

OCR A - LEVEL CHEMISTRY A • H432

CHEMISTRY



EXAM QUESTION PACK

5.1 RATES, EQUILIBRIUM AND PH

SCORE

/465

PERCENTAGE

%

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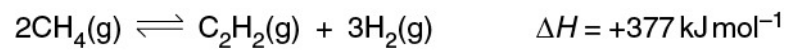
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1(a) Ethyne gas, C_2H_2 , is manufactured in large quantities for a variety of uses.

Much of this ethyne is manufactured from methane as shown in the equation below.



Write an expression for K_c for this equilibrium.

[1]

(b) A research chemist investigates how to improve the synthesis of ethyne from methane at a high temperature.

- The chemist adds CH_4 to a 4.00 dm^3 container.
- The chemist heats the container and allows equilibrium to be reached at constant temperature. The total gas volume does not change.
- The equilibrium mixture contains $9.36 \times 10^{-2} \text{ mol CH}_4$ and $0.168 \text{ mol C}_2\text{H}_2$.

(i) Calculate the amount, in mol, of H_2 in the equilibrium mixture.

amount of H_2 = _____ mol [1]

(ii) Calculate the equilibrium constant, K_c , at this temperature, including units.

Give your answer to **three** significant figures.

K_c = _____ units _____ [3]

(iii) Calculate the amount, in mol, of CH_4 that the chemist originally added to the container.

amount of CH_4 = _____ mol [1]

- (c) The chemist repeats the experiment three times.
In each experiment the chemist makes **one** change but uses the **same** initial amount of CH₄.

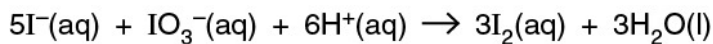
Complete the table to show the predicted effect of each change compared with the original experiment.

Only use the words **greater**, **smaller** or **same**.

Change	K_c	Equilibrium amount of C ₂ H ₂ (g) / mol	Initial rate
The container is heated at constant pressure			
A smaller container is used			
A catalyst is added to CH ₄ at the start			

[3]

2(a) A student carries out an initial rates investigation on the reaction below.



From the results, the student determines the rate equation for this reaction:

$$\text{rate} = k [\text{I}^{-}(\text{aq})]^2 [\text{IO}_3^{-}(\text{aq})] [\text{H}^{+}(\text{aq})]^2$$

(i) What is the overall order of reaction?

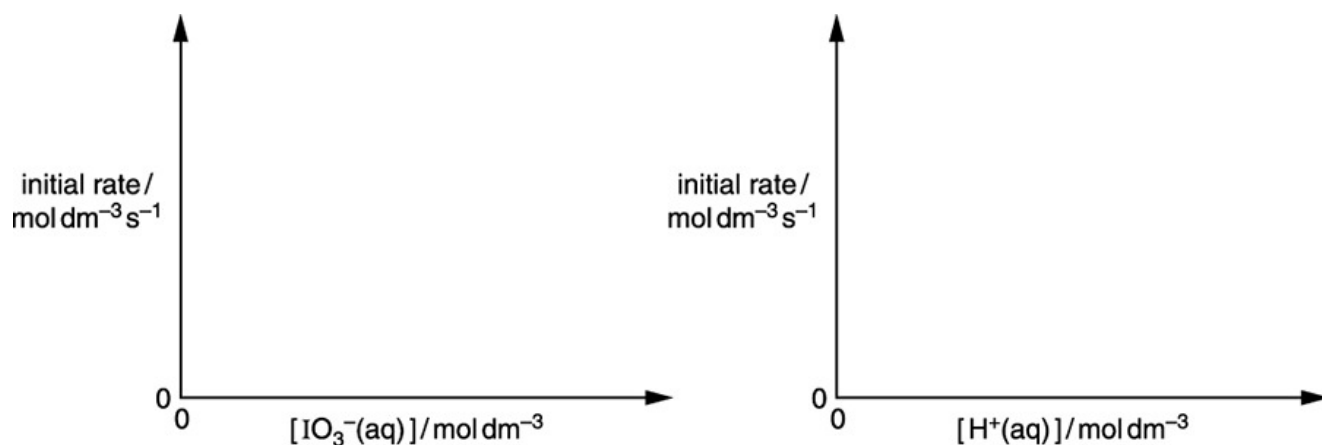
-----[1]

(ii) A proposed mechanism for this reaction takes place in several steps.

Suggest **two** reasons why it is unlikely that this reaction could take place in one step.

-----[2]

- (b) On the rate—concentration graphs below, sketch lines to show the relationship between initial rate and concentration for $\text{IO}_3^- (\text{aq})$ and $\text{H}^+ (\text{aq})$.



[2]

(c) The table below shows some of the student's results.

(i) Complete the table by adding the missing initial rates in the boxes.

	$[I^{-}(aq)] / \text{mol dm}^{-3}$	$[IO_3^{-}(aq)] / \text{mol dm}^{-3}$	$[H^{+}(aq)] / \text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
Experiment 1	0.015	0.010	0.020	0.60
Experiment 2	0.045	0.010	0.020	
Experiment 3	0.060	0.040	0.080	

[2]

(ii) Calculate the rate constant, k , for this reaction. Include units.

Give your answer to **two** significant figures.

$k =$ _____ units _____ [3]

(iii) The student repeats Experiment 1 using $0.020 \text{ mol dm}^{-3}$ methanoic acid, $\text{HCOOH}(aq)$ ($pK_a = 3.75$), instead of $0.020 \text{ mol dm}^{-3} \text{HCl}(aq)$ as a source of $H^{+}(aq)$.

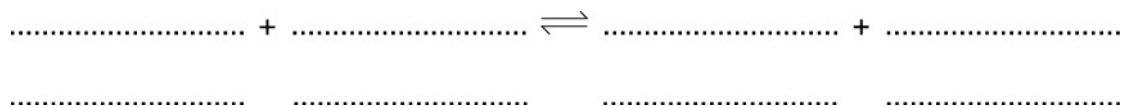
Determine the initial rate in this experiment. Show your working.

initial rate = _____ $\text{mol dm}^{-3} \text{ s}^{-1}$ [3]

3(a) Ethanoic acid, CH_3COOH , is a weak Brønsted—Lowry acid.

An acid—base equilibrium is set up when ethanoic acid is added to water.

Write the equation for the equilibrium that would be set up and label the two conjugate acid—base pairs.



[2]

(b) An aqueous solution of CH_3COOH has a pH of 3.060.

This solution contains both hydrogen ions and hydroxide ions.

(i) How can an aqueous solution of an acid contain hydroxide ions?

----- [1]

(ii) Calculate the concentration of hydroxide ions in this solution of ethanoic acid.

concentration of hydroxide ions = ----- mol dm^{-3} [2]

- (c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate. The resulting solution is able to act as a buffer solution.

(i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.

[1]

(ii) Explain why this buffer solution has formed.

[1]

(iii) Explain how this buffer solution controls pH when either an acid or an alkali is added.



 In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

[illegible]

(d) A biochemist plans to make up a buffer solution with a pH of 5.000.

The biochemist adds solid sodium ethanoate, CH_3COONa , to 400 cm^3 of 0.200 mol dm^{-3} ethanoic acid.

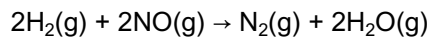
K_a for ethanoic acid = $1.75 \times 10^{-5}\text{ mol dm}^{-3}$

Calculate the mass of sodium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

Assume that the volume of the solution remains constant at 400 cm^3 on dissolving the sodium ethanoate.

[5]

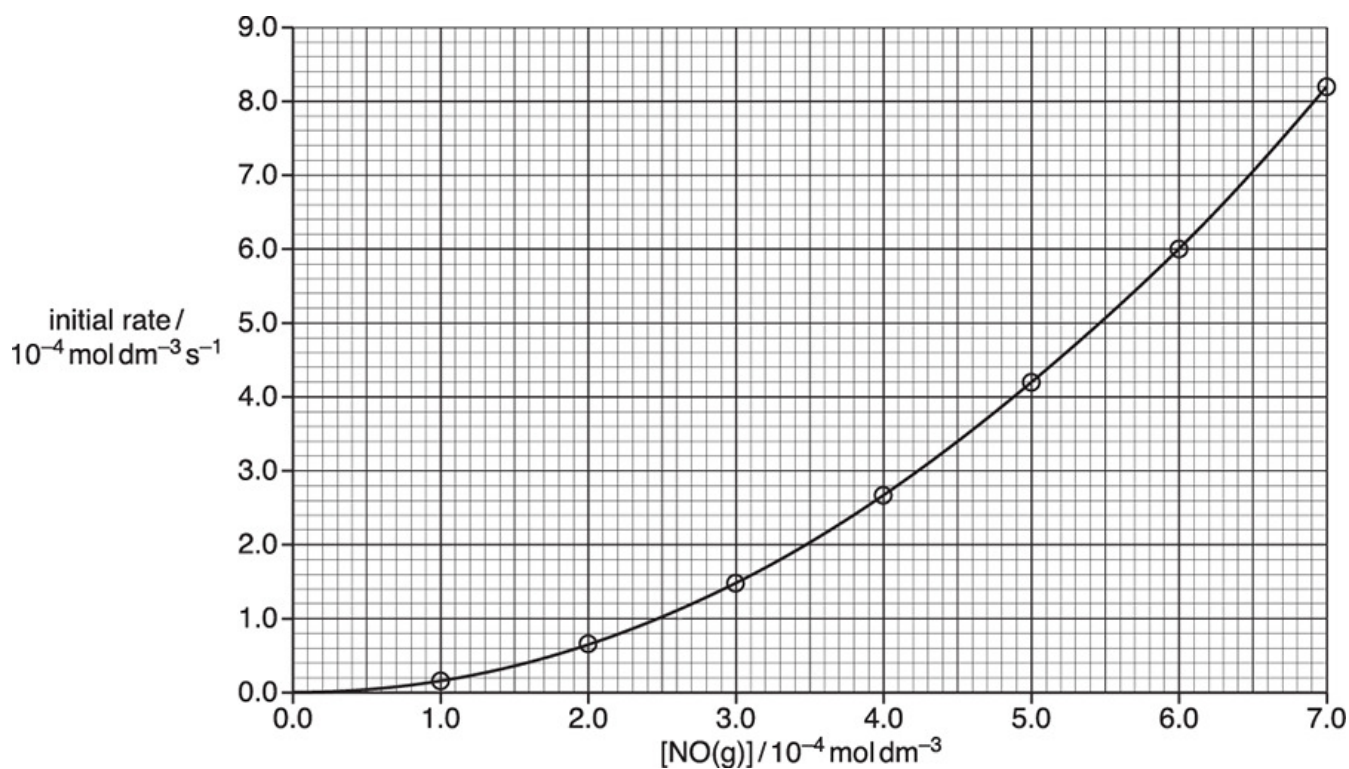
4(a) Hydrogen, H_2 , reacts with nitrogen monoxide, NO , as shown below:



The rate equation for this reaction is:

$$\text{rate} = k[\text{H}_2(\text{g})][\text{NO}(\text{g})]^2$$

The concentration of $\text{NO}(\text{g})$ is changed and a rate–concentration graph is plotted.



The chemist uses $\text{H}_2(\text{g})$ of concentration $2.0 \times 10^{-2} \text{ mol dm}^{-3}$.

Using values from the graph, calculate the rate constant, k , for this reaction.

Give your answer to **two** significant figures and in **standard form**.

Show your working.

$k =$ _____ units _____ [4]

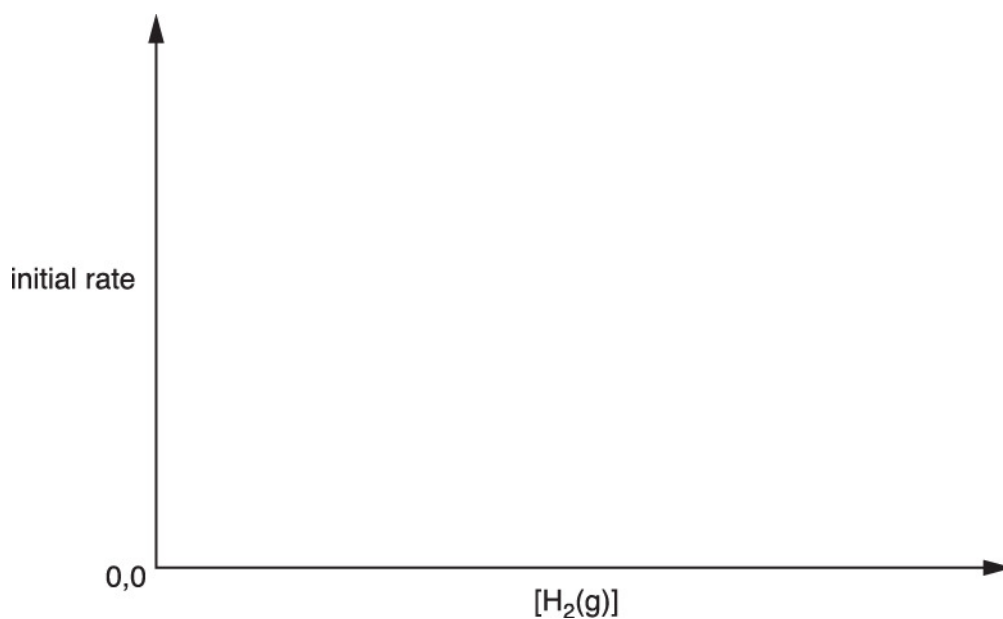
- (b) A chemist investigates the effect of changing the concentration of $\text{H}_2(\text{g})$ on the initial reaction rate at two different temperatures.

The reaction is first order with respect to $\text{H}_2(\text{g})$.

- (i) Using the axes below, sketch **two** graphs of the results.

Label the graphs as follows:

- L for the lower temperature
- H for the higher temperature.



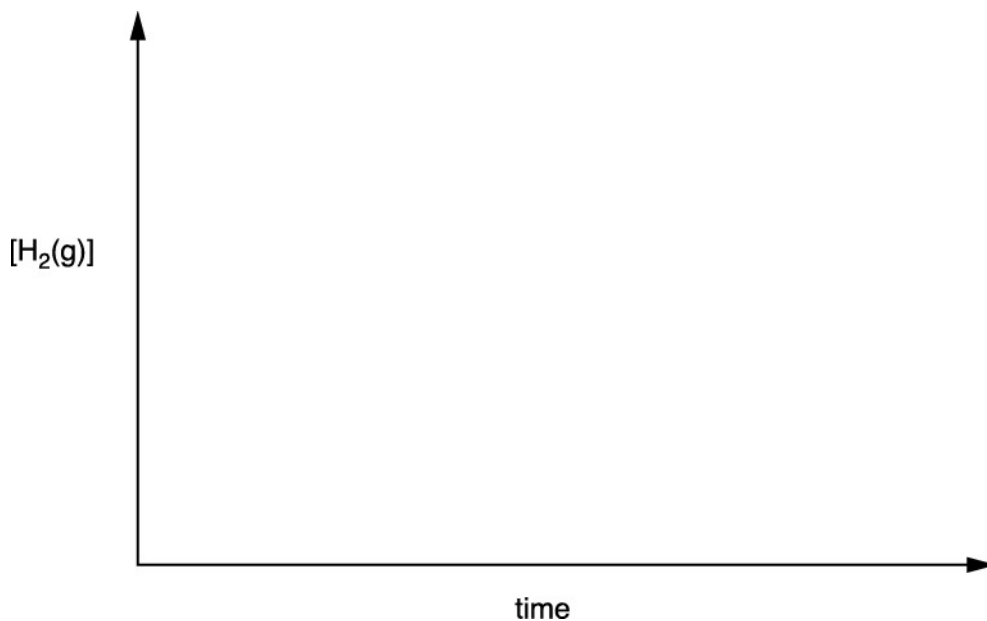
[2]

- (ii) State the effect of the higher temperature on the rate constant, k .

----- [1]

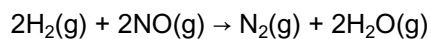
(c) The reaction can also be shown as being first order with respect to $\text{H}_2(\text{g})$ by continuous monitoring of $[\text{H}_2(\text{g})]$ during the course of the reaction.

- Using the axes below, sketch a graph to show the results.
- State how you would use the graph to show this first order relationship for $\text{H}_2(\text{g})$.



[2]

(d) The chemist proposes a three-step mechanism for the reaction:



(i) On the dotted line below, write the equation for step 3.

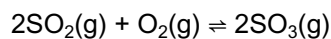
step 1:	$2\text{NO} \rightarrow \text{N}_2\text{O}_2$	fast
step 2:	$\text{H}_2 + \text{N}_2\text{O}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	slow
step 3:	-----	fast

[1]

(ii) Explain why this mechanism is consistent with the rate equation $\text{rate} = k[\text{H}_2(\text{g})][\text{NO}(\text{g})]^2$.

[1]

- 5 A chemist investigated methods to improve the synthesis of sulfur trioxide from sulfur dioxide and oxygen.



The chemist:

- mixed together 1.00 mol SO_2 and 0.500 mol O_2 with a catalyst at room temperature
- compressed the gas mixture to a volume of 250 cm^3
- allowed the mixture to reach equilibrium at constant temperature and without changing the total gas volume.

At equilibrium, 82.0% of the SO_2 had been converted into SO_3 .

- (i) Determine the concentrations of SO_2 , O_2 and SO_3 present at equilibrium and calculate K_c for this reaction.

$K_c =$ _____ units _____ [6]

- (ii) Explain what would happen to the pressure as the system was allowed to reach equilibrium.

----- [1]

- (iii) The value of K_c for this equilibrium decreases with increasing temperature.

Predict the sign of the enthalpy change for the forward reaction. State the effect on the equilibrium yield of SO_3 of increasing the temperature at constant pressure.

ΔH : -----

Effect on SO_3 yield: ----- [1]

- (iv) The chemist repeated the experiment at the same temperature with 1.00 mol SO_2 and an excess of O_2 .
The gas mixture was still compressed to a volume of 250 cm^3 .

State and explain, in terms of K_c , how the equilibrium yield of SO_3 would be different from the yield in the first experiment.

----- [3]

6(a) A student is supplied with $0.500 \text{ mol dm}^{-3}$ potassium hydroxide, KOH, and $0.480 \text{ mol dm}^{-3}$ propanoic acid, $\text{C}_2\text{H}_5\text{COOH}$.

The acid dissociation constant, K_a , for $\text{C}_2\text{H}_5\text{COOH}$ is $1.35 \times 10^{-5} \text{ mol dm}^{-3}$.

$\text{C}_2\text{H}_5\text{COOH}$ is a weak Brønsted–Lowry acid.

What is meant by a *weak acid* and *Brønsted–Lowry acid*?

----- [1]

(b) Calculate the pH of $0.500 \text{ mol dm}^{-3}$ potassium hydroxide.

pH = ----- [2]

(c) The student dilutes 25.0 cm^3 $0.480 \text{ mol dm}^{-3}$ $\text{C}_2\text{H}_5\text{COOH}$ by adding water until the total volume is 100.0 cm^3 .

(i) Write the expression for K_a for $\text{C}_2\text{H}_5\text{COOH}$.

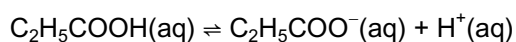
[1]

(ii) Calculate the pH of the diluted solution.

pH = _____ [3]

(d) A student prepares a buffer solution containing propanoic acid $\text{C}_2\text{H}_5\text{COOH}$ and propanoate ions, $\text{C}_2\text{H}_5\text{COO}^-$.
The concentrations of $\text{C}_2\text{H}_5\text{COOH}$ and $\text{C}_2\text{H}_5\text{COO}^-$ are both 1.00 mol dm^{-3} .

The following equilibrium is set up.



The acid dissociation constant, K_a , for $\text{C}_2\text{H}_5\text{COOH}$ is $1.35 \times 10^{-5} \text{ mol dm}^{-3}$.

(i) Calculate the pH of this buffer solution.

Give your answer to **two** decimal places.

pH = ... [1]

- (ii) A small amount of aqueous ammonia, $\text{NH}_3(\text{aq})$, is added to the buffer solution.

Explain, in terms of equilibrium, how the buffer solution would respond to the added $\text{NH}_3(\text{aq})$.

.....
.....
.....
..... [2]

- (iii) The student adds 6.075 g Mg to 1.00 dm^3 of this buffer solution.

Calculate the pH of the new buffer solution.

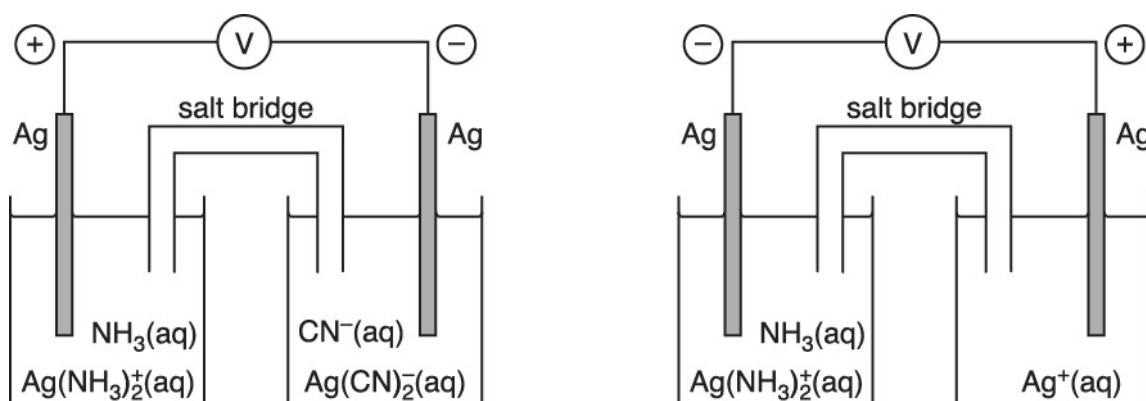
Give your answer to **two** decimal places

pH = ... [4]

C	$\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{NH}_3(\text{aq})$
D	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$
E	$\text{Ag}(\text{CN})_2^-(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{CN}^-(\text{aq})$

Table 6.1

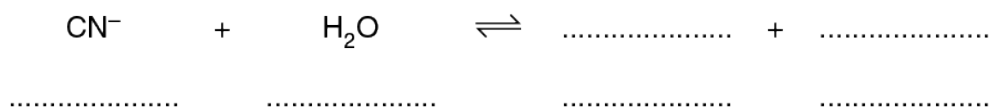
The two cells below were set up in an experiment to compare the standard electrode potentials of redox systems C, D and E. The signs on each electrode are shown.



The CN^- ion is the conjugate base of a very toxic weak acid.

In aqueous solutions of CN^- ions, an acid–base equilibrium is set up.

(i) Complete the equation for this equilibrium and label the conjugate acid–base pairs.



[1]

(ii) Explain, in terms of equilibrium, why acidic conditions should **not** be used with cells containing $\text{CN}^-(\text{aq})$ ions.

8 Zinc reacts with copper(II) sulfate solution, $\text{CuSO}_4(\text{aq})$.

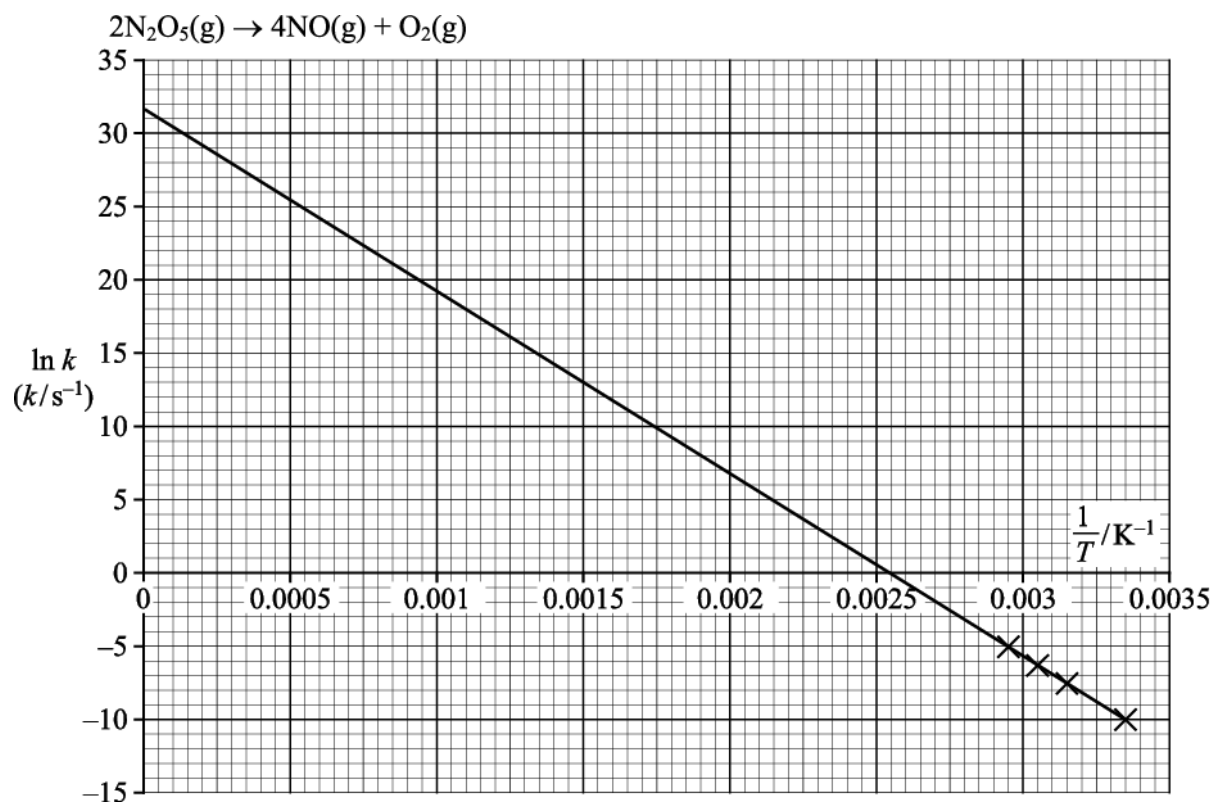
Which apparatus could be used to determine the effect of the concentration of $\text{CuSO}_4(\text{aq})$ on the rate of reaction?

- A balance
- B gas syringe
- C colorimeter
- D pH meter

Your answer

[1]

- 9 Using the graph, what is the value of the pre-exponential factor, A, for the decomposition of N_2O_5 ?



- A 3.45 s^{-1}
B 31.5 s^{-1}
C $1.04 \times 10^5 \text{ s}^{-1}$
D $4.79 \times 10^{13} \text{ s}^{-1}$

Your answer

[1]

- 10 A solution of propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, has a pH of 2.89 at 25°C .

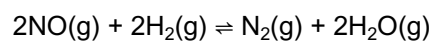
What is $[\text{H}^+]$ in this solution?

- A $1.7 \times 10^{-6} \text{ mol dm}^{-3}$
B $4.6 \times 10^{-4} \text{ mol dm}^{-3}$
C $1.3 \times 10^{-3} \text{ mol dm}^{-3}$
D 0.46 mol dm^{-3}

Your answer

[1]

11 NO(g), H₂(g), N₂(g) and H₂O(g) exist in equilibrium:



At room temperature and pressure, the equilibrium lies well to the right-hand side.

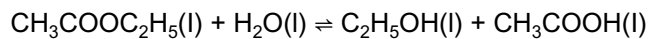
Which of the following could be the equilibrium constant for this equilibrium?

- A $1.54 \times 10^{-3} \text{ mol dm}^{-3}$
- B $6.50 \times 10^2 \text{ mol dm}^{-3}$
- C $1.54 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$
- D $6.50 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$

Your answer

[1]

12 Two students set up the equilibrium system below.



The students titrated samples of the equilibrium mixture with sodium hydroxide, $\text{NaOH}(\text{aq})$, to determine the concentration of CH_3COOH .

The students used their results to calculate a value for K_c .

The students' values for K_c were different.

Which of the reason(s) below could explain why the calculated values for K_c were different?

- 1: Each student carried out their experiment at a different temperature.
- 2: Each student used a different concentration of $\text{NaOH}(\text{aq})$ in their titration.
- 3: Each student titrated a different volume of the equilibrium mixture.

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

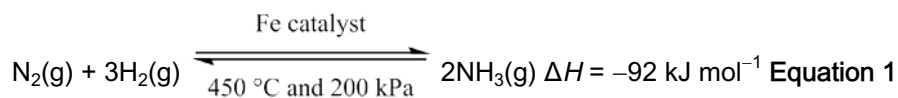
Your answer

☐

[1]

13(a) Ammonia is a gas with covalently-bonded molecules consisting of nitrogen and hydrogen atoms.

Ammonia can be made from the reaction of nitrogen and hydrogen in the Haber process.



What effect will increasing the temperature have on the composition of the equilibrium mixture **and** on the value of the equilibrium constant?

Explain your answer.

----- [2]

(b) A chemist mixes together 0.450 mol N_2 with 0.450 mol H_2 in a sealed container.

The mixture is heated and allowed to reach equilibrium.

At equilibrium, the mixture contains 0.400 mol N_2 and the total pressure is 500 kPa.

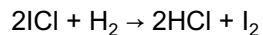
Calculate K_p .

Show **all** your working.

Include units in your answer.

$K_p =$ _____ units _____ [5]

14 Iodine monochloride, ICl, can react with hydrogen to form iodine.



This reaction was carried out several times using different concentrations of ICl or H₂. The initial rate of each experiment was calculated and the results are shown below. Initial concentrations are shown for each experiment.

	[ICl] / mol dm ⁻³	[H ₂] / mol dm ⁻³	Rate / mol dm ⁻³ s ⁻¹
Experiment 1	0.250	0.500	2.04×10^{-2}
Experiment 2	0.500	0.500	4.08×10^{-2}
Experiment 3	0.125	0.250	5.10×10^{-3}

(i) Calculate the rate constant, k , for this reaction. Include units in your answer.

Show **all** your working.

$k =$ _____ units _____ [4]

(ii) Calculate the rate of reaction when ICl has a concentration of 3.00×10^{-3} mol dm⁻³ and H₂ has a concentration of 2.00×10^{-3} mol dm⁻³.

Show **all** your working.

rate = _____ mol dm⁻³ s⁻¹ [1]

- (c) To prepare a buffer solution, 75.0 cm^3 of $0.220 \text{ mol dm}^{-3}$ butanoic acid is reacted with 50.0 cm^3 of $0.185 \text{ mol dm}^{-3}$ sodium hydroxide.

K_a for butanoic acid is $1.5 \times 10^{-5} \text{ mol dm}^{-3}$ at 25°C .

- (i) Calculate the pH of $0.185 \text{ mol dm}^{-3}$ sodium hydroxide at 25°C .

Give your answer to **two** decimal places.

pH = _____ [2]

- (ii) Calculate the pH of the buffer solution at 25°C .

Give your answer to **two** decimal places.

Show **all** your working.

pH = _____ [4]

- 16 For the reaction $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$, the rate equation is $\text{rate} = k[\text{H}_2][\text{NO}]^2$.

What is the effect on the rate of reaction when the concentration of H_2 is halved and the concentration of NO is doubled?

- A The reaction rate is halved.
- B The reaction rate is unchanged.
- C The reaction rate is doubled.
- D The reaction rate is quadrupled.

Your answer

[1]

- 17 The reaction $2AB \rightarrow 2A + B_2$ is first order with respect to AB.
The half-life of the reaction is 2 minutes.

0.100 mol of AB is dissolved in a solvent to form 100 cm^3 of a reaction mixture.

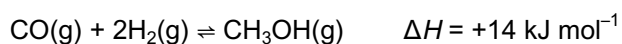
What is the concentration of AB, in mol dm^{-3} , after 6 minutes?

- A 0.0125
- B 0.0250
- C 0.125
- D 0.250

Your answer

[1]

- 18 The equilibrium system below is set up.



The equilibrium system is compressed at constant temperature.

What is the effect on the value of K_c and the amount, in moles, of CH_3OH ?

	K_c	Amount in moles of CH_3OH
A	increases	increases
B	decreases	decreases
C	no change	no change
D	no change	increases

Your answer

[1]

- 19 A buffer solution is based on methanoic acid, HCOOH ($K_a = 1.70 \times 10^{-4} \text{ mol dm}^{-3}$) and methanoate ions, HCOO^- .

In the buffer solution, the HCOOH concentration is half the HCOO^- concentration.

What is the pH of the buffer solution?

- A 2.47
- B 3.07
- C 3.47
- D 4.07

Your answer

[1]

- 20 Which statement is correct for a neutral solution at any temperature?

- A $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
- B The solution contains only H_2O
- C $[\text{H}^+] = [\text{OH}^-]$
- D $\text{pH} = 7$

Your answer

[1]

- 21 Two elements, **A** and **B**, react to form an ionic compound with the formula A_2B_3 . In this compound, **A** and **B** both have the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$.

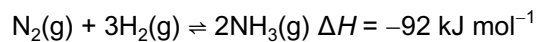
Deduce possible identities of the ions in A_2B_3 .

A:

B:

[2]

22(a) A research chemist investigates how the value of K_c changes with temperature.



- The chemist mixes 0.800 mol of $\text{N}_2(\text{g})$ and 2.400 mol of $\text{H}_2(\text{g})$ and leaves the mixture to reach equilibrium at 300 °C.
- The total volume of the equilibrium mixture is 5.00 dm³.
- At equilibrium, 0.360 mol of $\text{NH}_3(\text{g})$ has formed.

Calculate the value of K_c under these conditions.

Show all your working.

$K_c =$ _____ units _____ [6]

(b) Ammonia, NH_3 , is manufactured by the chemical industry from nitrogen and hydrogen gases.



- An iron catalyst is used which provides several benefits for sustainability.
- The chemical industry uses operational conditions that are different from the conditions predicted to give a maximum equilibrium yield.

The chemist adds more nitrogen to the equilibrium mixture in (b).



The temperature is kept at 300 K and the volume at 5.00 dm^3 .

The chemist predicts that the addition of nitrogen will increase the proportion of $\text{H}_2(\text{g})$ that reacts.

(i) Explain whether the chemist's prediction is correct.

----- [3]

(ii) Suggest why the chemist is more concerned with increasing the proportion of H_2 that reacts rather than the proportion of N_2 that reacts.

----- [1]

(b) A student carries out an investigation to find the activation energy, E_a , of a reaction.

From the results, the student determines the rate constant, k , at different temperatures, T .

The student then calculates $1 / T$ and $\ln k$, as shown in **Table 19.1**.

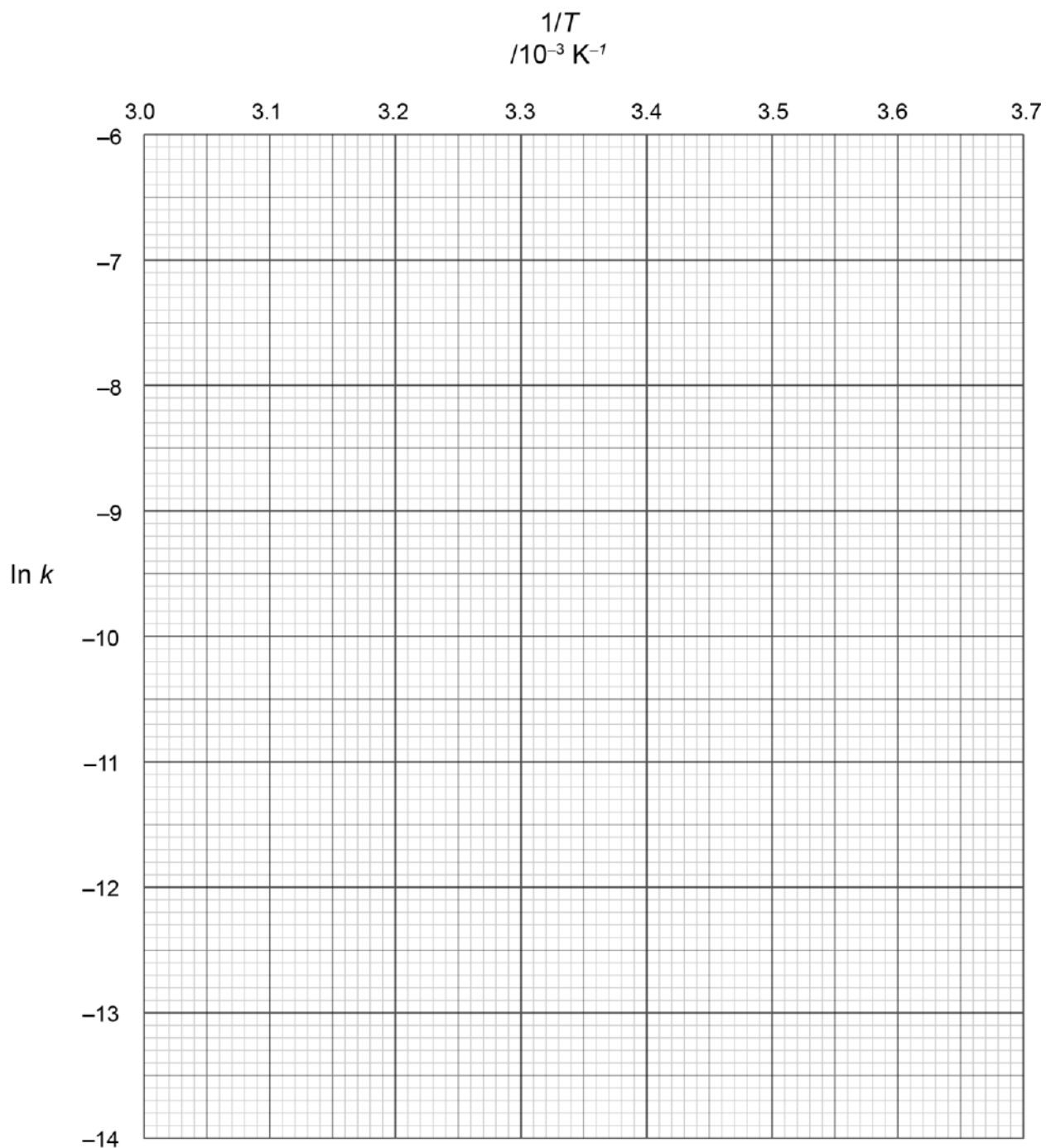
Temperature, T / K	Rate constant, k / s^{-1}	$1 / T / \text{K}^{-1}$	$\ln k$
278	1.50×10^{-6}	3.60×10^{-3}	-13.41
290	1.51×10^{-5}		-11.10
298	4.11×10^{-5}	3.34×10^{-3}	-10.10
308	1.99×10^{-4}	3.23×10^{-3}	
323	1.40×10^{-3}	3.10×10^{-3}	-6.57

Table 19.1

Add the missing values to **Table 19.1** and plot a graph of $\ln k$ against $1 / T$ on the graph paper opposite.

Using your graph, calculate the activation energy of the reaction.

Show your working.



activation energy, E_a = _____ kJ mol^{-1} [4]

24(a) This question is about acids and bases.

Nitric acid, HNO_3 , and nitrous acid, HNO_2 , are two Brønsted–Lowry acids containing nitrogen.

A student measures the pH of $0.0450 \text{ mol dm}^{-3}$ solutions of HNO_3 and HNO_2 ($\text{p}K_{\text{a}} = 3.35$) and found that the acids had different pH values.

(i) Explain why the pH values are different.

----- [1]

(ii) Calculate the pH value of $0.0450 \text{ mol dm}^{-3} \text{HNO}_3$ to **two** decimal places.

Show your working.

pH = ----- [1]

(iii) Calculate the pH value of $0.0450 \text{ mol dm}^{-3} \text{HNO}_2$ to **two** decimal places.

Show your working.

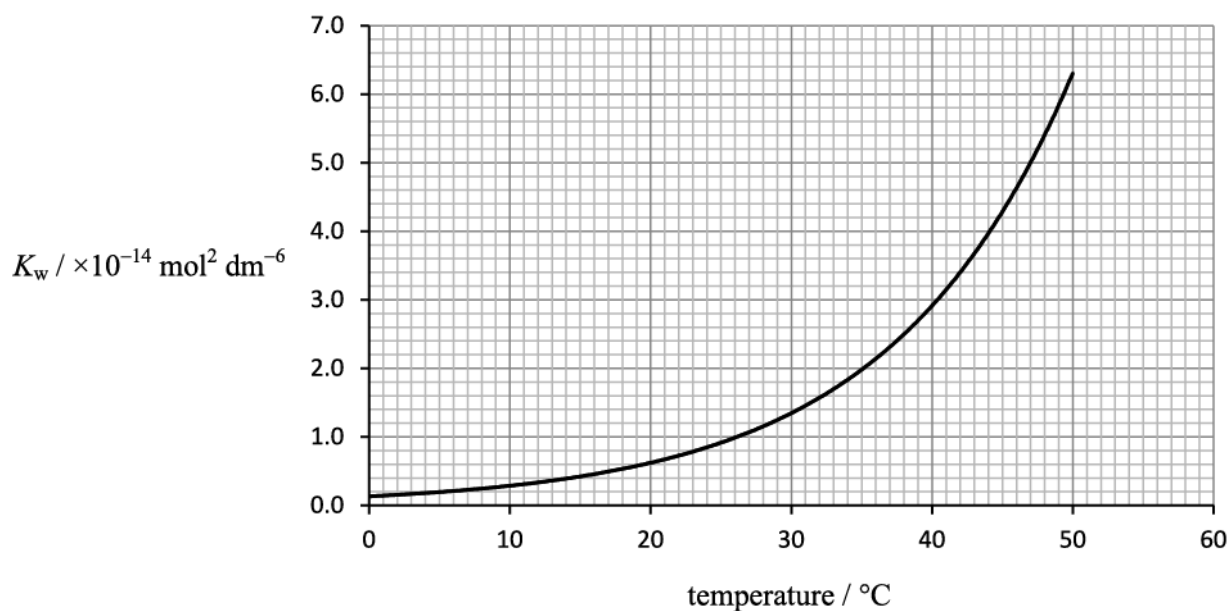
pH = ----- [3]

- (b) Rubidium hydroxide, RbOH, is a strong alkali. A technician is asked to prepare a 250.0 cm^3 solution of RbOH with a pH of 12.500.

Calculate the mass of RbOH that the technician needs to use.

mass = _____ g [4]

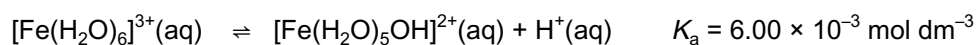
- 25 The dissociation of water is measured by the ionic product of water, K_w . The value of K_w varies with temperature as shown in the graph below.



Calculate the pH of water at body temperature, 37°C .

pH = _____ [3]

- 26 The complex ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, behaves as a weak Brønsted–Lowry acid in aqueous solution. The equation below represents the dissociation of aqueous $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions, together with the K_a value.



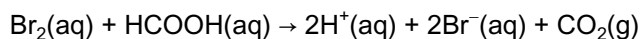
- (i) Write the expression for the acid dissociation constant, K_a , for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

[1]

- (ii) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ to **two** decimal places.

pH = _____ [2]

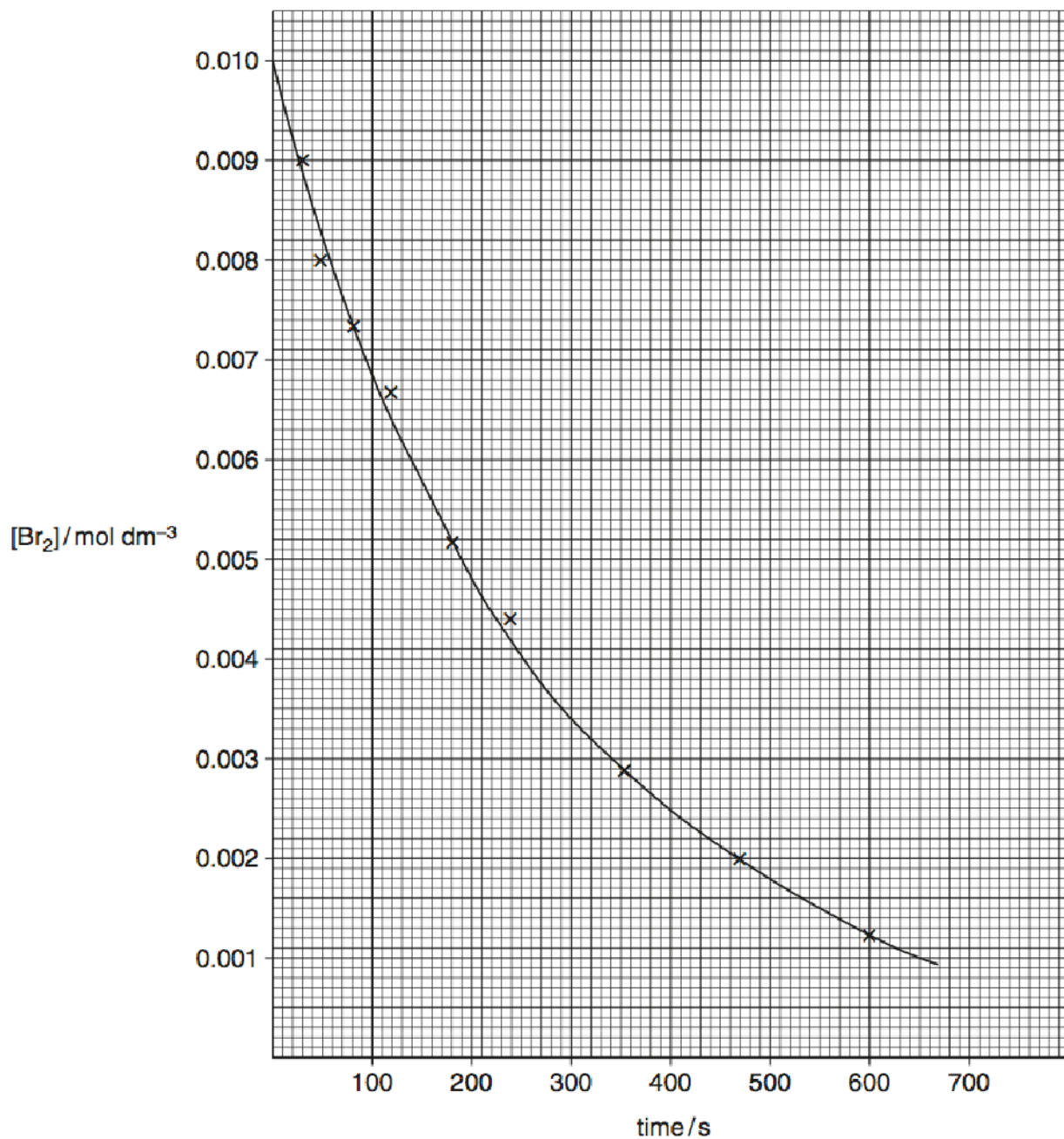
- 27 Methanoic acid and bromine react as in the equation below.



A student investigates the rate of this reaction by monitoring the concentration of bromine over time.

The student uses a large excess of HCOOH to ensure that the order with respect to HCOOH will be effectively zero.

From the experimental results, the student plots the graph below.



(a) Suggest how the concentration of the bromine could have been monitored.

----- [1]

(b) Suggest a different experimental method that would allow the rate of this reaction to be followed over time.

----- [1]

(c) Why would use of excess HCOOH ensure that the order with respect to HCOOH is effectively zero?

----- [1]

(d) * Using the graph, determine

- the initial rate of reaction
- the rate constant.

Your answer must show full working using the graph and the lines below as appropriate.

----- [6]

28 Methanoic acid is added to water. An acid–base equilibrium is set up containing two acid–base pairs.

Suggest a mechanism for the forward reaction in this equilibrium.

Your mechanism should use displayed formulae and curly arrows, and show all species present at equilibrium.

[2]

This question looks at number relationships. For calculations, show your working.

(i) What is the oxidation number of nitrogen in each species?



[1]

(ii) What mass of KMnO_4 is needed to prepare a 250.0 cm^3 solution with a concentration of $0.200 \text{ mol dm}^{-3}$ KMnO_4 ?

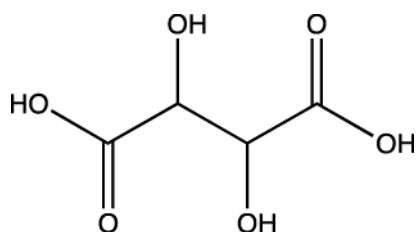
mass = _____ g [2]

(iii) What are the units of the rate constant for a reaction with an overall order of 3?

units = _____ [1]

(iv) How many molecules are in 38.25 g of tartaric acid?

Give your answer to an **appropriate** number of significant figures and in standard form.



tartaric acid

number of molecules = _____ [2]

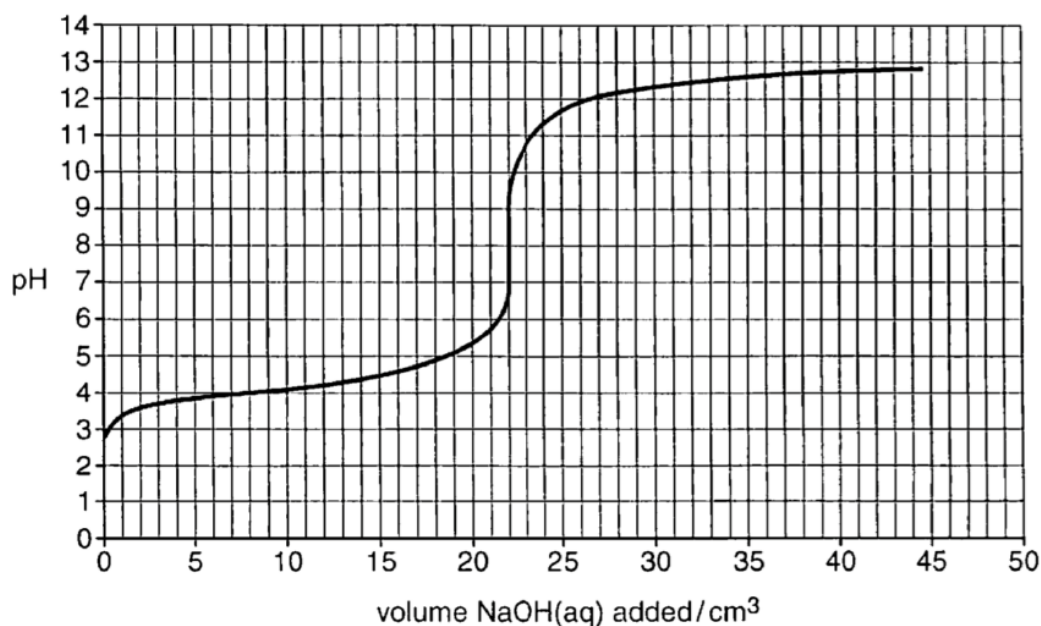
30(a) This question is about different weak acids.

A student carries out a titration to determine the concentration of a solution of ethanoic acid.

The method is outlined below.

- A 25.0 cm^3 sample of $\text{CH}_3\text{COOH}(\text{aq})$ is pipetted into a conical flask.
- The $\text{CH}_3\text{COOH}(\text{aq})$ is titrated by adding $0.125 \text{ mol dm}^{-3}$ NaOH from a burette.
- The pH of the solution is measured continuously, with stirring, as the $\text{NaOH}(\text{aq})$ is added.

The pH titration curve is shown below.



- (i) How could the student measure the pH continuously as the $\text{NaOH}(\text{aq})$ is added?

----- [1]

- (ii) Determine the unknown concentration, in mol dm^{-3} , of the $\text{CH}_3\text{COOH}(\text{aq})$.
Show your working.

(b) The table shows the pH ranges of four indicators.

Indicator	congo red	methyl red	brilliant yellow	alizarin yellow R
pH range	3.0–5.0	4.4–6.2	6.6–7.8	10.1–12.0

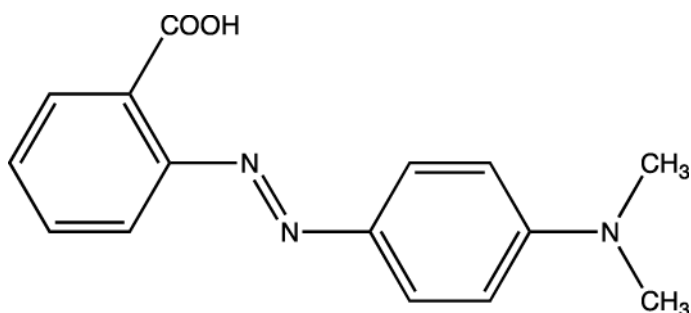
(i) Choose, with a reason, the indicator from the table that is most suitable for the student's titration in (a).

----- [1]

(ii) An indicator is a weak acid, HA, which has a different colour from its conjugate base, A^- .

For methyl red, the HA form is red and the A^- form is yellow.

The structure of methyl red is shown below.



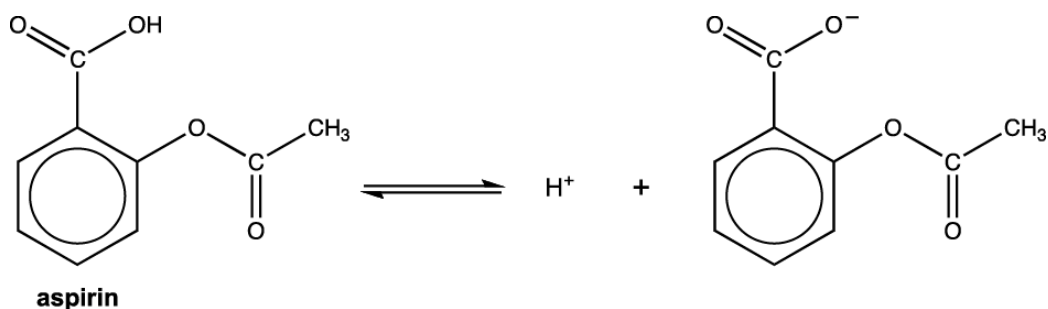
methyl red

Draw the structure of the conjugate base of methyl red and explain, in terms of equilibrium, the colours of methyl red at low pH, at high pH, and at the end point of a titration. You can use HA and A^- in your explanation.

explanation: -----

- (c) Aspirin is a weak acid with a pK_a value of 3.40 and a solubility in water of $1.00 \times 10^{-2} \text{ g cm}^{-3}$ at body temperature (37°C).

The equation for the dissociation of aspirin in aqueous solution is shown below.



- (i) Calculate the pH of a saturated solution of aspirin in water at body temperature.

pH = _____ [4]

- (ii) 'Soluble aspirin' is usually sold as the sodium or calcium salt of aspirin.

Suggest why salts of aspirin are more soluble than aspirin in water.

----- [1]

- (iii) The stomach contains hydrochloric acid at a pH of about 1–3.

Explain why swallowing soluble aspirin may lead to irritation of the stomach lining.

----- [2]

31(a) Ethers are a homologous series of organic compounds containing the R–O–R functional group.

The structures and names of two ethers are shown in Fig. 4.1.

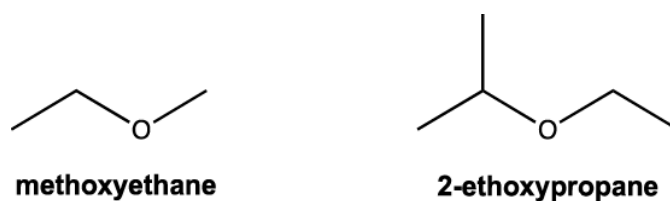


Fig. 4.1

Draw the **skeletal** formula of the ether, 2-ethoxy-3-methylbutane.

[1]

(b) Ethers can be prepared by nucleophilic substitution of haloalkanes with alkoxide ions, RO^- .

(i) Alkoxide ions can be prepared by reacting sodium with an alcohol. A gas is also formed.

Write an equation for the formation of methoxide ions from sodium and an alcohol.

-----[1]

(ii) Methoxyethane, shown in Fig. 4.1, can be prepared by reacting bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$, with methoxide ions, CH_3O^- .

Suggest the mechanism for the nucleophilic substitution of $\text{CH}_3\text{CH}_2\text{Br}$ with CH_3O^- .

Show curly arrows, charges, relevant dipoles, and products.

[3]

(iii) In this mechanism, explain how CH_3O^- ions have acted as a nucleophile.

State the type of bond fission that takes place.

-----[1]

(c) 2-Ethoxypropane, shown in Fig. 4.1, is analysed by ^1H NMR spectroscopy.

Complete the table to predict the ^1H NMR spectrum of 2-ethoxypropane.

You may **not** need to use all the rows.

Chemical shift, δ/ppm	Relative peak area	Splitting pattern

[4]

(d) In organic reactions, alkoxide ions can also act as a base.

The diagram below shows an incomplete mechanism for the reaction of a diester with methoxide ions, CH_3O^- (**Step 1**), followed by reaction of the intermediate with bromoethane (**Step 2**).

- (i) For **Step 1**, add curly arrows to show how CH_3O^- reacts with the diester to form the intermediate.
In the box, draw the structure of the organic product formed in **Step 2**.

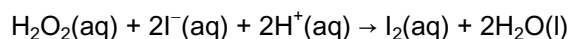


[3]

- (ii) Explain how CH_3O^- ions have acted as a base in this mechanism.

----- [1]

32(a) Hydrogen peroxide reacts with iodide ions in acid conditions, as shown below.



A student investigates the rate of this reaction by carrying out four experiments at the same temperature. The student's results are shown below.

Experiment	$[\text{H}_2\text{O}_2(\text{aq})] / \text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})] / \text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})] / \text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.0010	0.20	0.10	5.70×10^{-6}
2	0.0020	0.20	0.10	1.14×10^{-5}
3	0.0020	0.20	0.20	1.14×10^{-5}
4	0.0040	0.40	0.10	4.56×10^{-5}

The rate equation is: $\text{rate} = k [\text{H}_2\text{O}_2(\text{aq})] [\text{I}^-(\text{aq})]$

- Show that the student's results support this rate equation.
- Calculate the rate constant, k , for this reaction.

Give your answer to **two** significant figures, in standard form and with units.



In your answer you should make clear how the experimental results provide evidence for the rate equation.

-----[6]

- (b) The student concluded that $\text{H}^+(\text{aq})$ ions act as a catalyst.

Explain why the student's conclusion is **not** correct.

-----[1]

- (c) A four-step mechanism has been proposed for this reaction.
The rate-determining step is the first step.

- (i) State what is meant by the term *rate-determining step*.

-----[1]

- (ii) The equation for **Step 3** in the four-step mechanism is shown below.

Suggest equations for the other three steps.
State symbols are **not** required.

Step 1: -----

Step 2: -----

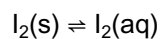
Step 3: $\text{HIO} + \text{I}^- \rightarrow \text{I}_2 + \text{OH}^-$

Step 4: -----

[3]

33(a) Iodine, I_2 , is a grey-black solid that is not very soluble in water.

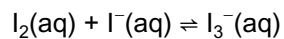
Equilibrium 1 is set up with the equilibrium position well to the left.



Equilibrium 1

Solid iodine is much more soluble in an aqueous solution of potassium iodide, $KI(aq)$, than in water.

Equilibrium 2 is set up.



Equilibrium 2

A student dissolves I_2 in $KI(aq)$.

The resulting 200 cm^3 equilibrium mixture contains:

$$4.00 \times 10^{-5} \text{ mol } I_2(aq)$$

$$9.404 \times 10^{-2} \text{ mol } I^-(aq)$$

$$1.96 \times 10^{-3} \text{ mol } I_3^-(aq).$$

Calculate K_c for **equilibrium 2**.

Give your answer to an **appropriate** number of significant figures.

$K_c =$ _____ units _____ [4]

- (b) The student adds an excess of aqueous silver nitrate, $\text{AgNO}_3(\text{aq})$, to the equilibrium mixture.

Predict what would be observed.

Explain the observations in terms of both **equilibrium 1** and **equilibrium 2** and any species formed.

[4]

- (c) Two redox reactions of iodine are described below.

Reaction 1: Iodine is reacted with oxygen to form a compound with a molar mass of 333.8 g mol^{-1} .

Reaction 2: In alkaline conditions, iodine disproportionates to form iodide ions, iodate(V) ions and water.

Construct equations for these **two** reactions.

State symbols are **not** required.

Reaction 1:

Reaction 2:

34(a) A chemist carries out some experiments using nitrous acid, $\text{HNO}_2(\text{aq})$.

HNO_2 is a weak acid with a K_a value of $4.69 \times 10^{-4} \text{ mol dm}^{-3}$ at the temperature of the chemist's experiments.

Write the expression for K_a for $\text{HNO}_2(\text{aq})$.

[1]

(b) Calculate the pH of $0.120 \text{ mol dm}^{-3} \text{HNO}_2(\text{aq})$.

Give your answer to **two** decimal places.

pH = _____ [2]

(c) The chemist prepares 1 dm^3 of a buffer solution by mixing 200 cm^3 of $0.200 \text{ mol dm}^{-3} \text{HNO}_2$ with 800 cm^3 of $0.0625 \text{ mol dm}^{-3}$ sodium nitrite, NaNO_2 .

(i) Calculate the pH of the buffer solution.

Give your answer to **two** decimal places.

pH = _____ [4]

(ii) Explain how this buffer solution controls pH when:

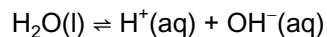
- a small amount of HCl(aq) is added
- a small amount of NaOH(aq) is added.



 In your answer, include the equation for the equilibrium in the buffer solution and explain how **this** equilibrium system controls the pH.

[4]

(d) The dissociation of water is shown below.



At 60 °C, the ionic product of water, K_w , is $9.311 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$.

At 25 °C, the ionic product of water, K_w , is $1.000 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$.

(i) Explain whether the dissociation of water is an exothermic or endothermic process.

----- [1]

(ii) Predict, using a calculation, whether a pH of 7 at 60 °C is neutral, acidic or alkaline.

----- [2]

(iii) pK_w , pK_a and pH are logarithmic scales.

Calculate pK_w at 60 °C.

Give your answer to **two** decimal places.

$pK_w =$ ----- [1]

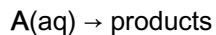
(iv) 20.0 cm^3 of $0.0270 \text{ mol dm}^{-3}$ NaOH is diluted with water and the solution made up to 100 cm^3 at 60 °C.

Calculate the pH of the diluted solution of NaOH at 60 °C.

Give your answer to **two** decimal places.

pH = ----- [3]

35 The reaction below is first order with respect to A.



When the initial concentration of A is 1 mol dm^{-3} , the half-life is 20 minutes.

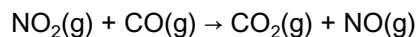
What is the half-life when the initial concentration of A is 2 mol dm^{-3} ?

- A 10 minutes
- B 20 minutes
- C 40 minutes
- D 60 minutes

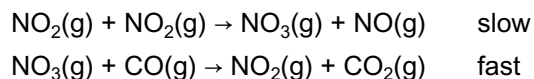
Your answer

[1]

36 Nitrogen dioxide, NO_2 reacts with carbon monoxide, CO, as shown in the equation.



A proposed mechanism for this reaction is shown below.



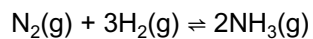
Which rate equation is consistent with this mechanism?

- A $\text{rate} = k[\text{NO}_2]$
- B $\text{rate} = k[\text{NO}_2][\text{CO}]$
- C $\text{rate} = k[\text{NO}_2]^2$
- D $\text{rate} = k[\text{NO}_2]^2[\text{CO}]$

Your answer

[1]

37 Ammonia, NH_3 , is formed in the reversible reaction below.



A mixture at equilibrium contains 0.320 mol N_2 , 0.960 mol H_2 and 0.120 mol NH_3 .

What is the mole fraction of H_2 in the equilibrium mixture?

- A 0.279
- B 0.686
- C 0.837
- D 2.06

Your answer

[1]

38 A $0.040 \text{ mol dm}^{-3}$ solution of a weak monobasic acid is 1.0% dissociated.

What is the value of K_a for the acid?

- A $2.0 \times 10^{-7} \text{ mol dm}^{-3}$
- B $4.0 \times 10^{-6} \text{ mol dm}^{-3}$
- C $4.0 \times 10^{-4} \text{ mol dm}^{-3}$
- D $4.0 \times 10^{-2} \text{ mol dm}^{-3}$

Your answer

[1]

- 39 Methane is an important raw material for manufacturing chemicals. Hydrogen can be manufactured from methane and steam as shown below in **equation 17.1**.



The rate of reaction is increased by using a catalyst.

A chemist investigates the equilibrium shown in **equation 17.1** as outlined below.



- A chemist mixes together 1.000 mol CH_4 and 1.400 mol of H_2O in a sealed container.
- The mixture is heated to constant temperature and allowed to reach equilibrium. The equilibrium mixture contains 0.200 mol of CH_4 and the total pressure is 30.0 atm.

Use this information to calculate K_p for the equilibrium in **equation 17.1**.

Show all your working.

[7]

40(a) This question is about vitamin C, $\text{C}_6\text{H}_8\text{O}_6$.

Vitamin C is a weak monobasic acid with a K_a value of $6.76 \times 10^{-5} \text{ mol dm}^{-3}$.

(i) Write the expression for K_a for vitamin C.

[1]

(ii) Calculate $\text{p}K_a$ for vitamin C, to **two** decimal places.

[1]

(iii) A bottle of vitamin C supplements contains tablets, each containing 500 mg of vitamin C.

A student dissolves three vitamin C tablets in water and makes up the solution to a volume of 250.0 cm^3 .

Calculate the pH of the solution.

Give your answer to **two** decimal places.

pH = _____ [4]

(b) Low acidity vitamin C tablets are less acidic than tablets containing just vitamin C.

A student dissolves a low acidity vitamin C tablet in water.

- The tablet contains a mixture of 300 mg of vitamin C, $C_6H_8O_6$, and the sodium salt of vitamin C, $C_6H_7O_6Na$.
- The pH of the solution is 4.02.

(i) Calculate the ratio $C_6H_7O_6^- : C_6H_8O_6$ in the solution.

Show your working.

$$\frac{[C_6H_7O_6^-]}{[C_6H_8O_6]} = \frac{\dots\dots\dots}{1} \quad [3]$$

(ii) Calculate the mass of $C_6H_7O_6Na$, in mg, in the low acidity vitamin C tablet.

mass = _____ mg [1]

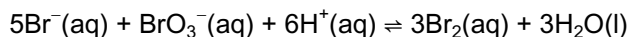
(c) The sodium salt of vitamin C can be made by reacting vitamin C with aqueous sodium hydroxide.

An aqueous solution of sodium hydroxide had a pH of 12.72 at 298 K.

Calculate the concentration, in mol dm^{-3} , of the NaOH solution.

concentration = _____ mol dm^{-3} [2]

*Bromine, Br₂, is formed in the redox reaction shown below.



A student plans an investigation, using the initial rates method, to determine the rate equation and rate constant for this reaction.

The student is supplied with solutions containing the following:

- 0.300 mol dm⁻³ Br⁻(aq)
- 0.300 mol dm⁻³ BrO₃⁻(aq)
- 0.300 mol dm⁻³ H⁺(aq).

The student is also supplied with distilled water and normal laboratory glassware.

The student uses a total volume of 30 cm³ for each experiment and measures the initial rate of formation of Br₂(aq).

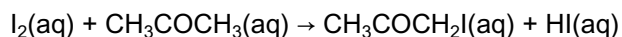
The results of the student's experiments are shown below.

Experiment	[Br ⁻ (aq)] / mol dm ⁻³	[BrO ₃ ⁻ (aq)] / mol dm ⁻³	[H ⁺ (aq)] / mol dm ⁻³	Initial rate / 10 ⁻³ mol dm ⁻³ s ⁻¹
1	0.100	0.100	0.100	1.20
2	0.025	0.100	0.100	0.30
3	0.100	0.050	0.100	0.60
4	0.100	0.050	0.050	0.15

Show how the student could obtain the concentrations for experiments 1–4 and determine the rate constant for this reaction.

[6]

42(a) A student investigates the rate of reaction between iodine, I_2 , and propanone, CH_3COCH_3 , in the presence of H^+ ions. The student uses $HCl(aq)$ to supply H^+ ions.



The student follows the method outlined below.

1. The student starts the reaction by mixing the following solutions.

1.00 cm³ of 1.00 mol dm⁻³ $I_2(aq)$

49.5 cm³ of 1.00 mol dm⁻³ $CH_3COCH_3(aq)$

49.5 cm³ of 1.00 mol dm⁻³ $HCl(aq)$

2. The student places a sample of the reaction mixture in a colorimeter, immediately starts a stopwatch, and records the absorbance.

3. The student records the absorbance every 100 s. The results are shown below.

Time/s	Absorbance
0	0.80
100	0.67
200	0.51
300	0.44
400	0.28
500	0.18
600	0.05

Explain why absorbance decreases during the experiment.

[1]

(b) Absorbance is proportional to the concentration of I₂.

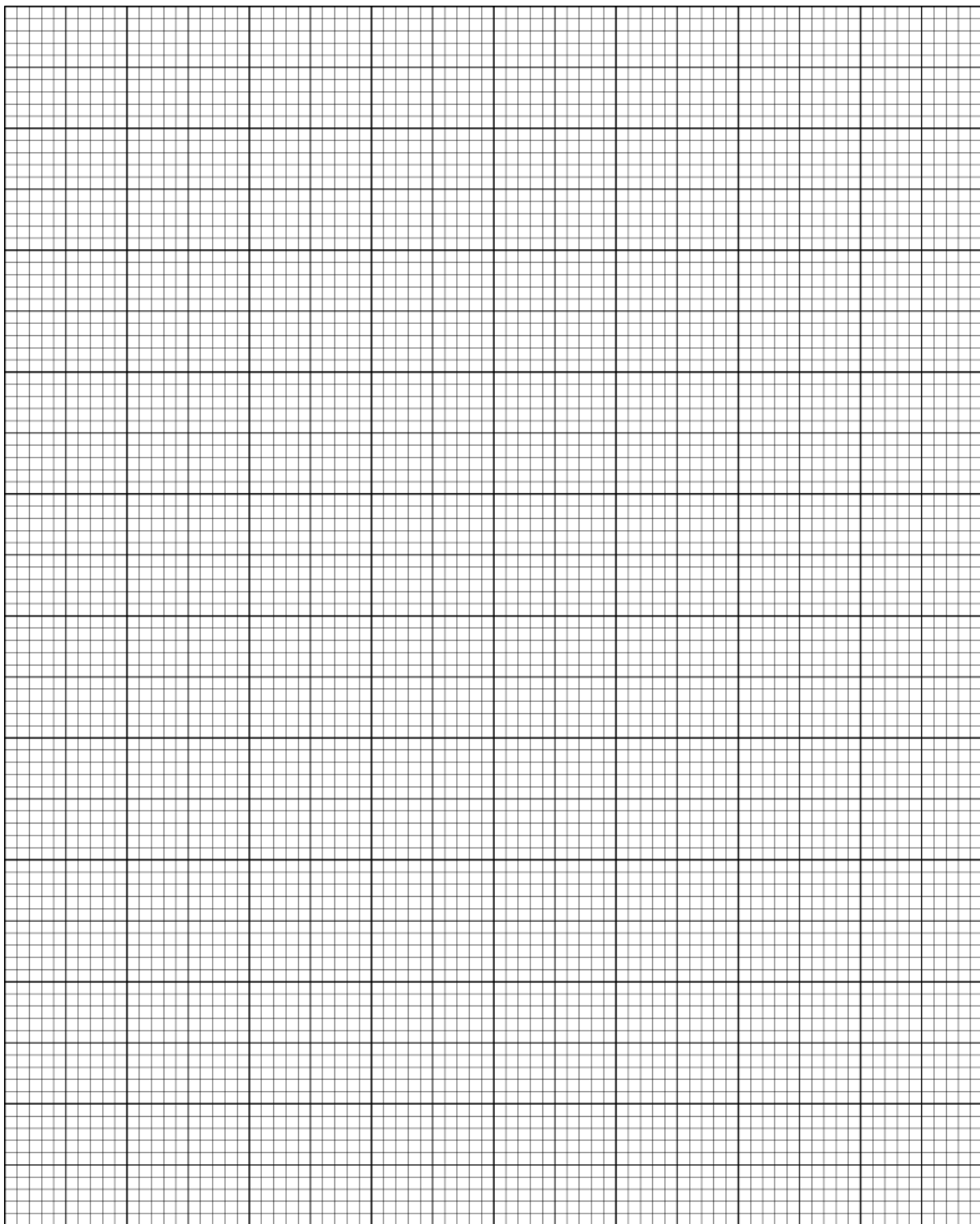
Calculate the concentration of I₂ at the start of the experiment and after 500 s.

Time/s	Absorbance	[I ₂ (aq)]/mol dm ⁻³
0	0.80	
500	0.18	

[2]

(c)

(i) Plot a graph of absorbance against time and draw a line of best fit.



[3]

(ii) Use your graph to find the order of reaction with respect to iodine.

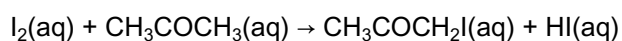
Explain your reasoning.

Order

Explanation

.....
..... [2]

(d) A three step mechanism has been proposed for this reaction.

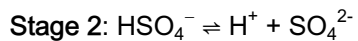
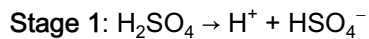


Complete the mechanism by adding equations for **Step 1** and **Step 3** in the boxes below.

Step 1 (slow)	
Step 2 (fast)	$\begin{array}{c} \text{OH}^+ \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array} \longrightarrow \begin{array}{c} \text{OH} \\ \\ \text{H}_3\text{C}-\text{C}=\text{CH}_2 \end{array} + \text{H}^+$
Step 3 (fast)	

[2]

43 When concentrated sulfuric acid is added to water, dissociation takes place in two stages.



(i) $0.100 \text{ mol dm}^{-3}$ sulfuric acid has a pH of 0.96.

Explain this observation. Your answer should include a calculation.

[3]

(ii) A student adds an excess of aqueous sodium carbonate to dilute sulfuric acid.

- Predict what the student would observe.
- Explain what happens to the equilibrium in **Stage 2** as the aqueous sodium carbonate is added.

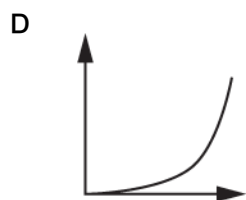
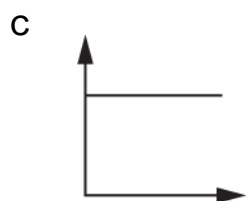
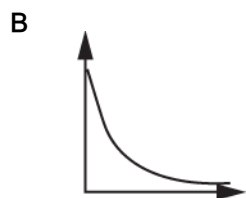
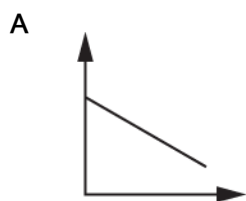
Observation -----

Explanation -----

[2]

44 A reaction is zero order with respect to a reactant A.

Which concentration–time graph for reactant A is the correct shape?



Your answer

[1]

45 HA and HB are two strong monobasic acids.

25.0 cm³ of 6.0 mol dm⁻³ HA is mixed with 45.0 cm³ of 3.0 mol dm⁻³ HB.

What is the H⁺(aq) concentration, in mol dm⁻³, in the resulting solution?

- A 1.9
- B 2.1
- C 4.1
- D 4.5

Your answer

[1]

- 46 A mixture of N_2 and O_2 gases has a total pressure of 1.42 atm.
The mole fraction of N_2 is 0.700.

What is the partial pressure, in atm, of O_2 in the mixture?

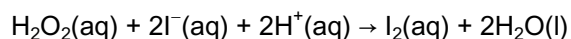
- A 0.211
- B 0.426
- C 0.493
- D 0.994

Your answer

[1]

47(a) This question is about reactions of hydrogen peroxide, H_2O_2 .

Hydrogen peroxide, H_2O_2 , iodide ions, I^- , and acid, H^+ , react as shown in the equation below.



A student carries out several experiments at the same temperature, using the initial rates method, to determine the rate constant, k , for this reaction.

The results are shown below.

Experiment	Initial concentrations			Rate / $10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$
	$[\text{H}_2\text{O}_2(\text{aq})]$ / mol dm^{-3}	$[\text{I}^-(\text{aq})]$ / mol dm^{-3}	$[\text{H}^+(\text{aq})]$ / mol dm^{-3}	
1	0.0100	0.0100	0.100	2.00
2	0.0100	0.0200	0.100	4.00
3	0.0200	0.0100	0.100	4.00
4	0.0200	0.0100	0.200	4.00

(i) Determine the rate equation and calculate the rate constant, k , including units.

$k =$ ----- units ----- [3]

(ii) The rate constant, k , for this reaction is determined at different temperatures, T .

Explain how the student could determine the activation energy, E_a , for the reaction graphically using values of k and T .

[3]

- (b) Peroxycarboxylic acids are organic compounds with the COOOH functional group.

Peroxyethanoic acid, CH₃COOOH, is used as a disinfectant.

- (i) Suggest the structure for CH₃COOOH.

The COOOH functional group must be clearly displayed.

[1]

- (ii) Peroxyethanoic acid can be prepared by reacting hydrogen peroxide with ethanoic acid.

This is a heterogeneous equilibrium.



A 250 cm³ equilibrium mixture contains concentrations of 0.500 mol dm⁻³ H₂O₂(aq) and 0.500 mol dm⁻³ CH₃COOH(aq).

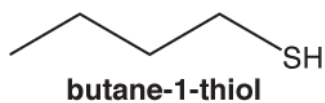
Calculate the amount, in mol, of peroxyethanoic acid in the equilibrium mixture.

amount = -----mol [3]

48 This question is about organic molecules that have a strong smell.

Thiols are foul-smelling, organic sulfur compounds with the functional group -SH .

Butane-1-thiol, shown below, contributes to the strong smell of skunks.



(i) Thiols are weak acids.

Write the expression for the acid dissociation constant, K_a , for butane-1-thiol.

[1]

(ii) Thiols react with carboxylic acids to form thioesters.

Write an equation for the reaction of butane-1-thiol with ethanoic acid.

Use structures for all organic compounds with the functional groups clearly displayed.

[2]

(iii) When beer is exposed to light, 3-methylbut-2-ene-1-thiol is formed, which gives an unpleasant smell and flavour to the beer.

Draw the **skeletal** formula for 3-methylbut-2-ene-1-thiol.

[1]

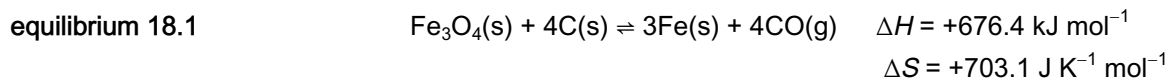
- (iv) Propane-1,3- dithiol reacts with carbonyl compounds in a condensation reaction to form a cyclic organic sulfur product.

Write an equation for the reaction of propane-1,3-dithiol with propanone.

Use structures for organic compounds.

[2]

- 49 Iron can be extracted from its ore Fe_3O_4 using carbon.
Several equilibria are involved including **equilibrium 18.1**, shown below.



- (i) Why is **equilibrium 18.1** a *heterogeneous* equilibrium?

----- [1]

- (ii) Write the expression for K_p for **equilibrium 18.1**.

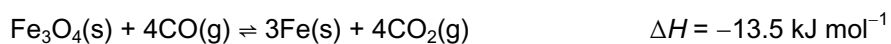
[1]

- (iii) The forward reaction in **equilibrium 18.1** is only feasible at high temperatures.

- Show that the forward reaction is **not** feasible at 25 °C.
- Calculate the minimum temperature, in K, for the forward reaction to be feasible.

minimum temperature = ...K [3]

- (iv) Another equilibrium involved in the extraction of iron from Fe_3O_4 is shown below.



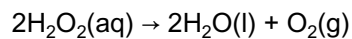
Enthalpy changes of formation, $\Delta_f H$, for $\text{Fe}_3\text{O}_4(\text{s})$ and $\text{CO}_2(\text{g})$ are shown in the table.

Compound	$\Delta_f H / \text{kJ mol}^{-1}$
$\text{Fe}_3\text{O}_4(\text{s})$	-1118.5
$\text{CO}_2(\text{g})$	-393.5

Calculate the enthalpy change of formation, $\Delta_f H$, for CO(g).

$\Delta_f H$, for CO(g) = ... kJ mol⁻¹
[3]

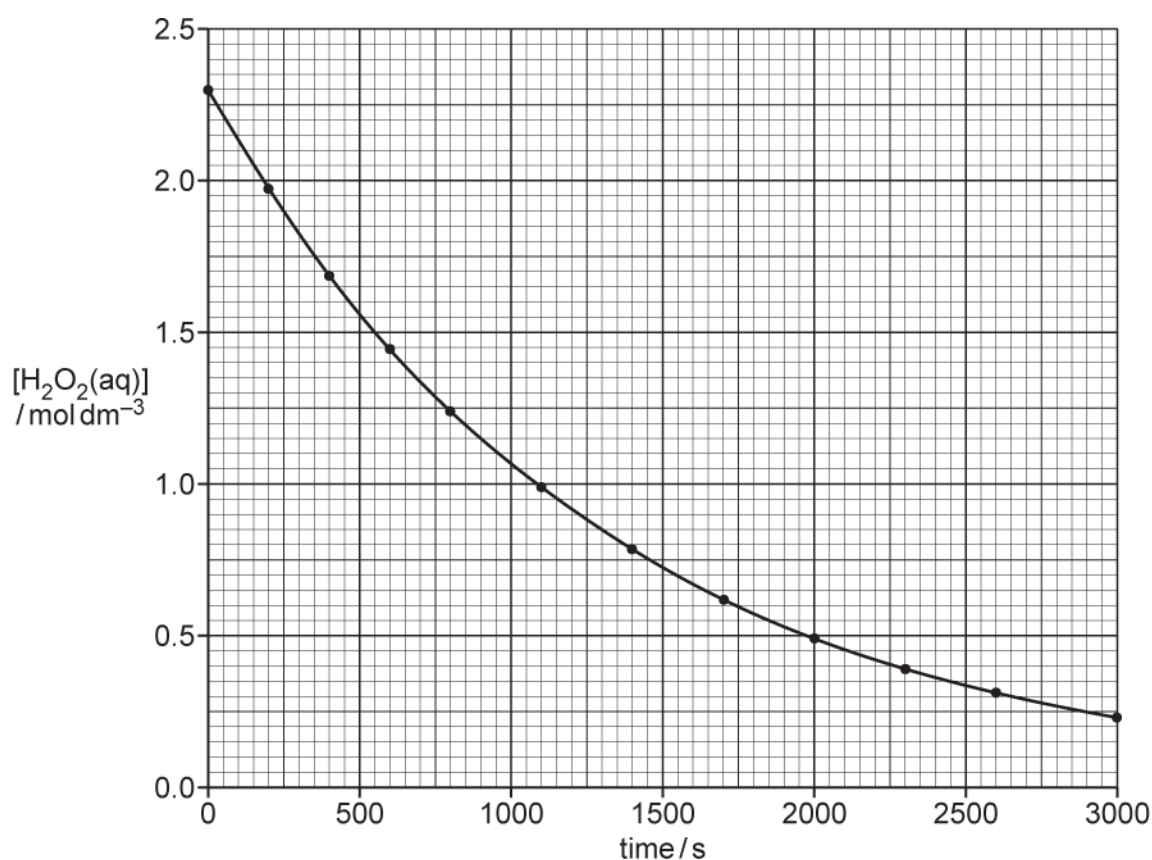
50(a) Aqueous solutions of hydrogen peroxide, $\text{H}_2\text{O}_2(\text{aq})$, decompose as in the equation below.



A student investigates the decomposition of $\text{H}_2\text{O}_2(\text{aq})$ by measuring the volume of oxygen gas produced over time. All gas volumes are measured at room temperature and pressure.

The student uses 25.0 cm^3 of 2.30 mol dm^{-3} H_2O_2 .

From the results, the student determines the concentration of $\text{H}_2\text{O}_2(\text{aq})$ at each time. The student then plots a concentration–time graph.



Suggest apparatus that would allow this gas volume to be collected, indicating clearly the scale of working.

[3]
$$2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$$

The student uses 25.0 cm^3 of $2.30 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$.

Suggest a different experimental method that would allow the rate of this reaction to be followed over time.

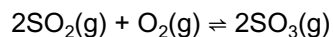
[1]



Your answer must show full working on the graph and on the lines below.

[6]

51 A chemist investigates the equilibrium reaction between sulfur dioxide, oxygen, and sulfur trioxide, shown below.



- The chemist mixes together SO_2 and O_2 with a catalyst.
- The chemist compresses the gas mixture to a volume of 400 cm^3 .
- The mixture is heated to a constant temperature and is allowed to reach equilibrium without changing the total gas volume.

The equilibrium mixture contains 0.0540 mol SO_2 and 0.0270 mol O_2 .

At the temperature used, the numerical value for K_c is $3.045 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$.

(i) Write the expression for K_c and the units of K_c for this equilibrium.

[2]

(ii) Determine the amount, in mol, of SO_3 in the equilibrium mixture at this temperature.

Give your final answer to an **appropriate** number of significant figures.

Show all your working.

equilibrium amount of SO_3 mol [4]

52(a) This question is about the properties and reactions of ethanoic acid, CH_3COOH .

Ethanoic acid is a weak acid with an acid dissociation constant, K_a , of $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ at 25°C .

A student uses a pH meter to measure the pH of a solution of CH_3COOH at 25°C .

The measured pH is 2.440.

Calculate the concentration of ethanoic acid in the solution.

Give your answer to **three** significant figures.

concentration = _____ mol dm^{-3} [3]

(b) Ethanoic acid is a weak acid with an acid dissociation constant, K_a , of $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ at 25°C .

Ethanoic acid is added to another weak acid, fluoroethanoic acid, FCH_2COOH ($K_a = 2.19 \times 10^{-3} \text{ mol dm}^{-3}$).

An equilibrium is set up containing two acid-base pairs.

Complete the equilibrium and label the conjugate acid-base pairs as A1, B1 and A2, B2.



[2]

(c) The student plans to prepare a buffer solution that has a pH of 4.50. The buffer solution will contain ethanoic acid, CH_3COOH , and sodium ethanoate, CH_3COONa .

The student plans to add 9.08 g CH_3COONa to 250 cm^3 of $0.800 \text{ mol dm}^{-3}$ CH_3COOH . The student assumes that the volume of the solution does not change.

- (i) Show by calculation whether, or not, the student's experimental method would produce the required pH.

Show **all** your working.

[5]

- (ii) When the student prepares the buffer solution, the volume of solution increases slightly.

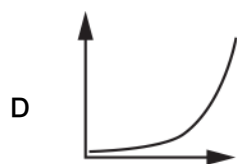
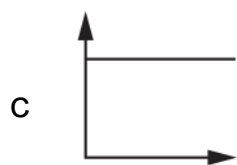
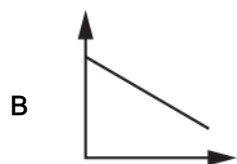
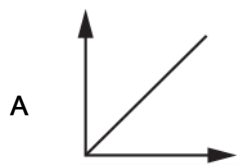
Suggest whether the pH of the buffer solution would be the same, greater than, or less than your calculated value in (c)(i).

Explain your reasoning.

[2]

53 A reaction is first order with respect to a reactant X.

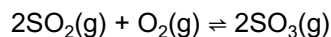
Which rate–concentration graph for reactant X is the correct shape?



Your answer

[1]

54 The reversible reaction of sulfur dioxide and oxygen to form sulfur trioxide is shown below.



An equilibrium mixture contains 2.4 mol SO_2 , 1.2 mol O_2 and 0.4 mol SO_3 .
The total pressure is 250 atm.

What is the partial pressure of SO_3 ?

- A 15 atm
- B 25 atm
- C 100 atm
- D 200 atm

Your answer

[1]

55 A buffer solution is prepared by mixing 200 cm^3 of 2.00 mol dm^{-3} propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, with 600 cm^3 of 1.00 mol dm^{-3} sodium propanoate, $\text{CH}_3\text{CH}_2\text{COONa}$.

K_a for $\text{CH}_3\text{CH}_2\text{COOH} = 1.32 \times 10^{-5} \text{ mol dm}^{-3}$

What is the pH of the buffer solution?

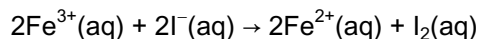
- A 4.58
- B 4.70
- C 5.06
- D 5.18

Your answer

[1]

56(a) This question is about reaction rates.

Aqueous iron(III) ions, $\text{Fe}^{3+}(\text{aq})$, react with aqueous iodide ions, $\text{I}^{-}(\text{aq})$, as shown below.



A student carries out three experiments to investigate how different concentrations of $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^{-}(\text{aq})$ affect the initial rate of this reaction. The results are shown below.

Experiment	$[\text{Fe}^{3+}(\text{aq})]$ / mol dm^{-3}	$[\text{I}^{-}(\text{aq})]$ / mol dm^{-3}	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	4.00×10^{-2}	3.00×10^{-2}	8.10×10^{-4}
2	8.00×10^{-2}	3.00×10^{-2}	1.62×10^{-3}
3	4.00×10^{-2}	6.00×10^{-2}	3.24×10^{-3}

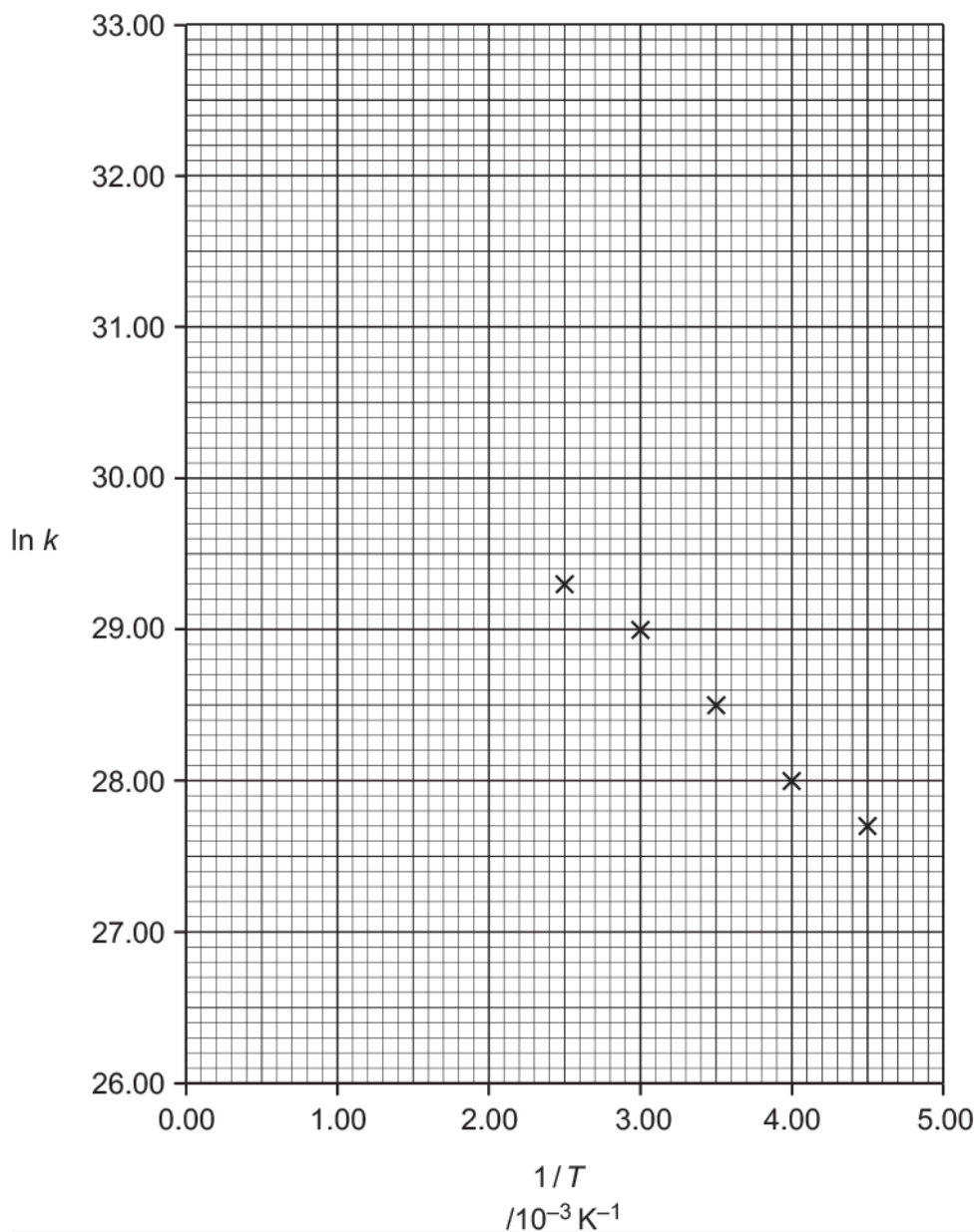
* Determine the rate constant and a possible two-step mechanism for this reaction that are consistent with these results.

[6]

- (b) A student carries out an investigation to find the activation energy, E_a , and the pre-exponential factor, A , of a reaction.

The student determines the rate constant, k , at different temperatures, T .

The student then plots a graph of $\ln k$ against $1/T$ as shown below.



- (i) Draw a best-fit straight line and calculate the activation energy, in J mol^{-1} .
Give your answer to **three** significant figures.

Show your working.

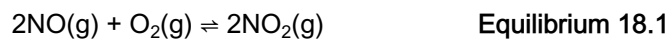
activation energy, $E_a = + \dots\dots\dots \text{J mol}^{-1}$ [3]

- (ii) Use the graph to calculate the value of the pre-exponential factor, A .

Show your working.

pre-exponential factor, $A = \dots\dots\dots$ [2]

57(a) Nitrogen monoxide, NO, and oxygen, O₂, react to form nitrogen dioxide, NO₂, in the reversible reaction shown in equilibrium 18.1.



Write an expression for K_c for this equilibrium and state the units.

$K_c =$

Units = ...

[2]

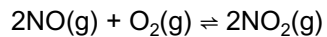
(b) A chemist mixes together nitrogen and oxygen and pressurises the gases so that their total gas volume is 4.0 dm³.

- The mixture is allowed to reach equilibrium at constant temperature and volume.
- The equilibrium mixture contains 0.40 mol NO and 0.80 mol O₂.
- Under these conditions, the numerical value of K_c is 45.

Calculate the amount, in mol, of NO₂ in the equilibrium mixture.

amount of NO₂ = ... mol [4]

(c) The values of K_p for **equilibrium 18.1** at 298 K and 1000 K are shown below.



Equilibrium 18.1

Temperature / K	K_p / atm^{-1}
298	$K_p = 2.19 \times 10^{12}$
1000	$K_p = 2.03 \times 10^{-1}$

(i) Predict, with a reason, whether the forward reaction is exothermic or endothermic.

-----[1]

(ii) The chemist increases the pressure of the equilibrium mixture at the same temperature.

State, and explain in terms of K_p , how you would expect the equilibrium position to change.

-----[3]

58(a) This question is about acids and bases found in the home.

Ethanoic acid, CH_3COOH , is the acid present in vinegar.

A student carries out an experiment to determine the $\text{p}K_{\text{a}}$ value of CH_3COOH .

- The concentration of CH_3COOH in the vinegar is $0.870 \text{ mol dm}^{-3}$.
- The pH of the vinegar is 2.41.

(i) Write the expression for the acid dissociation constant, K_{a} , of CH_3COOH .

[1]

(ii) Calculate the $\text{p}K_{\text{a}}$ value of CH_3COOH .

Give your answer to **two** decimal places.

$\text{p}K_{\text{a}} = \dots\dots\dots$ [3]

(iii) Determine the percentage dissociation of ethanoic acid in the vinegar.

Give your answer to **three** significant figures.

percentage dissociation = $\dots\dots\dots$ % [1]

(b) Many solid drain cleaners are based on sodium hydroxide, NaOH.

- A student dissolves 1.26 g of a drain cleaner in water and makes up the solution to 100.0 cm³.
- The student measures the pH of this solution as 13.48.

Determine the percentage, by mass, of NaOH in the drain cleaner.

Give your answer to **three** significant figures.

percentage = ... % **[4]**

59 Succinic acid (CH₂COOH)₂ is esterified by ethanol, C₂H₅OH, in the presence of an acid catalyst to form an equilibrium mixture.

Succinic acid is esterified by ethanol, C₂H₅OH, in the presence of an acid catalyst to form an equilibrium mixture.

The equilibrium constant, K_c , for this equilibrium can be calculated using the amounts, in moles, of the components in the equilibrium mixture, using **expression 5.1**.

$$K_c = \frac{n((\text{CH}_2\text{COOC}_2\text{H}_5)_2) \times n(\text{H}_2\text{O})^2}{n((\text{CH}_2\text{COOH})_2) \times n(\text{C}_2\text{H}_5\text{OH})^2} \quad \text{Expression 5.1}$$

A student carries out an experiment to determine the value of K_c for this equilibrium.

- The student mixes together 0.0500 mol of succinic acid and 0.150 mol of ethanol, with a small amount of an acid catalyst.
- The mixture is allowed to reach equilibrium.
- The student determines that 0.0200 mol of succinic acid are present in the equilibrium mixture.

(i) Which technique could be used to determine the equilibrium amount of succinic acid?

-----[1]

(ii) Write the equation for the equilibrium reaction that takes place.

-----[1]

(iii) Draw the skeletal formula of the ester present in the equilibrium mixture.

[1]

(iv) K_c is the equilibrium constant in terms of equilibrium concentrations.

Why can **expression 5.1** be used to calculate K_c for this equilibrium?

----- [1]

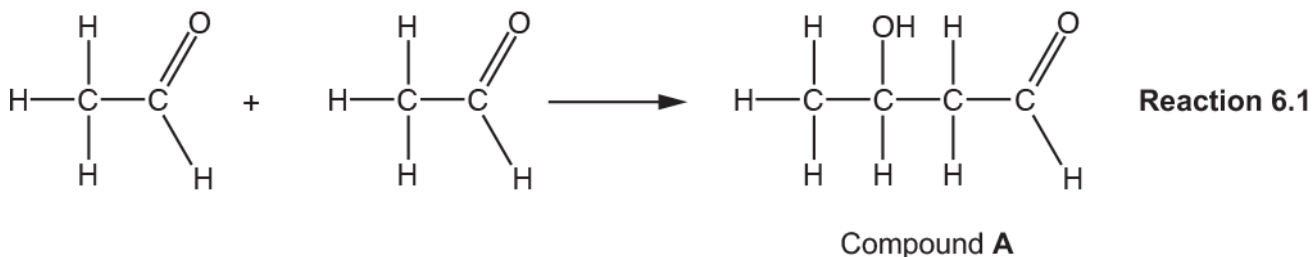
(v) Calculate the value of K_c for this reaction.

Show your working.

$K_c =$ ----- [3]

Compound A is formed when ethanal is mixed with $\text{OH}^-(\text{aq})$ ions, which act as a catalyst.

The balanced equation is shown in **reaction 6.1** below.



(i) Give the systematic name for compound A.

----- [1]

(ii) What type of reaction has taken place?

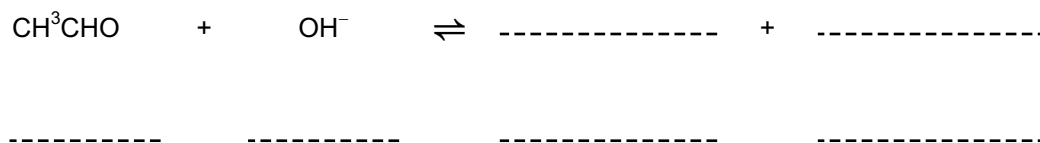
----- [1]

(iii) **Reaction 6.1** takes place in two steps. OH^- ions act as a catalyst.

In **step 1**, ethanal reacts with OH^- ions to set up an acid–base equilibrium.

In **step 2**, compound A is formed.

- Complete the equilibrium for **step 1** and label the conjugate acid–base pairs as: A1, B1 and A2, B2.



- Suggest the equation for **step 2**.

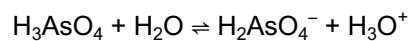
[3]

(iv) A similar reaction takes place when propanone, $(\text{CH}_3)_2\text{CO}$, is mixed with $\text{OH}^-(\text{aq})$ ions.

Draw the structure of the organic product of this reaction.

[1]

61 The equation shows the dissociation of the acid H_3AsO_4 in water.



Which pair is a conjugate acid–base pair?

A H_3AsO_4 and H_2O

B H_2AsO_4^- and H_3O^+

C H_3AsO_4 and H_3O^+

D H_3O^+ and H_2O

Your answer

[1]

62 This question is about making ammonia, NH_3 .

The industrial manufacture of NH_3 from N_2 and H_2 is carried out at an increased temperature and in the presence of a catalyst.

Explain, using Boltzmann distributions, why increasing the temperature and using a catalyst both increase the reaction rate.

63(a) The equilibrium constant K_p and temperature T (in K) are linked by the mathematical relationship shown in equation 5.1 (R = Gas constant in $\text{J mol}^{-1} \text{K}^{-1}$ and ΔH is enthalpy change in J mol^{-1}).

$$\ln K_p = -\frac{\Delta H}{R} \times \frac{1}{T} + \frac{\Delta S}{R} \quad \text{Equation 5.1}$$

The table shows the values of K_p at different temperatures for an equilibrium.

Complete the table by adding the missing values of $\frac{1}{T}$ and $\ln K_p$.

Temperature, T / K	400	500	600	700	800
K_p	3.00×10^{58}	5.86×10^{45}	1.83×10^{37}	1.46×10^{31}	1.14×10^{26}
$\frac{1}{T} / \text{K}^{-1}$	2.50×10^{-3}				
$\ln K_p$	135				

[2]

- (b) State and explain how increasing the temperature affects the position of this equilibrium and whether the forward reaction is exothermic or endothermic.

[1]

(c)

Plot a graph of $\ln K_p$ against $\frac{1}{T}$ using the axes provided on the opposite page.

Use your graph and **equation 5.1** to determine ΔH , in kJ mol^{-1} , for this equilibrium.

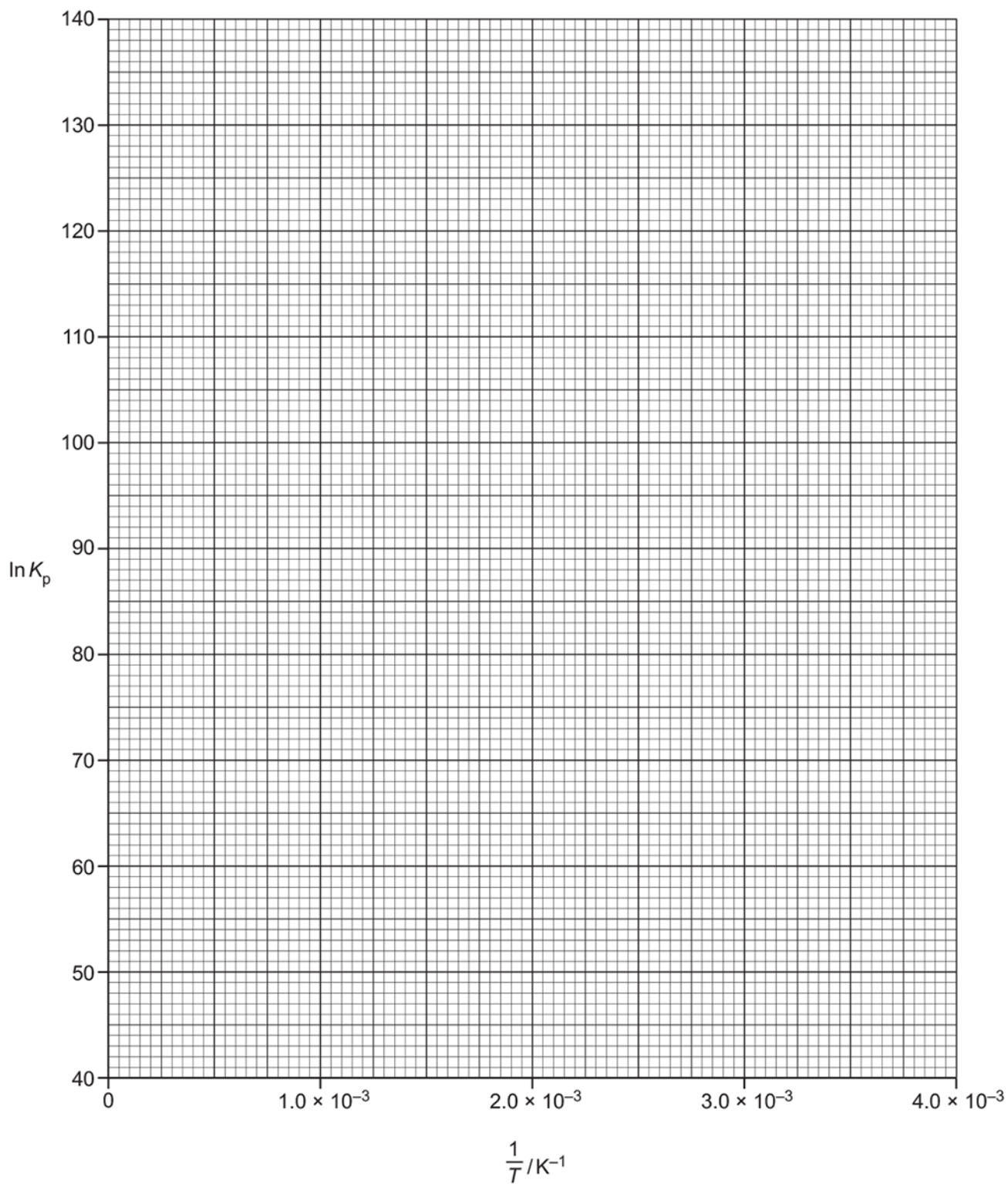
Give your answer to 3 significant figures.

$\Delta H = \dots\dots\dots \text{kJ mol}^{-1}$ [4]

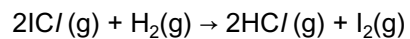
(d)

Explain how ΔS could be calculated from a graph of $\ln K_p$ against $\frac{1}{T}$.

----- [2]



64 The equation for the reaction of ICl and H_2 is shown below.



The rate constant k for this reaction is $1.63 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

What is the overall order of the reaction?

- A 0
- B 1
- C 2
- D 3

Your answer

[1]

65 Which statement(s) is/are correct when a catalyst is added to a system in dynamic equilibrium?

- 1 The rates of the forward and reverse reactions increase by the same amount.
- 2 The concentrations of the reactants and products do not change.
- 3 The value of K_c increases

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

Your answer

[1]

- 66 This question is about reactions and uses of the weak acids methanoic acid, HCOOH , and ethanoic acid, CH_3COOH .

The K_a values of HCOOH and CH_3COOH are shown in Table 18.1.

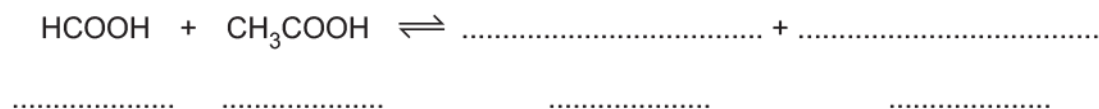
Weak acid	$K_a / \text{mol dm}^{-3}$
HCOOH	1.82×10^{-4}
CH_3COOH	1.78×10^{-5}

Table 18.1

A student adds methanoic acid to ethanoic acid.

An equilibrium is set up containing two acid-base pairs.

Complete the equilibrium and label the conjugate acid-base pairs as A1, B1 and A2, B2.



[2]

67(a) What is the partial pressure of O_2 (in Pa) in a gas mixture containing 21% O_2 by volume and with a total pressure of 1.0×10^5 Pa?

partial pressure of O_2 = ... Pa [1]

(b) A reaction is first order with respect to H^+ . At a pH of 1, the initial rate is $2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

What is the initial rate at a pH of 3?

initial rate = ... $\text{mol dm}^{-3} \text{ s}^{-1}$ [1]

68(a) Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is added to some foods as a preservative.

A student prepares benzoic acid as outlined below.

- Step 1** The student mixes 4.00 cm^3 of phenylmethanol, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, (density = 1.04 g cm^{-3}) with sodium carbonate and aqueous potassium manganate(VII), as an oxidising agent. The mixture is heated under reflux.
- Step 2** The resulting mixture is cooled and then acidified with concentrated HCl . Impure crystals of benzoic acid appear.
- Step 3** The student recrystallises the impure crystals to obtain 1.59 g of pure benzoic acid.

In **Step 1**, sodium carbonate, Na_2CO_3 , makes the reaction mixture alkaline.

Write an ionic equation to show how carbonate ions form an alkaline solution in water.

[1]

- (b) In **Step 2**, explain why the mixture must be acidified so that crystals of benzoic acid appear.

[1]

- (c) Write the overall equation for the preparation of benzoic acid from phenylmethanol.

Use [O] for the oxidising agent.

[1]

(d) Calculate the percentage yield of benzoic acid.

Give your answer to 3 significant figures.

percentage yield = ... % [3]

(e) In **Step 3**, describe how the student can recrystallise the impure crystals to obtain pure benzoic acid.

[2]

69 A graph of $\ln k$ against $\frac{1}{T}$ (T in K) for a reaction has a gradient with the numerical value of -4420 .

What is the activation energy, in kJ mol^{-1} , for this reaction?

- A -532
- B -36.7
- C $+36.7$
- D $+5.32 \times 10^5$

Your answer

[1]

70(a) This question is about weak acids.

The K_a values of three weak acids are shown in Table 20.1.

Weak acid	$K_a / \text{mol dm}^{-3}$
iodic(V) acid, $\text{HIO}_3(\text{aq})$	1.78×10^{-1}
propanoic acid, $\text{C}_2\text{H}_5\text{COOH}(\text{aq})$	1.35×10^{-5}
hydrocyanic acid, $\text{HCN}(\text{aq})$	6.17×10^{-10}

Table 20.1

Calculate the pH of $0.0800 \text{ mol dm}^{-3} \text{C}_2\text{H}_5\text{COOH}(\text{aq})$.

Give your answer to 2 decimal places.

pH = ... [2]

- (b) A student adds a total of 45.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{NaOH}(\text{aq})$ to 25.0 cm^3 of $0.0800 \text{ mol dm}^{-3} \text{C}_2\text{H}_5\text{COOH}(\text{aq})$ and monitors the pH throughout.

- (i) Show by calculation that 20.0 cm^3 of $\text{NaOH}(\text{aq})$ is required to reach the end point.

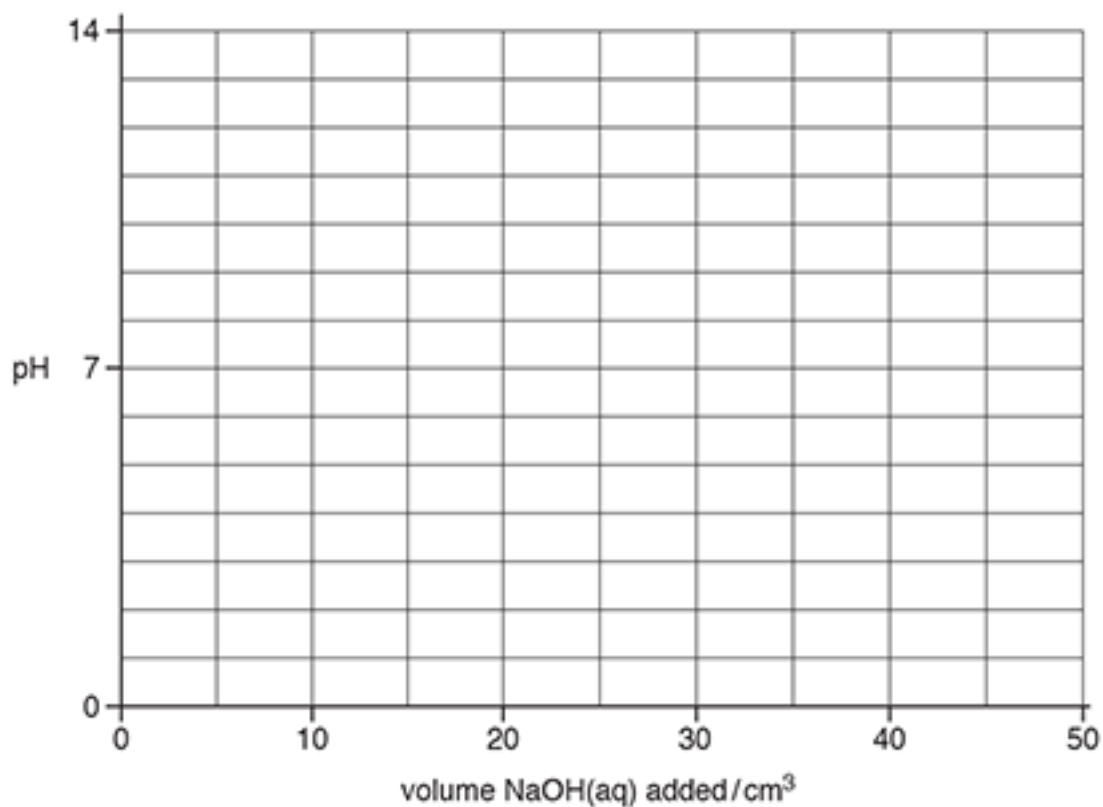
[1]

- (ii) Calculate the pH of the final solution.

Give your answer to 2 decimal places.

pH = ... [4]

- (iii) On the axes below, sketch a pH curve for the pH changes during the addition of 45.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ NaOH(aq) to 25.0 cm^3 of $0.0800 \text{ mol dm}^{-3}$ $\text{C}_2\text{H}_5\text{COOH(aq)}$.



[3]

- (iv) The student considers using the four indicators in **Table 20.2** for the titration.

Indicator	pH range
Cresol red	0.2 – 1.8
Bromophenol blue	3.0 – 4.6
Cresol purple	7.6 – 9.2
Indigo carmine	11.6 – 14.0

Table 20.2

Explain which indicator would be most suitable for the titration.

.....

.....

.....

.....

.....

[1]

- (v) The student repeats the experiment starting with 25.0 cm³ of 0.0800 mol dm⁻³ HCN(aq) and adding a total of 45.0 cm³ of 0.100 mol dm⁻³ NaOH(aq).

Predict **one** similarity and **one** difference between the pH curve with C₂H₅COOH(aq) and the pH curve with HCN(aq). Use the information in **Table 20.1**, and your answer to **(b)(iii)**.

Similarity

Difference

.....

[2]

- (c) The student calculates the pH of $0.0800 \text{ mol dm}^{-3} \text{ HIO}_3(\text{aq})$. The student assumes that the equilibrium concentration of $\text{HIO}_3(\text{aq})$ is the same as the initial concentration of $\text{HIO}_3(\text{aq})$.

The student measures the pH, and finds that the measured pH value is different from the calculated pH value.

Explain why the measured pH is different from the calculated pH.

----- [1]

- 71 Phosphoric acid is a tribasic acid.

What is the mass of $\text{Ca}(\text{OH})_2$ that completely neutralises 100 cm^3 of $0.100 \text{ mol dm}^{-3}$ phosphoric acid?

- A 0.49 g
B 0.74 g
C 1.11 g
D 2.22 g

Your answer

[1]

- 72 A graph is plotted of $\ln(k)$ against $1/T$.
(k = rate constant, T = temperature in K)

The gradient has the numerical value of $-55\,000$.

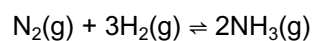
What is the activation energy, in kJ mol^{-1} ?

- A $+1.5 \times 10^{-7}$
B $+2.22 \times 10^{-6}$
C +6.62
D +457

Your answer

[1]

73 The reversible reaction of nitrogen and hydrogen to form ammonia is shown below.



In the equilibrium mixture, the partial pressure of N_2 is 18.75 MPa and the partial pressure of H_2 is 2.50 MPa.
The total pressure is 25 MPa.

What is the value of K_p , in MPa^{-2} ?

- A 1.2×10^{-4}
- B 0.048
- C 0.075
- D 21

Your answer

[1]

74 20 cm^3 of 0.10 mol dm^{-3} hydrochloric acid is added to 10 cm^3 of 0.10 mol dm^{-3} sodium hydroxide.

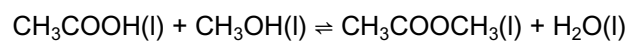
What is the pH of the resulting mixture?

- A 1.00
- B 1.18
- C 1.30
- D 1.48

Your answer

[1]

- 75 A student investigates the reaction between ethanoic acid, $\text{CH}_3\text{COOH}(\text{l})$ and methanol, $\text{CH}_3\text{OH}(\text{l})$, in the presence of an acid catalyst. The equation is shown below.



The student carries out an experiment to determine the value of K_c for this reaction.

The student mixes 9.6 g of CH_3OH with 12.0 g of CH_3COOH and adds the acid catalyst.

When the mixture reaches equilibrium, 0.030 mol of CH_3COOH remains.

Calculate K_c for this equilibrium.

$K_c = \dots\dots\dots$ [4]

76 Healthy human blood needs to be maintained at a pH of 7.40 for the body to function normally.

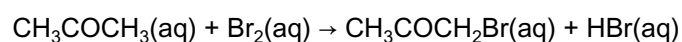
*Carbonic acid, H_2CO_3 , is a weak acid which, together with hydrogencarbonate ions, HCO_3^- , acts as a buffer to maintain the pH of blood.

The $\text{p}K_a$ value for the dissociation of carbonic acid is 6.38.

Explain, in terms of equilibrium, how the carbonic acid–hydrogencarbonate mixture acts as a buffer in the control of blood pH, and calculate the $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio in healthy blood.

[6]

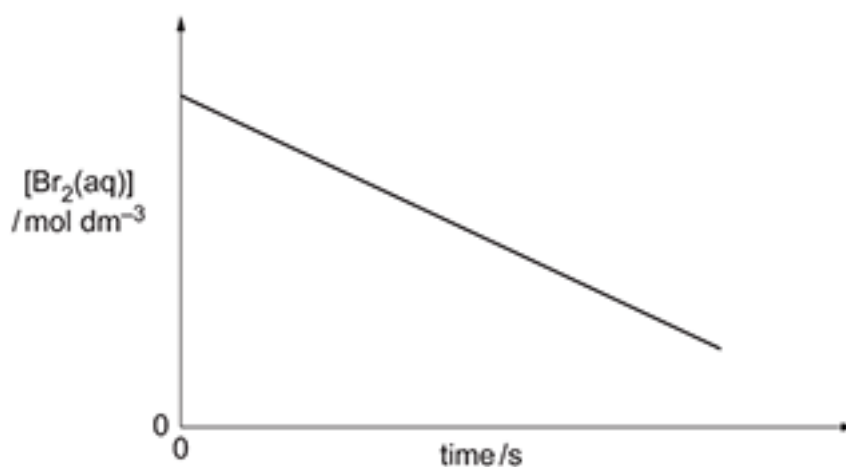
- 77 Three students carry out a rates investigation on the reaction between bromine and propanone in the presence of hydrochloric acid.



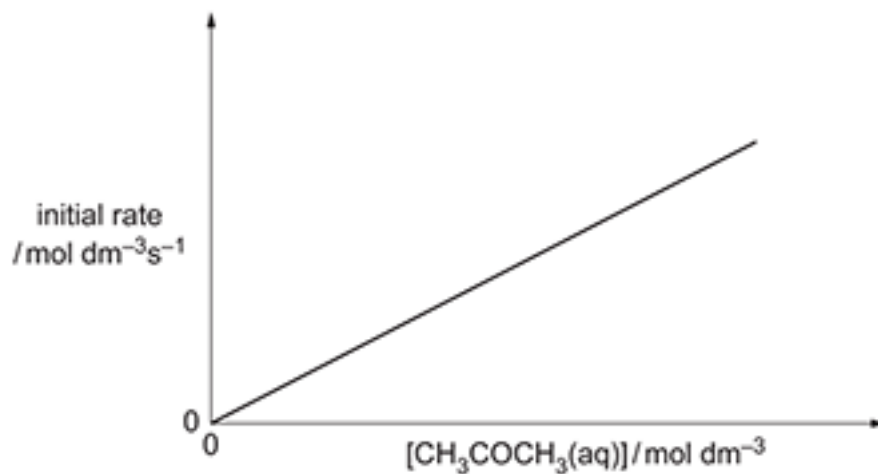
Each student investigates the effect of changing the concentration of one of the reactants whilst keeping the other concentrations constant.

Their results are shown below.

Results of student 1



Results of student 2



Results of student 3

Experiment	$[\text{Br}_2(\text{aq})] / \text{mol dm}^{-3}$	$[\text{CH}_3\text{COCH}_3(\text{aq})] / \text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})] / \text{mol dm}^{-3}$	Initial rate / $10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
1	0.004	1.60	0.20	1.25
2	0.004	1.60	0.40	2.50

Explain how the reaction orders can be determined from the students' results, and determine the rate equation and rate constant.

Blank lined paper for writing.

- 78 This question is about two different types of acid found in organic compounds, carboxylic acids and sulfonic acids, as shown in Fig. 6.1.

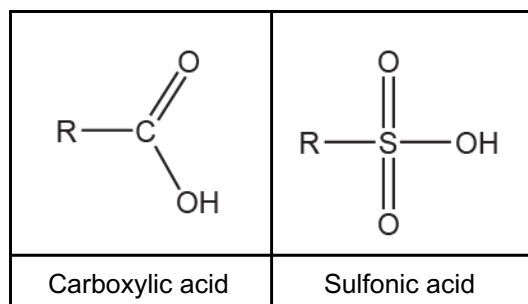


Fig. 6.1

Ethanoic acid, CH_3COOH , and methanesulfonic acid, $\text{CH}_3\text{SO}_2\text{OH}$, are both monobasic acids. The $\text{p}K_{\text{a}}$ values are shown in the table.

Acid		$\text{p}K_{\text{a}}$
Ethanoic acid	CH_3COOH	4.76
Methanesulfonic acid	$\text{CH}_3\text{SO}_2\text{OH}$	-1.90

A student suggests that $1.0 \text{ mol dm}^{-3} \text{CH}_3\text{SO}_2\text{OH}$ should have a lower pH value than $1.0 \text{ mol dm}^{-3} \text{CH}_3\text{COOH}$.

Write an equation, showing conjugate acid–base pairs, for the equilibrium of $\text{CH}_3\text{SO}_2\text{OH}$ with water and explain, with reasons, whether the student is correct.

Label the conjugate acid–base pairs: A1, B1 and A2, B2.

[4]

- 79 Methanol, CH₃OH, can be made industrially by the reaction of carbon monoxide with hydrogen, as shown in **equilibrium 1**.



At 298 K, the free energy change, ΔG , for the production of methanol in **equilibrium 1** is $-2.48 \times 10^4 \text{ J mol}^{-1}$.

ΔG is linked to K_p by the relationship: $\Delta G = -RT \ln K_p$.

R = gas constant

T = temperature in K.

Calculate K_p for **equilibrium 1** at 298 K.

Give your answer to 3 significant figures.

$K_p = \dots\dots\dots$ units $\dots\dots\dots$ [3]

- 80 This question is about reactions and uses of the weak acids methanoic acid, HCOOH , and ethanoic acid, CH_3COOH .

The K_a values of HCOOH and CH_3COOH are shown in Table 18.1.

Weak acid	$K_a / \text{mol dm}^{-3}$
HCOOH	1.82×10^{-4}
CH_3COOH	1.78×10^{-5}

Table 18.1

Use Table 18.1 to answer the following questions.

- (i) The student measures the pH of $\text{CH}_3\text{COOH}(\text{aq})$ as 2.72.

Show that the concentration of the $\text{CH}_3\text{COOH}(\text{aq})$ is $0.204 \text{ mol dm}^{-3}$.

[2]

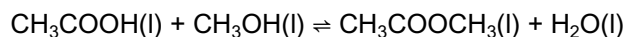
- (ii) The student plans to make a buffer solution of pH 4.00 from a mixture of $\text{CH}_3\text{COOH}(\text{aq})$ and sodium ethanoate, $\text{CH}_3\text{COONa}(\text{aq})$.

The student mixes 400 cm^3 of $0.204 \text{ mol dm}^{-3}$ $\text{CH}_3\text{COOH}(\text{aq})$ with 600 cm^3 of $\text{CH}_3\text{COONa}(\text{aq})$.

Calculate the concentration of $\text{CH}_3\text{COONa}(\text{aq})$ needed to prepare this buffer solution of pH 4.00.

concentration = ... mol dm⁻³ [4]

- 81 A student investigates the reaction between ethanoic acid, $\text{CH}_3\text{COOH}(\text{l})$ and methanol, $\text{CH}_3\text{OH}(\text{l})$, in the presence of an acid catalyst. The equation is shown below.

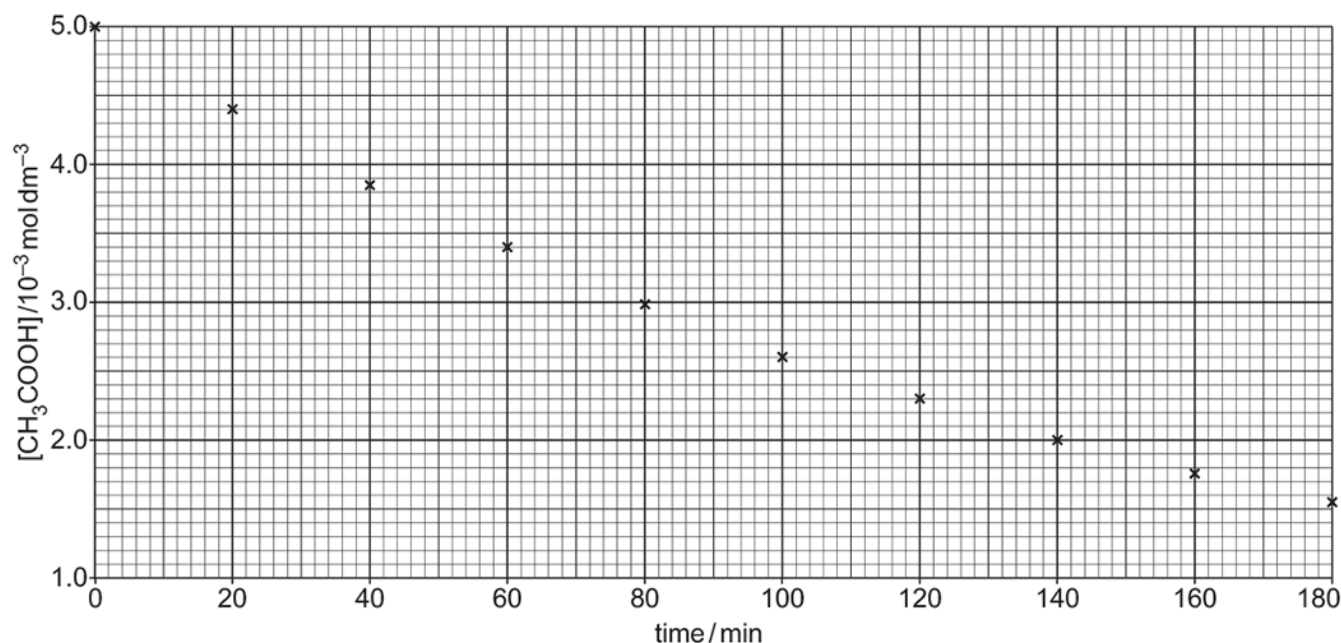


The student carries out an experiment to determine the order of reaction with respect to CH_3COOH .

The student uses a large excess of CH_3OH . The temperature is kept constant throughout the experiment.

The student takes a sample from the mixture every 20 minutes, and then determines the concentration of the ethanoic acid in each sample.

From the experimental results, the student plots the graph below.



- (i) Explain why the student uses a large excess of methanol in this experiment.

[1]

- (ii) Use the half-life of this reaction to show that the reaction is first order with respect to CH_3COOH .

Show your working on the graph and below.

----- [2]

(iii) Determine the initial rate of reaction.

initial rate = ... mol dm⁻³ min⁻¹ [2]

END OF QUESTION PAPER

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
1	a		$(K_c =) \frac{[C_2H_2][H_2]^3}{[CH_4]^2} \checkmark$	1	Square brackets are essential State symbols not required. IGNORE incorrect state symbols Examiner's Comments The K_c expression was shown correctly by almost all candidates, the only mistakes being the very occasional inverted expression or use of '+' within the denominator.
	b	i	amount of $H_2 = 3 \times 0.168$ $= 0.504$ (mol) $\checkmark$	1	Examiner's Comments The correct answer of 0.504 mol was seen in the majority of scripts but examiners were also presented with many other responses. The key was use of the 1:3 molar ratio of C_2H_2 and H_2 formed in the equilibrium mixture, with simple multiplication of 0.168 by 3 giving the correct answer. The commonest incorrect answer was 0.1404 from $3/2 \times 9.36 \times 10^{-2}$: from use the molar ratio of moles CH_4 formed and H_2 formed. Answer: 0.504 mol
		ii	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = $0.153 \text{ mol}^2 \text{ dm}^{-6}$, award 3 marks IF answer = 0.153 with incorrect units, award 2 marks ----- IF answer from 3(b)(i) for $n(H_2) \neq 0.504$, mark by ECF. Equilibrium concentrations (from $n(H_2) = 0.504 \text{ mol dm}^{-3}$) $[CH_4] = 2.34 \times 10^{-2} \text{ (mol dm}^{-3}\text{)}$ AND $[C_2H_2] = 4.20 \times 10^{-2} \text{ (mol dm}^{-3}\text{)}$ AND $[H_2] = 0.126 \text{ (mol dm}^{-3}\text{)} \checkmark$ Calculation of K_c and units $K_c = \frac{4.20 \times 10^{-2} \times (0.126)^3}{(2.34 \times 10^{-2})^2} = 0.153 \checkmark \text{ mol}^2$	3	FULL ANNOTATIONS MUST BE USED ----- IF there is an alternative answer, check to see if there is any ECF credit possible using working below ----- ALLOW $\div$ by 4 of equilibrium amounts in all expressions, i.e. ALLOW $[CH_4] = \frac{9.36 \times 10^{-2}}{4} \text{ mol dm}^{-3}$ AND $[C_2H_2] = \frac{0.168}{4} \text{ mol dm}^{-3}$ AND $[H_2] = \frac{0.504}{4} \text{ mol dm}^{-3} \checkmark$ ALLOW ECF from incorrect concentrations or from moles From moles: 9.36×10^{-2}, 0.168 and 0.504,

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			dm^{-6} ✓ 3 significant figures are required		$K_c = 2.45$ by ECF ALLOW $\text{dm}^{-6} \text{mol}^2$ DO NOT ALLOW mol^2/dm^6 ALLOW ECF from incorrect K_c expression for both calculation and units ----- COMMON ECF From 3(b)(i) answer of 0.1404, $K_c = 3.32 \times 10^{-3}$ 2 marks + units $K_c = 0.0531$ No ÷ 4 throughout 1 mark + units Examiner's Comments Many candidates are well-rehearsed for this type of question. Candidates were expected to use the equilibrium amounts, convert to concentrations by dividing by 4 and to use these values to obtain the K_c value. A common mistake was omission of the concentration stage, leading to a value of 2.45. More calculator errors were seen than in the past, perhaps caused by the cubed power within the numerator. Candidates without a cubed function key on the calculator can simply multiply a value with itself three times. Few candidates failed to express their numerical value for K_c to three significant figures. The units caused few problems although some inverted units were seen. Answer: $0.153 \text{ mol}^2 \text{ dm}^{-6}$

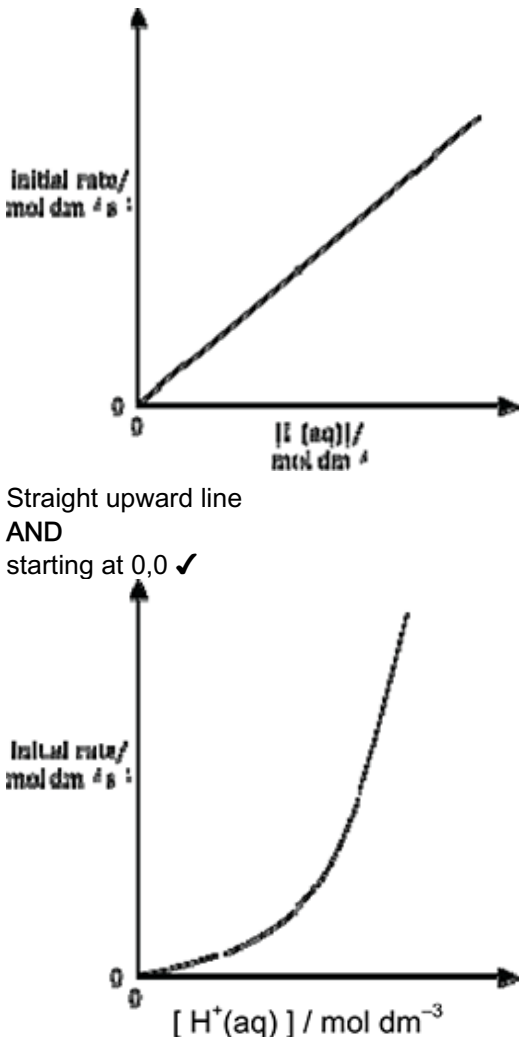
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance																				
		iii	Initial amount of CH ₄ amount of CH ₄ = $9.36 \times 10^{-2} + 2 \times 0.168$ = 0.4296 OR 0.43(0) (mol) ✓	1	NO ECF possible (all data given in question) Examiner's Comments Although this part was more challenging than the initial molar ratio in (b)(i), many candidates were able to work out the amount of CH ₄ that had reacted as $2 \times 9.36 \times 10^{-2}$ and to then add this to the remaining amount of CH ₄ : 9.36×10^{-2} . This part did cause a lot of difficult for weaker candidates with a range of incorrect numerical answers being seen. Answer: 0.4296 mol																				
	C		<table><tr><th>Change</th><th>K_c</th><th>Equilibrium amount of C₂H₂ / mol</th><th>Initial rate</th></tr><tr><td>temperature increased</td><td>greater</td><td>greater</td><td>greater</td></tr><tr><td>smaller container</td><td>same</td><td>smaller</td><td>greater</td></tr><tr><td>catalyst added</td><td>same</td><td>same</td><td>greater</td></tr><tr><td></td><td>✓</td><td>✓</td><td>✓</td></tr></table>	Change	K _c	Equilibrium amount of C ₂ H ₂ / mol	Initial rate	temperature increased	greater	greater	greater	smaller container	same	smaller	greater	catalyst added	same	same	greater		✓	✓	✓	3	Mark by COLUMN ALLOW obvious alternatives for greater / smaller / same, e.g. increases / decreases; more / less Examiner's Comments This part tested candidates understanding of how three quantities would change from changes to experimental conditions. This was marked by column. Of the three quantities, K _c and rate were correct more often than the equilibrium amount of C ₂ H ₂ . This question discriminated extremely well. Strangely, some candidates chose to use their own words instead of those provided and examiners often saw words such as 'increases' and 'decreases'. As the meaning was clear, such responses were still credited.
Change	K _c	Equilibrium amount of C ₂ H ₂ / mol	Initial rate																						
temperature increased	greater	greater	greater																						
smaller container	same	smaller	greater																						
catalyst added	same	same	greater																						
	✓	✓	✓																						
			Total	9																					

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
2	a	i	5 OR 5th (order) ✓	1	Examiner's Comments This part was almost universally correct.
		ii	(stoichiometry in) rate equation does not match (stoichiometry) in overall equation ✓ Collision unlikely with more than 2 ions / species / particles ✓	2	ALLOW moles / ions / species / particles / molecules / atoms throughout (<i>i.e. emphasis on particles</i>) IGNORE more reactants in overall equation If number of species is stated, ALLOW 3–5 only (<i>rate equation contains 5 ions</i>) DO NOT ALLOW negative ions would repel (<i>there is a mixture of positive and negative ions</i>) IGNORE more than two reactants collide (<i>not related to rate equation</i>) Examiner's Comments Able candidates were often able to suggest one of the two acceptable reasons in the mark scheme: different coefficients in the rate and overall equation or the unlikelihood of more than 2 species colliding. Although the reacting species were all ions, the examiners did allow various terms provided that they were indicative of particles. Reactants was not allowed as the reactants in the two equations were the same and collisions are specific to particles.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b		 initial rate/ mol dm⁻³ s⁻¹ 0 0 $[I^{-}(aq)] / \text{mol dm}^{-3}$ Straight upward line AND starting at 0,0 ✓ initial rate/ mol dm⁻³ s⁻¹ 0 0 $[H^{+}(aq)] / \text{mol dm}^{-3}$ Curve with increasing gradient, AND starting at 0,0 ✓	2	ALLOW lines starting close to 0,0 ALLOW 2nd order line with 'straight' section early or late as long as an upward curve is seen between. Examiner's Comments It was common to see correct lines for both graphs. Incorrect sketches often showed curves reminiscent of a half life relationship of an inverse 2nd order curve.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c	i	5.4(0) ✓ 614.4(0) ✓	2	IGNORE sign ALLOW 614 OR 610 Examiner's Comments Able candidate usually obtained both marks but average and weaker candidates often experienced problems, particularly with the rate for Experiment 3. The commonest mistakes stemmed from not using the squared terms in the rate equation, resulting in rates of 1.80 for Experiment 2 and 9.60 for Experiment 3. Other incorrect answers for Experiment 3, such as 21.6 were the result of multiplying the rate in Experiment 1 by various multiples of 4. Answers: Experiment 2, $5.40 \text{ mol dm}^{-3} \text{ s}^{-1}$; Experiment 3, $614.40 \text{ mol dm}^{-3} \text{ s}^{-1}$

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 6.7×10^8 OR 670000000 dm¹² mol⁻⁴ s⁻¹, award 3 marks IF answer = 6.7×10^8 OR 670000000 with incorrect units, award 2 marks <i>k</i> to <2 SF: 666666666.7 ✓ OR <i>k</i> to 2 SF: 6.7×10^8 OR 670000000 ✓✓ units: dm¹² mol⁻⁴ s⁻¹ ✓	3	ALLOW ECF from incorrect initial rates if 1st experimental results have not been used. (Look to 4(c)(i) to check) <i>i.e.</i> IF other rows have been used, then calculate the rate constant from data chosen. For <i>k</i>, ALLOW 1 mark for the following: 6.6×10^8 recurring 6.6×10^8 2 SF answer for <i>k</i> BUT one power of 10 out <i>i.e.</i> 6.7×10^9 OR 6.7×10^7 ALLOW units in any order, e.g. mol⁻⁴ dm¹² s⁻¹ Examiner's Comments Almost all candidates used the information from Experiment 1 to calculate a value for the rate constant. Most were able to obtain 6.6 recurring with most middle and able candidates correctly rounding their answer to the required two significant figures. Weaker responses showed incorrect powers of 10, rounding to two decimal places (in this case three significant figures) and incorrect rounding to 6.6. Rounding and significant figures are a basic GCSE mathematical skill. Candidates are well advised to check any significant figure or decimal place requirements in calculations before moving on the next question. Candidates coped well with the unfamiliar units for the rate constant of a fifth order reaction. The examiners accepted units in any order but the more correct positive before negative order of indices was usually seen. Answer: 6.7×10^8 dm¹² mol⁻⁴ s⁻¹

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iii	$(K_a =) 10^{-3.75}$ OR $1.78 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ $[H^+] = \sqrt{1.78 \times 10^{-4} \times 0.0200}$ $= 1.89 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} \checkmark$ initial rate $= 6.7 \times 10^8 \times 0.01 \times 0.015^2 \times (1.89 \times 10^{-3})^2$ $= 5.33 \times 10^{-3} \text{ to } 5.38 \times 10^{-3} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ OR $5.3 \times 10^{-3} \text{ to } 5.4 \times 10^{-3} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ $\checkmark$ Actual value will depend on amount of acceptable rounding in steps and whether figures kept in calculator even if rounding is written down. ALLOW any value in range given above.	3	FULL ANNOTATIONS MUST BE USED For ALL marks, ALLOW 2 SF up to calculator value correctly rounded $1.77827941 \times 10^{-4}$ ALLOW $\sqrt{10^{-3.75} \times 0.0200}$ for first marking point ALLOW $1.88 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ ALLOW ECF from calculated $[H^+ \text{ (aq)}]$ and calculated answer for k from 4(c)(ii) e.g. If no square root taken, $[H^+] = 3.56 \times 10^{-6} \text{ mol dm}^{-3}$ and $rate = 1.91 \times 10^{-8}$ OR 1.9×10^{-8} by ECF Examiner's Comments This question linked two areas of the specification, pH calculations of weak acids with reaction rates. Overall candidates coped admirably with the challenge and most calculated the $[H^+]$ successfully. Weaker candidates often made no further progress but many candidates then moved forwards to correctly calculate the initial rate. The examiners used the candidate answer from 4(c)(ii) for ECF purposes. Because of the range of possible intermediate roundings in this calculation, a generous range of values was allowed for the initial rate. Answer: $5.33 \times 10^{-3} \text{ to } 5.38 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
			Total	13	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
3	a	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+$ $+ \text{CH}_3\text{COO}^- \checkmark$ Acid 1 Base 2 Acid 2 Base 1 ✓	2	IGNORE state symbols (even if incorrect) ALLOW 1 AND 2 labels the other way around. ALLOW 'just acid' and 'base' labels if linked by lines so that it is clear what the acid—base pairs are ALLOW A and B for 'acid' and 'base' IF proton transfer is wrong way around ALLOW 2nd mark for idea of acid—base pairs, <i>i.e.</i> $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH}_2^+$ $+ \text{OH}^- \times$ Base 2 Acid 1 Acid 2 Base 1 ✓ NOTE For the 2nd marking point (acid—base pairs), this is the ONLY acceptable ECF <i>i.e.</i>, NO ECF from impossible chemistry Examiner's Comments Most candidates showed an acid-base equilibrium involving proton transfer and then identified the acid-base pairs. The acid-base pairs were usually correctly identified but the proton transfer was sometimes shown the wrong way round. Common errors included omission of a positive charge on H_3O^+ and an equilibrium involving OH^- ions rather than water. Neither approach could be credited.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b	i	Water dissociates / ionises OR $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ OR $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ ✓	1	ALLOW $K_w = [\text{H}^+][\text{OH}^-]$ OR $[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ (mol}^2 \text{ dm}^{-6}\text{)}$ IGNORE breaking for dissociation IGNORE water contains H^+ and OH^- IGNORE $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ <i>i.e. no equilibrium sign</i> IGNORE $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ <i>i.e. no equilibrium sign</i> Examiner's Comments The key required feature was the dissociation of water but many instead discussed dissociation of the acid.
		ii	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 1.15×10^{-11}, award 2 marks ----- $[\text{H}^+] = 10^{-3.06} = 8.71 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ $[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{8.71 \times 10^{-4}} = 1.15 \times 10^{-11} \text{ (mol dm}^{-3}\text{)} \checkmark$ ALLOW answer to two or more significant figures 2SF: 1.1×10^{-11}; 4SF: 1.148×10^{-11}; calculator $1.148153621 \times 10^{-11}$	2	IF there is an alternative answer, check to see if there is any ECF credit possible using working below. ----- ALLOW 2 SF: 8.7×10^{-4} up to calculator value of 8.7096359×10^{-4} correctly rounded ALLOW alternative approach using pOH: $\text{pOH} = 14 - 3.06 = 10.94 \checkmark$ $[\text{OH}^-] = 10^{-10.94} = 1.15 \times 10^{-11} \text{ (mol dm}^{-3}\text{)} \checkmark$ Examiner's Comments The majority of candidates correctly calculated the hydroxide ion concentration via K_w. Another less popular but successful approach was via pOH. Either approach could result in both marks. Weaker candidates were successful in calculating the hydrogen ion concentration but this was then often shown also as the hydroxide ion concentration in the final answer. Answer: $1.15 \times 10^{-11} \text{ mol dm}^{-3}$

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c	i	$2\text{CH}_3\text{COOH} + \text{CaCO}_3 \rightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{CO}_2 + \text{H}_2\text{O} \checkmark$	1	IGNORE state symbols ALLOW $\rightleftharpoons$ provided that reactants on LHS For $\text{CO}_2 + \text{H}_2\text{O}$, ALLOW H_2CO_3 ALLOW $\text{Ca}(\text{CH}_3\text{COO})_2$ ALLOW $(\text{CH}_3\text{COO}^-)_2\text{Ca}^{2+}$ BUT DO NOT ALLOW if either charge is missing or incorrect Examiner's Comments The equations seen were certainly better than in previous sessions, perhaps as candidates will have practised similar questions from past papers. Ionic signs within the formula of calcium ethanoate were allowed but both were then needed. Common errors included an incorrect formula of calcium ethanoate with one ethanoate group only and an unbalanced ethanoic acid on the left-hand side of the equation.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	solution contains CH_3COOH AND CH_3COO^- ✓	1	ALLOW names: ethanoic acid for CH_3COOH ethanoate for CH_3COO^- ALLOW calcium ethanoate OR $(\text{CH}_3\text{COO})_2\text{Ca}$ for CH_3COO^- IGNORE 'acid, salt, conjugate base; responses must identify the acid and conjugate base as ethanoic acid and ethanoate IGNORE ethanoic acid is in excess (<i>in question</i>) BUT DO ALLOW some ethanoic acid is left over / present / some ethanoic acid has reacted IGNORE equilibrium: $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$ <i>Dissociation of ethanoic acid only</i> Examiner's Comments The mark scheme was specific in wanting the names or formulae of the components of the buffer solution and also the idea that some ethanoic acid remains. More general responses in terms of an acid and its conjugate base were not credited.
		iii	Quality of written communication, QWC 2 marks are available for explaining how the equilibrium system allows the buffer solution to control the pH on addition of H^+ and OH^- (see below) ----- $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$ ✓ ----- CH_3COOH reacts with added alkali OR $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow$ OR added alkali reacts with H^+ OR $\text{H}^+ + \text{OH}^- \rightarrow$ ✓	5	FULL ANNOTATIONS MUST BE USED ----- -- Note: If there is no equilibrium equation then the two subsequent equilibrium marks are not available: max 2 DO NOT ALLOW $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ DO NOT ALLOW more than one equilibrium equation. ----- ALLOW response in terms of H^+, A^- and HA IF more than one equilibrium shown, it must be clear which one is being referred to by labeling the equilibria.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			Equilibrium → right OR Equilibrium → CH_3COO^- ✓ (QWC) CH_3COO^- reacts with added acid ✓ Equilibrium → left OR Equilibrium → CH_3COOH ✓ (QWC)		ALLOW weak acid reacts with added alkali DO NOT ALLOW acid reacts with added alkali ALLOW conjugate base reacts with added acid DO NOT ALLOW salt / base reacts with added acid Examiner's Comments The role of buffers in controlling pH is a common recall question and most candidates had prepared their rehearsed answers. Well-prepared candidates were thus able to collect full or nearly full marks for this part. There was a significant minority of candidates who had obviously not learnt this part of the specification and, despite their best efforts to invent answers, there was rarely anything that the examiners could credit. This was a great pity because marks were effectively being thrown away. Candidates are recommended to construct their responses using the weak acid equilibrium equation only. Some candidates shown both the correct relevant equilibrium but also others, including for calcium ethanoate. Subsequent explanations in terms of equilibrium were then ambiguous as the examiner could not tell which equilibrium was being discussed. Some candidates thankfully did label and reference multiple equilibria so that some credit could be awarded.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
d	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 11.48 OR 11.5 (g), award 5 marks ----- $[H^+] = 10^{-5} \text{ (mol dm}^{-3}\text{)} \checkmark$ ----- $[CH_3COO^-] = \frac{1.75 \times 10^{-5}}{0.350 \text{ mol dm}^{-3}} \checkmark \times 0.200 = 10^{-5} \checkmark$ $n(CH_3COONa / CH_3COO^-) \text{ in } 400 \text{ cm}^3$ $= 0.350 \times \frac{400}{1000} = 0.14(0) \text{ (mol)} \checkmark$ ----- mass $CH_3COONa = 0.140 \times 82.0 = 11.48$ OR 11.5 (g) $\checkmark$ For ECF, $n(CH_3COONa/CH_3COO^-)$ must have been calculated in step before	5	FULL ANNOTATIONS MUST BE USED ----- IF there is an alternative answer, check to see if there is any ECF credit possible. Incorrect use of $[H^+] = \sqrt{([CH_3COOH] \times K_a)}$ scores zero BUT IGNORE if an alternative successful method is present Incorrect use of K_w, 1 max for $[H^+] = 10^{-5} \text{ (mol dm}^{-3}\text{)}$ BUT IGNORE if an alternative successful method is present ----- ALLOW $n(CH_3COONa / CH_3COO^-)$ $= \frac{1.75 \times 10^{-5}}{10^{-5}} \checkmark \times 0.08 = 0.14(0) \text{ (mol)}$ $\checkmark \checkmark$ Note: There is no mark just for $n(CH_3COOH) \text{ in } 400 \text{ cm}^3 = 0.200 \times \frac{400}{1000} = 0.08 \text{ (mol)}$ ----- As alternative for the 4th and 5th marks, ALLOW: mass of $CH_3COONa \text{ in } 1 \text{ dm}^3 = 0.350 \times 82.0 = 28.7 \text{ g} \checkmark$ mass of $CH_3COONa \text{ in } 400 \text{ cm}^3 = 28.7 \times \frac{400}{1000} = 11.48 \text{ g} \checkmark$ ----- COMMON ECF 4.592 OR 4.6 g AWARD 4 marks use of 400 / 1000 twice ALLOW variants of Henderson—Hasselbalch equation. $pK_a = -\log(1.75 \times 10^{-5}) = 4.757 \checkmark$ Calc: 4.75696. ...

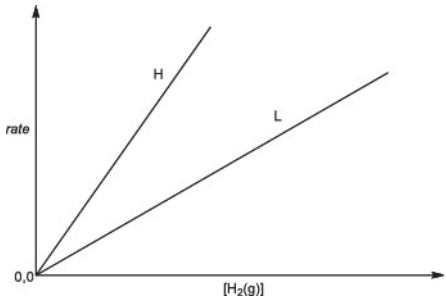
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pH} - \text{p}K_a = 5 - 4.757$ $= 0.243$ $\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 10^{0.243} = 1.75 \checkmark$ $[\text{CH}_3\text{COO}^-] = 1.75 \times 0.200 = 0.350 \text{ mol dm}^{-3} \checkmark$ $n(\text{CH}_3\text{COONa}/\text{CH}_3\text{COO}^-) \text{ in } 400 \text{ cm}^3$ $= 0.350 \times \frac{400}{1000} = 0.14(0) \text{ (mol)} \checkmark$ ----- $\text{mass CH}_3\text{COONa} = 0.140 \times 82.0 = 11.48$ OR 11.5 (g) $\checkmark$ Examiner's Comments Able candidates answered this question with comparative ease, collecting all five marks for a carefully constructed answer. This was in contrast to weaker candidate who struggled, often resorting to the 'square root' method for calculating the pH of a weak acid. The calculation started off with an easy mark for calculating the hydrogen ion concentration from the pH. Unfortunately, this 'square root' method then resulted in another hydrogen ion concentration which contradicted the original. Other weak candidates resorted to use of K_w. The result was that weaker candidates would often score no marks at all for this part. Many candidates were aware of the importance of the acid/base ratio in buffer calculations and were able to gain at least some marks for this part. The commonest error in partially successful responses was with the scaling factor of 400/1000, being either omitted to give an answer of 28.7 g, or used twice to give an answer of 4.952 g Answer: 11.48 g
			Total	17	

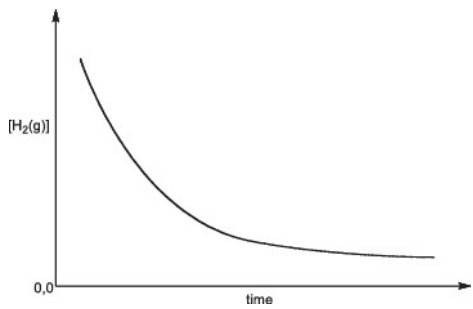
Mark Scheme

Question		Answer/Indicative content	Marks	Guidance																																
4	a	NOTE: First 3 marks are ONLY available from an expression using [NO]² Units are marked independently ----- Using values ON THE CURVE in CORRECT expression 1 mark Use of any two correct values for rate and [NO] from graph e.g. for 5.0 × 10⁻⁴ and 4.2 × 10⁻⁴, $k = \frac{6.0 \times 10^{-4}}{(2.0 \times 10^{-2}) \times (6.0 \times 10^{-4})^2}$ OR 4.2 × 10⁻⁴ = k (2.0 × 10⁻²) × (5.0 × 10⁻⁴)² ✓ ----- Calculation of k 2 marks FOR 1 MARK k calculated correctly from values obtained from graph BUT NOT in standard form AND / OR more than 2 SF e.g. $k = \frac{6.0 \times 10^{-4}}{(2.0 \times 10^{-2}) \times (6.0 \times 10^{-4})^2} = 83333.33$ ✓ OR FOR 2 MARKS k calculated correctly from values obtained from graph AND in standard form AND TO 2 SF e.g. k = 83333.33 gives 8.3 × 10⁴ ✓ ----- UNITS FOR 1 MARK: dm⁶ mol⁻² s⁻¹ ✓	4	Note: rate and [NO] are any correct pair of readings from the graph, The [NO] below are the most commonly seen. For these [NO] values, these are the ONLY rates allowed <table><tr><th>[NO]</th><th>rate</th><th>k</th><th>k</th></tr><tr><td>1.0 × 10⁻⁴</td><td>0.1 × 10⁻⁴ to 0.2 × 10⁻⁴</td><td>50000 100000</td><td>5.0 × 10⁴ 1.0 × 10⁵</td></tr><tr><td>2.0 × 10⁻⁴</td><td>0.6 × 10⁻⁴ to 0.7 × 10⁻⁴</td><td>75000 87500</td><td>7.5 × 10⁴ 8.8 × 10⁴</td></tr><tr><td>3.0 × 10⁻⁴</td><td>1.5 × 10⁻⁴</td><td>83333</td><td>8.3 × 10⁴</td></tr><tr><td>4.0 × 10⁻⁴</td><td>2.7 × 10⁻⁴</td><td>84375</td><td>8.4 × 10⁴</td></tr><tr><td>5.0 × 10⁻⁴</td><td>4.2 × 10⁻⁴</td><td>84000</td><td>8.4 × 10⁴</td></tr><tr><td>6.0 × 10⁻⁴</td><td>6.0 × 10⁻⁴</td><td>83333</td><td>8.3 × 10⁴</td></tr><tr><td>7.0 × 10⁻⁴</td><td>8.2 × 10⁻⁴</td><td>83673</td><td>8.4 × 10⁴</td></tr></table> IF OTHER values are given, mark using the same principle. If any doubt, contact TL. NOTE: IGNORE any numbers used from tangents ----- SPECIAL CASES that ALLOW ECF for calculation of k from ONLY ONE of the following (2 marks) 1. Powers of 10 incorrect or absent in initial k expression 2. [H₂]²[NO] used instead of [H₂][NO]². 3. Any value within ±0.2 of actual values from graph ----- ALLOW units in any order, e.g. mol⁻² dm⁶ s⁻¹ Examiner's Comments This part required candidates to calculate a rate constant from a rate–concentration graph and a rate equation. Most candidates were able to obtain correct values from the rate–concentration graph, with a tolerance of ±0.1 allowed, and to calculate a value for the rate constant; three or four marks were common. In the calculation, almost all candidates were able to rearrange the rate equation	[NO]	rate	k	k	1.0 × 10 ⁻⁴	0.1 × 10 ⁻⁴ to 0.2 × 10 ⁻⁴	50000 100000	5.0 × 10 ⁴ 1.0 × 10 ⁵	2.0 × 10 ⁻⁴	0.6 × 10 ⁻⁴ to 0.7 × 10 ⁻⁴	75000 87500	7.5 × 10 ⁴ 8.8 × 10 ⁴	3.0 × 10 ⁻⁴	1.5 × 10 ⁻⁴	83333	8.3 × 10 ⁴	4.0 × 10 ⁻⁴	2.7 × 10 ⁻⁴	84375	8.4 × 10 ⁴	5.0 × 10 ⁻⁴	4.2 × 10 ⁻⁴	84000	8.4 × 10 ⁴	6.0 × 10 ⁻⁴	6.0 × 10 ⁻⁴	83333	8.3 × 10 ⁴	7.0 × 10 ⁻⁴	8.2 × 10 ⁻⁴	83673	8.4 × 10 ⁴
[NO]	rate	k	k																																	
1.0 × 10 ⁻⁴	0.1 × 10 ⁻⁴ to 0.2 × 10 ⁻⁴	50000 100000	5.0 × 10 ⁴ 1.0 × 10 ⁵																																	
2.0 × 10 ⁻⁴	0.6 × 10 ⁻⁴ to 0.7 × 10 ⁻⁴	75000 87500	7.5 × 10 ⁴ 8.8 × 10 ⁴																																	
3.0 × 10 ⁻⁴	1.5 × 10 ⁻⁴	83333	8.3 × 10 ⁴																																	
4.0 × 10 ⁻⁴	2.7 × 10 ⁻⁴	84375	8.4 × 10 ⁴																																	
5.0 × 10 ⁻⁴	4.2 × 10 ⁻⁴	84000	8.4 × 10 ⁴																																	
6.0 × 10 ⁻⁴	6.0 × 10 ⁻⁴	83333	8.3 × 10 ⁴																																	
7.0 × 10 ⁻⁴	8.2 × 10 ⁻⁴	83673	8.4 × 10 ⁴																																	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					and to calculate a value for the rate constant, although this was not always expressed to two significant figures and to standard form. A significant number of candidates omitted one or both the powers of 10 for rate and concentration in their calculation. Answers: The value of k allowed depended on the values of rate and concentration that had been used from the supplied graph and the required value of k was usually either 8.3×10^4 or $8.3 \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. This part was almost universally correct. The commonest error was two upwardly sloping curves, starting from the origin, and this response was awarded one mark.
	b	i	 One straight upward line AND starting at 0,0 ✓ 2nd straight upward line starting at 0,0 and steeper AND Steeper line labelled H OR less steep line labelled L ✓	2	ALLOW 1 mark for two upward sloping curves starting at origin AND upper curve labelled H and lower curve labelled L NOTE: ALLOW some leeway for lines starting from origin ALLOW straight line not drawn with ruler, i.e. is a straight line rather than a curve ALLOW similar labelling as long as it is clear which line is which
		ii	increases ✓	1	Examiner's Comments Almost all candidates were aware that a rate constant increases in value with increasing temperature.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c		MARK INDEPENDENTLY -----  Downward curve ✓ Half life is constant ✓	2	ALLOW curve touching y axis ALLOW curve touching x axis ALLOW Two half lives are the same IGNORE 'regular' half life (not necessarily the same) Examiner's Comments This part was answered extremely well, with the expected downward slope and a comment about a constant half-life. Comparatively few incorrectly shaped lines were seen.
	d	i	$\text{H}_2 + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O}$ ✓	1	ONLY correct answer DO NOT ALLOW multiples Examiner's Comments Most candidates were aware that the equations for the three steps must add to give the overall equation and the majority of candidates obtained the correct equation.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	Steps 1 AND Step 2 together give $2\text{NO} + \text{H}_2$ ✓	1	ALLOW Step 1 AND Step 2 together give species in same ratio as in rate equation ALLOW rate-determining step / slow step for Step 2 ALLOW H_2 reacts with N_2O_2 which is formed from 2NO NOTE: The response must link Step 1 with Step 2 Steps can be referenced from the species in each step Examiner's Comments Candidates found this part far more difficult. Most were clearly expecting to answer in terms of the species in the slow step being present in the rate equation and many responded in this way. This strategy will only work if the slow step is also the first step. Only the best candidates were able to interpret the data, explaining that N_2O_2 in the slow step had been formed from 2NO in the preceding fast step.
			Total	11	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
5	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = $57.6 \text{ dm}^3 \text{ mol}^{-1}$, award 6 marks IF answer = 57.6 with incorrect units, award 5 mark ----- Equilibrium amounts in mol 2 MARKS $n(\text{SO}_2) = 0.180$ ALL 3 correct: ✓✓ (mol) $n(\text{O}_2) = 0.090$ ANY 2 correct: ✓ (mol) $n(\text{SO}_3) = 0.820$ (mol) Equilibrium concentrations (moles $\times$ 4) 1 MARK $\text{SO}_2 = 0.720 \text{ (mol dm}^{-3}\text{)}$ AND $\text{O}_2 = 0.360 \text{ (mol dm}^{-3}\text{)}$ AND $\text{SO}_3 = 3.28 \text{ (mol dm}^{-3}\text{)}$ ✓ Calculation of K_c and units 3 MARKS $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$ OR $\frac{3.28^2}{(0.720)^2 \times (0.360)}$ ✓ $= 57.6 \text{ ✓ dm}^3 \text{ mol}^{-1} \text{ ✓}$ <i>At least 3SF is required</i>	6	FULL ANNOTATIONS NEEDED IF there is an alternative answer, check to see if there is any ECF credit possible using working below ----- ALLOW ECF from incorrect moles of SO_2, O_2 AND SO_3 ALL three concentrations required for this mark ALLOW ECF from incorrect concentrations NO ECF for numerical value with a square missing For K_c, ALLOW 3 significant figures up to calculator value of 57.64746228 correctly rounded For units, ALLOW $\text{mol}^{-1} \text{ dm}^3$ DO NOT ALLOW dm^3 / mol ALLOW ECF from incorrect K_c expression for both calculation and units COMMON ERRORS 0.0294 3 marks + units mark from $\text{SO}_2 = 0.820$, $\text{O}_2 = 0.410$, $\text{SO}_3 = 0.180$ (mol) Examiner's Comments Many candidates are now well-rehearsed for this type of question. Candidates were expected to determine the equilibrium amounts, convert to concentrations by multiplying by 4 or dividing by 0.250, and to use the concentration values to obtain the K_c value. Three easy marks were available for the K_c expression, a correct calculation using calculated concentrations, and the units. As expected the equilibrium amounts caused the biggest problems for

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					candidates. Most correctly obtained 0.180 mol for SO₂ and 0.820 mol for SO₃ (although some had these reversed or even the same). The amount of O₂ was often incorrect with 0.410 mol (0.500 – 0.090), rather than 0.090 mol, being commonly seen. The majority used 1000/250 or ÷ 0.250 to calculate concentrations from their equilibrium amounts. Some omitted this stage whilst other just divided by 250 or multiplied instead of dividing. Throughout, the examiners marked consequentially so that an individual error was not repeatedly penalised. Consequently the majority of candidates scored 4–6 marks for this part. Answer: $K_c = 57.6 \text{ dm}^3 \text{ mol}^{-1}$
		ii	(Pressure) decreases AND fewer molecules / moles ✓	1	For fewer moles, ALLOW 3 mol → 2 mol ALLOW more moles of reactants Examiner's Comments Surprisingly this part presented problems to many candidates. The examiners were expecting to see a response in terms of a decreased pressure from the presence of fewer gas molecules. However, many candidates responded with an increase or even the same pressure. This question discriminated extremely well.
		iii	ΔH is negative / '–' / –ve AND yield of SO ₃ decreases ✓	1	IGNORE exothermic and endothermic Examiner's Comments Candidates had far more success with this part, with the vast majority responding with a negative ΔH value and decreased yield of SO₃. Weaker candidates often used exothermic (or even endothermic) instead and obtained the incorrect effect.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iv	IGNORE le Chatelier responses ----- <i>Each marking point is independent</i> K_c K_c does not change (with pressure / concentration) ✓ <i>Comparison of conc terms with more O_2</i> $[O_2]$ / concentration of oxygen is greater OR denominator / bottom of K_c expression is greater ✓ <i>QWC: yield of SO_3 linked to K_c</i> (Yield of) SO_3 is greater / increases AND	3	FULL ANNOTATIONS NEEDED ALLOW K_c only changes with temperature IF 1st marking point has been awarded, IGNORE comments about 'K_c decreasing' or 'K_c increasing' and assume that this refers to how the ratio subsequently changes. i.e DO NOT CON 1st marking point. IGNORE O_2 is greater / increases ALLOW (Yield of) SO_3 is greater / increases AND
		iv	numerator / top of K_c expression is greater / increases ✓		to reach / restore K_c value ✓ Examiner's Comments Explaining shifts in equilibrium in terms of K_c is far more difficult than the simpler le Chatelier approach. The examiners were impressed by the responses from able candidates with some excellent explanations comparing the values of the denominator and numerator between the two experiments and the consequential effect on the concentration of SO_3. Many responses did state that K_c is unaffected by changes in concentration or pressure but the explanation then used le Chatelier's principle. This part discriminated extremely well and unfortunately weaker candidates often failed to score.
			Total	11	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
6	a		Proton / H ⁺ donor AND Partially dissociates / ionises ✓	1	Examiner's Comments For most candidates, this was an easy mark, although some only responded for a weak acid (partial dissociation) or for a Brønsted–Lowry acid (proton donor).
	b		FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 13.7(0), award 2 marks ----- $[H^+] = \frac{1.00 \times 10^{-14}}{0.5(00)} \text{ OR } 2(.00) \times 10^{-14} \text{ (mol dm}^{-3}\text{)} \checkmark$ $\text{pH} = -\log 2(.00) \times 10^{-14} = 13.7(0) \checkmark$	2	 For pOH method:, ALLOW pOH = $-\log[OH^-] = 0.3(0) \checkmark$ (calculator 0.301029995) ALLOW pH = $14 - 0.3 = 13.7 \checkmark$ ALLOW 13.7 up to calculator value of 13.69897 correctly rounded. ALLOW ECF from incorrect [H ⁺ (aq)] provided that pH > 7 Examiner's Comments The majority of candidates correctly calculated the pH via K_w . Another less popular but successful approach was via pOH. Either approach could result in both marks. Weaker candidates sometimes calculated the pH as 0.30 (from $-\log 0.500$). This gained no credit. Answer: pH = 13.70

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c	i	$(K_a =) \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]} \checkmark$	1	IGNORE $\frac{[H^+]^2}{[C_2H_5COOH]}$ OR $\frac{[H^+][A^-]}{[HA]}$ ALLOW $[H_3O^+]$ for $[H^+]$ IGNORE state symbols Examiner's Comments Almost all candidates successfully wrote the expression for K_a. Responses using $[H^+(aq)]^2$ were not credited. Rarely, the expression was shown inverted or square brackets were omitted from one or more of the terms. Candidates are recommended to carefully check the formulae as this easy mark was sometimes not awarded for a missing C atom within a formula (even in the scripts of able candidates).
		ii	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.9(0), award 3 marks $[C_2H_5COOH] = 0.12(0) \text{ mol dm}^{-3} \checkmark$ $[H^+] = \sqrt{K_a \times [C_2H_5COOH]} = \sqrt{1.35 \times 10^{-5} \times 0.12(0)}$ OR $1.27 \times 10^{-3} \text{ (mol dm}^{-3}) \checkmark$	3	ALLOW HA for C_2H_5COOH and A^- for $C_2H_5COO^-$ ALLOW ECF from incorrectly calculated $[C_2H_5COOH]$ ALLOW 1.27×10^{-3} to calculator value of $1.272792206 \times 10^{-3}$ correctly rounded
		ii	$pH = -\log 1.27 \times 10^{-3} = 2.9(0) \checkmark$ NOTE: The final two marks are ONLY available from attempted use of K_a AND $[C_2H_5COOH]$		

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
			$-\log(1.35 \times 10^{-5} \times 0.120)$ <i>No</i> ✓ pH = 5.19 1 mark $-\log(1.35 \times 10^{-5} \times 0.480)$ <i>Original conc, no</i> ✓ pH = 4.87 0 marks $-\log(1.35 \times 10^{-5}) = 4.87$ $-\log K_a$ Examiner's Comments This part discriminated extremely well. The added stage of an initial dilution to a stock weak acid pH calculation created problems for many candidates. Although most were able to use the correct square root expression to obtain a value for $[H^+(aq)]$, the concentration used was often incorrect. Although just a four times dilution from $0.480 \text{ mol dm}^{-3}$ to $0.120 \text{ mol dm}^{-3}$, many candidates obtained 0.120 using learnt equations rather than the simple ratio. Others used the original concentration of $0.480 \text{ mol dm}^{-3}$ or incorrectly calculated concentrations, commonly seen as 0.0480, 0.0120 or even 0.192 (from $\times 4$). Some candidates calculated $[H^+(aq)]$ using $0.480 \text{ mol dm}^{-3}$ but then divided by 4 before calculating the pH. Able candidates invariably obtained the correct pH but many obtained pH values from the values above such as a pH of 2.59 (from $0.480 \text{ mol dm}^{-3}$), for which partial credit could be awarded. Answer: pH = 2.90

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	d	i	$\text{pH} = -\log 1.35 \times 10^{-5} = 4.87 \checkmark$	1	ONLY correct answer DO NOT ALLOW 4.9 (<i>Question asks for 2 DP</i>) Examiner's Comments Some candidates correctly calculated the pH here as $-\log K_a$ but most used the standard buffer pH method, using a 1:1 acid–base ratio. Weak candidates often first took the square root of the K_a value, obtaining a pH of 2.43. Unfortunately, some candidates rounded a correct pH to 4.9, despite a two decimal place requirement being emphasised in the question. Answer: pH = 4.87
		ii	Added ammonia $\text{C}_2\text{H}_5\text{COOH}$ removes added NH_3 / alkali / base OR $\text{C}_2\text{H}_5\text{COOH} + \text{NH}_3 / \text{OH}^- \rightarrow$ OR NH_3 / alkali reacts with / accepts H^+ OR $\text{H}^+ + \text{NH}_3 \rightarrow$ OR $\text{H}^+ + \text{OH}^- \rightarrow \checkmark$	2	ALLOW use of HA / weak acid / acid for $\text{C}_2\text{H}_5\text{COOH}$; ALLOW use of NH_4OH for NH_3
		ii	Equilibrium $\rightarrow \text{C}_2\text{H}_5\text{COO}^-$ OR Equilibrium $\rightarrow$ right $\checkmark$		ALLOW A^- for $\text{C}_2\text{H}_5\text{COO}^-$ ASSUME that equilibrium applies to that supplied in the question, i.e. IGNORE any other equilibria Examiner's Comments The role of buffers in controlling pH is a common recall question and most candidates had prepared their rehearsed answers. Although this question asked for the addition of ammonia as a specific base, all but the weakest candidates identified that this was a question about addition of a base. The commonest and best answers stated that NH_3 accepts a proton to form NH_4^+ (with many ionic equations seen). The correct equilibrium shift was usually included.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	iii CHECK WORKING CAREFULLY AS CORRECT NUMERICAL ANSWER IS POSSIBLE FROM WRONG VALUES ----- ALLOW HA and A⁻ throughout Amount of Mg (1 mark) $n(\text{Mg}) = \frac{6.075}{24.3} = 0.25(0) \text{ mol} \quad \checkmark$ ----- Moles / concentrations (2 marks) $n(\text{C}_2\text{H}_5\text{COOH}) = 1.00 - (2 \times 0.25) = 0.50 \text{ (mol)} \quad \checkmark$ $n(\text{C}_2\text{H}_5\text{COO}^-) = 1.00 + (2 \times 0.25) = 1.50 \text{ (mol)} \quad \checkmark$ ----- [H⁺] and pH (1 mark) $[\text{H}^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.50} \text{ OR } 4.5 \times 10^{-6} \text{ (mol dm}^{-3}\text{)}$ $\text{pH} = -\log 4.5 \times 10^{-6} = 5.35 \text{ 2 dp required} \quad \checkmark$ NOTE: IF there is no prior working, ALLOW 4 MARKS for $[\text{H}^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.50}$ AND pH = 5.35 IF the ONLY response is pH = 5.35, award 1 mark ONLY Award a maximum of 1 mark (for $n(\text{Mg}) = 0.25 \text{ mol}$) for: pH value from K_a square root approach (weak acid pH) pH value from $K_w / 10^{-14}$ approach (strong base pH) ----- ALLOW alternative approach based on Henderson–Hasselbalch equation for final 1 mark $\text{pH} = \text{p}K_a + \log \frac{1.5}{0.5} \text{ OR } \text{p}K_a - \log \frac{0.5}{1.5}$ $\text{pH} = 4.87 + 0.48 = 5.35 \quad \checkmark$	4	FULL ANNOTATIONS MUST BE USED ----- For $n(\text{Mg})$, 1 mark ALLOW ECF for ALL marks below from incorrect $n(\text{Mg})$ ECF ONLY available from concentrations that have - subtracted 0.50 OR 0.25 from 1 for $[\text{C}_2\text{H}_5\text{COOH}]$ - added 0.50 OR 0.25 to 1 for $[\text{C}_2\text{H}_5\text{COO}^-]$ i.e. For moles / concentration 1 mark (1 mark lost) 1 $n(\text{C}_2\text{H}_5\text{COOH}) = 0.75$ AND $n(\text{C}_2\text{H}_5\text{COO}^-) = 1.25$ 2 $n(\text{C}_2\text{H}_5\text{COOH}) = 0.50$ AND $n(\text{C}_2\text{H}_5\text{COO}^-) = 1.25$ 3 $n(\text{C}_2\text{H}_5\text{COOH}) = 0.75$ AND $n(\text{C}_2\text{H}_5\text{COO}^-) = 1.50$ ----- ALLOW ECF ONLY for the following giving 1 additional mark and a total of 3 marks 1 $[\text{H}^+] = 1.35 \times 10^{-5} \times \frac{0.75}{1.25}$ pH = $-\log 8.1 \times 10^{-6} = 5.09$ 2 $[\text{H}^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.25}$ pH = $-\log 5.4 \times 10^{-6} = 5.27$ 3 $[\text{H}^+] = 1.35 \times 10^{-5} \times \frac{0.75}{1.50}$ pH = $-\log 6.75 \times 10^{-6} = 5.17$ Examiner's Comments This buffer calculation was aimed as stretch and challenge and the majority of candidates struggled to derive the concentrations of $\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{COO}^-$. An easy mark for the amount of magnesium added was available for almost all candidates. The problem was then to derive the amount and concentration of $\text{CH}_3\text{CH}_2\text{COOH}$ that would be obtained 0.500 mol^{-3}. Many did

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			ALLOW $-\log K_a$ for pK_a		not identify that Mg and $\text{CH}_3\text{CH}_2\text{COOH}$ react in a 1:2 molar ratio, subtracting 0.25, instead of 0.50, from the original concentration. Rarely did candidates realise that the $\text{CH}_3\text{CH}_2\text{COO}^-$ concentration would increase from the initial concentration of 1 mol dm^{-3}. Others assumed that no $\text{CH}_3\text{CH}_2\text{COO}^-$ was present at the start. Consequently, candidates often used a variety of acid–base ratios in their buffer calculation. Instead of the correct ratio of 0.5/1.5, it was very common to see 0.75/1.25, 0.75/0.25, and especially 0.5/1, 0.75/1 and 0.25/1.0. The very best candidates tackled the problem with apparent ease but this was seen comparatively rarely in scripts of other candidates. Answer: $\text{pH} = 5.35$
			Total	14	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
7		i	$\text{AND } \text{Base}_1^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$ Acid 1 Acid 2+ Base 1 ✓ CN	1	State symbols NOT required ALLOW CNH and HO^- (i.e. any order) ALLOW 1 and 2 labels the other way around. ALLOW 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid-base pairs are. Examiner's Comments The majority of candidates were able to complete the equation for acid–base equilibrium and to identify the acid–base pairs. Candidates are advised to use numbers to label the acid–base pairs, such as 'acid 1' and 'base 1'. Attempts at using 'acid' and 'conjugate base' are ambiguous when more than one acid–base pair is involved. Although credited, it was strange to see hydrogen cyanide often written as CNH.
		ii	H^+ reacts with CN^- OR HCN forms OR equation: $\text{H}^+ + \text{CN}^- \rightarrow \text{HCN}$ (ALLOW $\rightleftharpoons$) OR CN^- accepts a proton / H^+ OR equilibrium shifts right AND CN^- is removed ✓	1	ALLOW Acid reacts with / removes OH^- ions (to form HCN) ALLOW CNH (i.e. any order) IGNORE other equilibrium comments Examiner's Comments The majority of candidates recognised that acid conditions would lead to protonation of CN^- forming toxic HCN.
			Total	2	
8			C	1	
			Total	1	
9			D	1	
			Total	1	
10			C	1	
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
11			D	1	
			Total	1	
12			D	1	
			Total	1	
13	a		The forward reaction is exothermic, so an increase in temperature favours the backward reaction (<i>owtte</i>) ... (1) ... therefore there will be more N₂ and H₂ OR less NH₃ in the equilibrium mixture, AND therefore the value of the equilibrium constant will decrease (<i>owtte</i>) (1)	2	allow names of compounds allow reactants / product instead of compounds 2nd mark only available if deduced from 1st mark allow ecf for 2nd mark
	b		FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = $2.37 \times 10^{-6} \text{ kPa}^{-2}$ award 5 marks IF answer = 2.37×10^{-6} with incorrect units award 4 marks At equilibrium, $n(\text{H}_2) = 0.300 \text{ (mol)}$ AND $n(\text{NH}_3) = 0.100 \text{ (mol)}$ (1) 0.400 $p(\text{N}_2) = \frac{0.400}{0.800} \times 500 = 250 \text{ kPa}$ AND 0.300 $p(\text{H}_2) = \frac{0.300}{0.800} \times 500 = 187.5 \text{ kPa}$ AND 0.100 $p(\text{NH}_3) = \frac{0.100}{0.800} \times 500 = 62.5 \text{ kPa}$ (1) $K_p = \frac{p(\text{NH}_3)^2}{p(\text{N}_2) \times p(\text{H}_2)^3} = \frac{62.5^2}{250 \times 187.5^3}$ (1) $= 2.37 \times 10^{-6} \text{ (1) kPa}^{-2} \text{ (1)}$	5	Final answer must be correct and have the correct units to score all five marks allow calculator value for K_p correctly rounded to three or more significant figures. If there is an alternative answer, check to see if there is any ECF credit possible using working below Correct values substituted into correct expression for K_p gains first three marks.
			Total	7	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
14		i	FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = $0.163 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ OR $0.1632 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ award 4 marks IF answer = 0.163 OR 0.1632 with incorrect units award 3 marks Order w.r.t. IC/ = 1 and order w.r.t H_2 = 1 (1) rate = $k[\text{IC}]/[\text{H}_2]$ (1) $k = \frac{2.04 \times 10^{-2}}{0.250 \times 0.500} = 0.163 \text{ OR } 0.1632$ (1) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1)	4	If there is an alternative answer, check to see if there is any ECF credit possible using working below both orders = 1 mark correct rate equation or rearranged form = 1 mark candidates may use experimental data from experiments 2 or 3 to calculate the rate constant do not allow 0.16
		ii	rate = $k[\text{IC}]/[\text{H}_2]$ (from (i)) = $0.163 \times 3 \times 10^{-3} \times 2 \times 10^{-3} = 9.78 \times 10^{-7}$ (mol $\text{dm}^{-3} \text{ s}^{-1}$) (1)	1	allow ecf from (i) Note use of 0.1632 from (i) gives $9.79(2) \times 10^{-7}$
			Total	5	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
15	a		$[H^+] = 10^{-pH} = 10^{-2.19} = 6.46 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ $[CH_3CH(OH)COOH] = \frac{[H^+]^2}{K_a} = \frac{(6.46 \times 10^{-3})^2}{1.38 \times 10^{-4}}$ $= 0.0302 \text{ (mol dm}^{-3}\text{)}$ $n(CH_3CH(OH)COOH) = \frac{0.302 \times 250}{1000} = 0.0755 \text{ mol}$ Mass of $CH_3CH(OH)COOH = 0.0755 \times 90 = 6.80 \text{ g}$ Dissolve 6.80 g of the solid in distilled water (less than 250 cm^3) in a beaker (then) transfer the solution to a 250 cm^3 volumetric flask AND ensure that all solution is washed out of beaker (washings transferred to volumetric flask) (then) make solution up to 250 cm^3 with distilled water AND ensure thorough mixing by inverting the flask several times	8	ALLOW 5 marks for 6.80 g through any calculation. ALLOW ECF for incorrect calculation of mass. Mass used must be linked to calculation.
	b		$CH_3CH(OH)COO^- + CH_3CH_2CH_2COOH_2^+$ $CH_3CH(OH)COOH$ AND $CH_3CH(OH)COO^-$ $CH_3CH_2CH_2COOH$ AND $CH_3CH_2CH_2COOH_2^+$ Both pairs identified	2	State symbols NOT required ALLOW labels 'acid 1', 'base 1' etc. ALLOW ECF for second mark
	c	i	$[H^+] = \frac{1 \times 10^{-14}}{0.185} = 5.405 \times 10^{-14}$ (Use of K_w) $pH = -\log(5.405 \times 10^{-14}) = 13.27$	2	ALLOW $5.405405405 \times 10^{-14}$ and correct rounding to 5.4×10^{-14} ALLOW alternative approach using pOH: $pOH = -\log(0.185) = 0.73$ $pH = 14 - 0.73 = 13.27$ Correct answer scores BOTH marks ALLOW 13.267

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	$n(A^-) = 9.25 \times 10^{-3} \text{ (mol)}$ $n(HA) = 0.0165 - 9.25 \times 10^{-3} = 7.25 \times 10^{-3} \text{ (mol)}$ $[H^+] = K_a \times \frac{[HA]}{[A^-]}$ $pH = -\log(1.5 \times 10^{-5} \times \frac{0.058}{0.074}) = 4.93$ $OR \text{ } pH = -\log(1.5 \times 10^{-5} \times \frac{1000 \times \frac{7.25 \times 10^{-3}}{125}}{1000 \times \frac{9.25 \times 10^{-3}}{125}}) = 4.93$ Final mark also via Henderson-Hasselbalch equation: $pH = pK_a - \log \frac{[HA]}{[A^-]} = 4.82 - (-0.11) = 4.93$ $OR \text{ } pH = pK_a + \log \frac{[A^-]}{[HA]} = 4.82 + 0.11 = 4.93$	4	ALLOW HA / acid and A ⁻ /salt throughout for butanoate and butanoic acid ALLOW $pK_a = -\log K_a$ OR $-\log 1.5 \times 10^{-5}$ OR 4.82 ALLOW ECF from incorrect values of $n(A^-)$ or $n(HA)$ ALLOW $pH = -\log(1.5 \times 10^{-5} \times \frac{7.25 \times 10^{-3}}{9.25 \times 10^{-3}}) = 4.93$
			Total	16	
16			C	1	
			Total	1	
17			C	1	
			Total	1	
18			D	1	
			Total	1	
19			D	1	
			Total	1	
20			C	1	
			Total	1	
21			A: Sc ³⁺ B: S ²⁻	2	
			Total	2	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
22	a	FIRST CHECK THE ANSWER ON ANSWER LINE IF answer = $0.812 \text{ dm}^6 \text{ mol}^{-2}$, award 6 marks IF answer = 0.812 with incorrect units, award 5 marks ----- Equilibrium amounts in mol 2 MARKS $n(\text{N}_2) = 0.62(0)$ $n(\text{N}_2) = 1.86$ Equilibrium concentrations in mol dm^{-3} (mol $\div$ 5) 1 MARK $\text{N}_2 = 0.124$ AND $\text{H}_2 = 0.372$ AND $\text{NH}_3 = 0.072$ Calculation of K_c and units 3 MARKS $K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})] \times [\text{H}_2(\text{g})]^3}$ OR $\frac{0.072^2}{0.124 \times 0.372^3}$ = $0.812 \text{ dm}^6 \text{ mol}^{-2}$ <i>At least 3SF is required</i>	6	FULL ANNOTATIONS NEEDED IF there is an alternative answer, check to see if there is any ECF credit possible using working below ----- ALLOW ECF from incorrect moles of N_2, H_2 AND / OR NH_3 ALL three concentrations required for mark ALLOW ECF from incorrect concentrations OR use of moles (omitting conc stage) NO ECF for numerical value with a square AND / OR cube missing For K_c, ALLOW 3 significant figures up to calculator value of 0.8121093077 correctly rounded For units, ALLOW $\text{mol}^{-2} \text{ dm}^6$ DO NOT ALLOW $\text{dm}^6/\text{mol}^{-2}$ ----- COMMON ERRORS 0.0325 3 marks + units mark from $\text{N}_2 = 0.620$, $\text{H}_2 = 1.86$, $\text{NH}_3 = 0.360$ (mol)

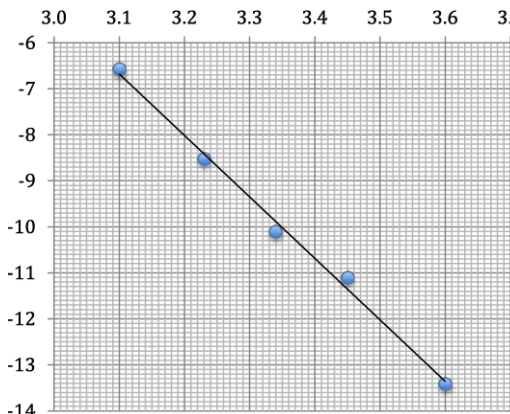
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b	i	IGNORE le Chatelier responses ----- <i>Each marking point is independent</i> K_c K_c does not change (with pressure / concentration) <i>Comparison of conc terms with more N_2</i> $[N_2]$ increases OR denominator / bottom of K_c expression increases <i>yield of NH_3 linked to K_c</i> Chemist is correct AND denominator decreases OR numerator increases to restore equilibrium K_c	3	FULL ANNOTATIONS NEEDED ALLOW K_c only changes with temperature IF 1st marking point has been awarded, IGNORE comments about 'K_c decreasing' or 'K_c increasing' and assume that this refers to how the ratio subsequently changes. i.e. DO NOT CON 1st marking point.
		ii	N_2 obtained from the air AND H_2 must be manufactured / does not occur naturally	1	N_2 is more readily available not insufficient. ALLOW an example of H_2 manufacture, e.g. from oil / gas / water BOTH responses required for mark.
			Total	10	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
23	a	<i>Please refer to the marking instruction point 10 for guidance on how to mark this question.</i> Level 3 (5–6 marks) A comprehensive conclusion which uses quantitative results for determination of the reaction orders AND determination of k with units AND proposes the two-step mechanisms. <i>There is a well-developed conclusion showing a line of reasoning which is clear and logically structured. The working for orders, rate equation, rate constant and two-step mechanism are clearly linked to the experimental evidence.</i> Level 2 (3–4 marks) Reaches a sound, but not comprehensive, conclusion based on the quantitative results. Correctly identifies the orders and rate equation AND calculates the rate constant with units OR proposes the two-step mechanism. <i>The conclusion has a line of reasoning presented with some structure. The working for orders, rate equation AND rate constant OR the two-step mechanism are linked to the experimental evidence.</i> Level 1 (1–2 marks) Reaches a simple conclusion for orders AND rate equation. <i>The working for orders, and rate equation are linked to the experimental data, but the evidence may not be clearly shown.</i> 0 marks No response or no response worthy of credit.	6	Indicative scientific points may include: Orders and rate equation • NO_2 and O_3 both 1st order OR $\text{rate} = k[\text{O}_3][\text{NO}_2]$ • Supported by experimental results Calculation of k, including units • k correctly calculated AND correct units, i.e. $k = 1.28 \times 10^{-2}$ • $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ OR $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$ Two-step mechanism • Two steps add up to give overall equation • Slow step / rate-determining step matches stoichiometry of rate equation. e.g. $\text{O}_3 + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}_3$ rate-determining step $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$ OR $\text{O}_3 + \text{NO}_2 \rightarrow 2\text{O}_2 + \text{NO}$ rate-determining step $\text{NO} + \text{O}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance																								
	b		<table><tr><th>Temperature, T / K</th><th>Rate constant, k / s^{-1}</th><th>$1 / T / K^{-1}$</th><th>$\ln k$</th></tr><tr><td>278</td><td></td><td></td><td></td></tr><tr><td>290</td><td></td><td>3.45×10^{-3}</td><td></td></tr><tr><td>298</td><td></td><td></td><td></td></tr><tr><td>308</td><td></td><td></td><td>-8.52</td></tr><tr><td>323</td><td></td><td></td><td></td></tr></table> two missing values: 3.45×10^{-3} AND -8.52 all points plotted correctly AND best straight line drawn through points gradient = $\pm 1.36 \times 10^4$ <i>acceptable range: $1.30-1.40 \times 10^4$</i> multiplication by 8.314 AND division by 10^3 to give $E_a = (+)113 \text{ (kJ mol}^{-1}\text{)}$	Temperature, T / K	Rate constant, k / s^{-1}	$1 / T / K^{-1}$	$\ln k$	278				290		3.45×10^{-3}		298				308			-8.52	323				4	 ALLOW mark for gradient if correct working shown within E_a calculation without gradient being calculated separately. ALLOW ECF from value of gradient BUT DO NOT ALLOW '-' sign for E_a
Temperature, T / K	Rate constant, k / s^{-1}	$1 / T / K^{-1}$	$\ln k$																										
278																													
290		3.45×10^{-3}																											
298																													
308			-8.52																										
323																													
			Total	10																									

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
24	a	i	HNO ₃ is a strong acid AND HNO ₂ is a weak acid	1	ALLOW HNO ₃ completely dissociates AND HNO ₂ partially dissociates ALLOW $\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^-$ AND $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$ IGNORE HNO ₃ is a stronger acid OR IGNORE HNO ₃ produces more H ⁺
		ii	pH = -log 0.0450 = 1.35 (2 DP required)	1	
		iii	FIRST CHECK THE ANSWER ON ANSWER LINE IF answer = 2.35, award all three calculation marks $K_a = 10^{-3.35}$ OR 4.47×10^{-4} (mol dm ⁻³) $[\text{H}^+] = \sqrt{(K_a \times [\text{HNO}_2])}$ OR $\sqrt{(K_a \times [\text{HA}])}$ OR $\sqrt{(K_a \times 0.0450)}$ OR 4.48×10^{-3} (mol dm ⁻³) pH = 2.35 (2 DP required)	3	ALLOW 2 SF to calculator value: $4.466835922 \times 10^{-4}$, correctly rounded IGNORE HNO ₃ in working Always ALLOW calculator value irrespective of working as number may have been kept in calculator. <i>Note: pH = 2.35 is obtained from all three values above</i> <i>From no square root, pH = 4.70. Worth K_a mark only.</i>
	b		FIRST CHECK THE ANSWER ON ANSWER LINE IF answer = 0.810 (g) award 4 marks $[\text{H}^+] = 10^{-12.500} = 3.16 \times 10^{-13}$ (mol dm ⁻³) $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.00 \times 10^{-14}}{3.16 \times 10^{-13}} = 0.0316$ (mol dm ⁻³) $n(\text{RbOH}) = 0.0316 \times \frac{250}{1000} = 7.91 \times 10^{-3}$ (mol) mass RbOH = $7.91 \times 10^{-3} \times 102.5 = 0.810$ (g)	4	Always ALLOW calculator value irrespective of working as number may have been kept in calculator. ALLOW alternative approach using pOH: pOH = 14.000 – 12.500 = 1.500 $[\text{OH}^-] = 10^{-1.500} = 0.0316$ ALLOW ECF from [H ⁺] derived using K _w and [OH ⁻] BUT DO NOT ALLOW an acid pH. ALLOW 0.81 g, up to calculator value but take care as rounding could be from any stage. <i>Last 3 SF figure is zero and is treated as a 'trailing zero' as specific number of SF has not been asked for.</i>
			Total	9	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
25			K_w value from graph from 2.2 to 2.4×10^{-14} ($\text{mol}^2 \text{dm}^{-6}$) Using 2.4×10^{-14} , $[\text{H}^+] = \sqrt{2.4 \times 10^{-14}}$ OR 1.55×10^{-7} $\text{pH} = -\log(1.55 \times 10^{-7}) = 6.81$ (using $K_w = 2.4 \times 10^{-14}$)	3	Actual $K_w = 2.38 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6}$ ALLOW ECF only if candidate uses a value between 2.0 and $2.6 \times 10^{-14} (\text{mol}^2 \text{dm}^{-6})$, i.e. from the approximately correct region of the graph ALLOW 6.8 (1DP) up to calculator value ALLOW ECF only if candidate has generated a value of $[\text{H}^+]$ by attempting to take a square root of a value between 2.0 and 3.0×10^{-14}
			Total	3	
26		i	$K_a = \frac{[[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}(\text{aq})][\text{H}^+(\text{aq})]}{[[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})]}$	1	state symbols not required
		ii	$[\text{H}^+] = \sqrt{6.00 \times 10^{-3} \times 0.100}$ OR $0.0245 (\text{mol dm}^{-3})$ $\text{pH} = -\log 0.0245 = 1.61$	2	ALLOW ECF from calculated $[\text{H}^+]$ provided that BOTH 6.0×10^{-3} AND 0.100 only have been used ALLOW calculation via quadratic equation → pH 1.66
			Total	3	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
27	a		Measure reduction of colour of bromine	1	
	b		Measure volume of CO ₂ (produced)	1	
	c		Concentration of HCOOH would be constant	1	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
	d	<i>* Please refer to the marking instruction point 10 for guidance on how to mark this question.</i> Level 3 (5–6 marks) A comprehensive conclusion which uses quantitative data from the graph to correctly identify and calculate initial rate AND half lives and reasoned order of Br₂ AND determination of <i>k</i> with units. <i>There is a well-developed conclusion showing a line of reasoning which is clear and logically structured. The working for initial rate, half life and order are clearly shown. Determination of <i>k</i> is clear and correct.</i> Level 2 (3–4 marks) Reaches a sound, but not comprehensive, conclusion based on quantitative data from the graph. Correctly identifies and calculates initial rate AND half lives and reasoned order of Br₂. <i>The conclusion has a line of reasoning presented with some structure. The initial rate and order is relevant and supported by correct evidence from the graph. There may be errors in the calculations which prevent the correct determination of <i>k</i>.</i> Level 1 (1–2 marks) Reaches a simple conclusion using at least one piece of quantitative data from the graph. Attempts calculation of initial rate OR half lives and reasoned order of Br₂. <i>The information selected from the graph is basic and communicated in an unstructured way. The calculations may not be clear and the evidence used from the graph may not be clearly shown.</i> 0 marks No response or no response worthy of credit.	6	Indicative scientific points may include: Initial rate - Evidence of tangent on graph drawn to line at $t = 0$ s AND gradient determined in range $4 \pm 1 \times 10^{-5}$ <i>initial rate</i> expressed as gradient value with units of $\text{mol dm}^{-3} \text{s}^{-1}$, e.g. <i>initial rate</i> = $4 \times 10^{-5} \text{mol dm}^{-3} \text{s}^{-1}$ Half lives and reasoned order of Br₂ - Half life measured on graph OR within text OR stated in range 180–200 s - Constant half life OR two stated half lives within ± 20 s AND conclusion that Br₂ is 1st order Determination of <i>k</i> with units - Rate constant <i>k</i> clearly linked to initial $k = \frac{\text{rate}}{[\text{Br}_2]} \quad \text{OR} \quad k = \frac{\ln 2}{t_{1/2}}$ <i>k</i> determined correctly from measured initial rate or measured half life with units of s^{-1}, e.g. $k = 4 \times 10^{-3} \text{s}^{-1}$ from initial rate of $4 \times 10^{-5} \text{mol dm}^{-3} \text{s}^{-1}$ OR $t_{1/2}$ of 175 s

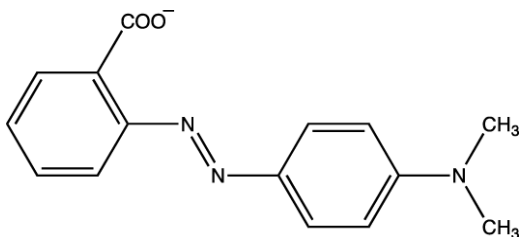
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			Total	9	
28			1 mark for correct reactants AND products AND correct positioning of + and – charges on products 1 mark for two correct curly arrows AND H₂O curly arrow starting from O lone pair	2	
			Total	2	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
29		i	$\text{N}_2\text{O}_4 = +4$ AND $\text{NO}_3^- = +5$ AND $\text{NH}_4^+ = -3$ ✓	1	ALL 3 oxidation numbers required DO NOT ALLOW missing '+' or '-' OR oxidation numbers shown as charges e.g. N^{5+}
		ii	FIRST CHECK THE ANSWER ON THE ANSWER LINE If answer = 7.9(0) (g) award 2 marks $n(\text{KMnO}_4) = \frac{0.200 \times 250}{1000} = 0.0500 \text{ (mol)}$ ✓ mass of $\text{KMnO}_4 = 0.0500 \times 158.0 = 7.9(0)$ (g) ✓	2	
		iii	$\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ ✓	1	
		iv	FIRST CHECK THE ANSWER ON THE ANSWER LINE If answer = 1.54×10^{23} award 2 marks □ $n(\text{tartaric acid}) = \frac{38.25}{150} = 0.255 \text{ (mol)}$ ✓ number of molecules = $0.255 \times 6.02 \times 10^{23}$ = 1.54×10^{23} ✓ (3 SF required from least significant data)	2	ALLOW ECF from $n(\text{tartaric acid})$ Common error: use of 148 (<i>missing 2H Structure</i>) → 1.56×10^{23}
			Total	6	

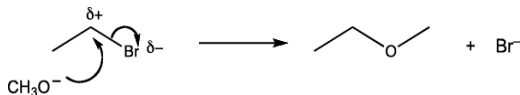
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
30	a	i	Using a pH probe on a data logger OR pH meter	1	
		ii	FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 0.11(0) (mol dm⁻³), award 2 marks ----- $n(\text{NaOH}) = \frac{0.125 \times 22.0}{1000} = 2.75 \times 10^{-3} \text{ (mol)}$ $\text{concentration of CH}_3\text{COOH} = \frac{2.75 \times 10^{-3} \times 1000}{25.0}$ $= 0.11(0) \text{ (mol dm}^{-3}\text{)}$	2	IF there is an alternative answer, check to see if there is any ECF credit possible using working below. ----- ANNOTATE WITH TICKS AND CROSSES, etc ALLOW ECF: $n(\text{NaOH}) \times 1000/25.00$
	b	i	Brilliant yellow AND Vertical section / rapid pH change matches the pH range / end point / colour change (of the indicator)	1	ALLOW pH range (of the indicator) matches equivalence point ALLOW end point / colour change matches equivalence point IGNORE colour change matches end point (<i>colour change is the same as end point</i>)
		ii	 Explanation: Acid / H⁺ reacts with A⁻ AND equilibrium (position) shifts towards HA (to give a red colour) Alkali / OH⁻ reacts with HA/H⁺ AND equilibrium (position) shifts towards A⁻ (to give a yellow colour) At end point, equal amounts of HA and A⁻ AND orange colour	4	ALLOW direction of equilibrium shift if equilibrium shown: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ i.e. 'towards HA' is equivalent to 'to left' i.e. 'towards A⁻' is equivalent to 'to right' ALLOW yellow–red colour

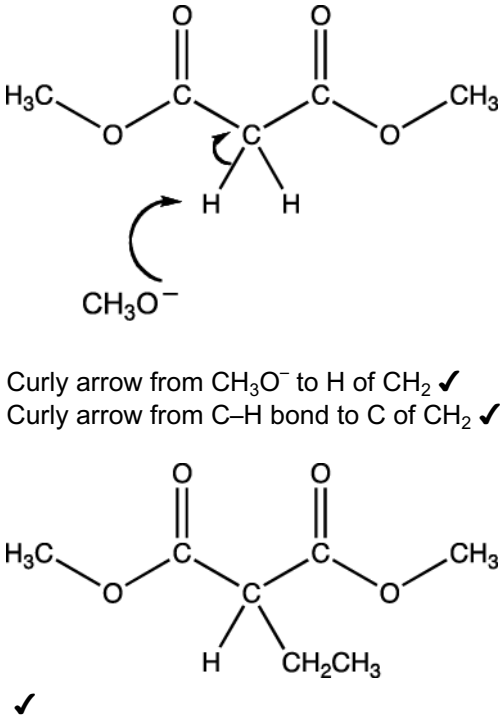
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c	i	FIRST CHECK THE ANSWER ON THE ANSWER LINE If answer = 2.33 award 4 marks $K_a = 10^{-3.40} = 3.98 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$ Concentration of aspirin $= \frac{1.00 \times 10^{-2}}{180} \times 1000$ $= 0.0556 \text{ (mol dm}^{-3}\text{)}$ $[H^+] = \sqrt{(K_a \times [HA])} = \sqrt{(3.98 \times 10^{-4} \times 0.0556)}$ $= 4.70 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ $\text{pH} = -\log 4.70 \times 10^{-3} = 2.33$	4	ALLOW ECF ALLOW ECF only from $[H^+]$ calculation using $[H^+] = \sqrt{(K_a \times [HA])}$
		ii	Salts are ionic AND attracted to polar H ₂ O	1	
		iii	COO⁻ reacts with H⁺ forming COOH Aspirin precipitates out	2	ALLOW equilibrium shifts to left
			Total	15	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance																				
31	a		✓	1																					
	b	i	$2\text{Na} + 2\text{CH}_3\text{OH} \rightarrow 2\text{Na}^+ + 2\text{CH}_3\text{O}^- + \text{H}_2$ ✓	1	ALLOW $2\text{Na} + 2\text{CH}_3\text{OH} \rightarrow 2\text{CH}_3\text{ONa} + \text{H}_2$																				
		ii	 Curly arrow from CH_3O^- to carbon atom of C-Br bond ✓ Dipole shown on C-Br bond, $\text{C}^{\delta+}$ and $\text{Br}^{\delta-}$ AND curly arrow from C-Br bond to the Br atom ✓ Products of reaction (must not be ambiguous) ✓	3	ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non-ambiguous. The curly arrow must start from O atom of CH_3O^- AND must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. ALLOW $\text{S}_{\text{N}}1$ Dipole shown on C-Br bond, $\text{C}^{\delta+}$ and $\text{Br}^{\delta-}$, and curly arrow from C-Br bond to the Br atom. Correct carbocation drawn. AND curly arrow from CH_3O^- to carbocation. The curly arrow must start from the oxygen atom of the CH_3O^-, and must start either from a lone pair or from the negative charge.																				
		iii	CH_3O^- donates an electron pair AND heterolytic fission ✓	1	ASSUME 'it' refers to CH_3O^-																				
	c		<table><tr><th>Chemical shift, δ/ppm</th><th>Relative peak area</th><th>Splitting pattern</th><th></th></tr><tr><td>0.5–1.9</td><td>3</td><td>Triplet</td><td>✓</td></tr><tr><td>3.0–4.3</td><td>2</td><td>Quartet</td><td>✓</td></tr><tr><td>0.5–1.9</td><td>6</td><td>Doublet</td><td>✓</td></tr><tr><td>3.0–4.3</td><td>1</td><td>Heptet</td><td>✓</td></tr></table>	Chemical shift, δ/ppm	Relative peak area	Splitting pattern		0.5–1.9	3	Triplet	✓	3.0–4.3	2	Quartet	✓	0.5–1.9	6	Doublet	✓	3.0–4.3	1	Heptet	✓	4	ALLOW δ values ± 0.2 ppm, as a range or a value within the range ALLOW multiplet for heptet
Chemical shift, δ/ppm	Relative peak area	Splitting pattern																							
0.5–1.9	3	Triplet	✓																						
3.0–4.3	2	Quartet	✓																						
0.5–1.9	6	Doublet	✓																						
3.0–4.3	1	Heptet	✓																						

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Question			Answer/Indicative content	Marks	Guidance
	d	i	 Curly arrow from CH_3O^- to H of CH_2 ✓ Curly arrow from C-H bond to C of CH_2 ✓	3	The curly arrow must start from O atom of CH_3O^- AND must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. ALLOW any unambiguous structure, skeletal, displayed, structural or combination.
		ii	CH_3O^- accepted a proton ✓	1	ASSUME 'it' refers to CH_3O^-
			Total	14	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
32	a	<i>initial rates data (3 marks)</i> NOTE: Each comparison MUST relate to the actual change in concentration / rate in the experiments H₂O₂: $[\text{H}_2\text{O}_2] \times 2$ rate $\times 2$ EXPTS AND (1 & 2) 1st order ✓ H⁺: $[\text{H}^+] \times 2$ rate does not change (2 & 3) AND Zero order ✓ I⁻: $[\text{I}^-] \times 2$ AND $[\text{H}_2\text{O}_2] \times 2$ rate $\times 4$ (2 & 4) OR $[\text{I}^-] \times 2$ AND $[\text{H}_2\text{O}_2] \times 4$ rate $\times 8$ (1 & 4) OR $[\text{I}^-] \times 2$ AND $[\text{H}_2\text{O}_2] \times 2$ rate $\times 4$ (3 & 4) AND 1st order ✓	3	FULL ANNOTATIONS MUST BE USED ----- THROUGHOUT, • Square brackets NOT REQUIRED around H₂O₂, H⁺ and I⁻ • ALLOW 'doubles' for $\times 2$; quadruples for $\times 4$ ALLOW direct comparison of concentrations and rate, e.g. $[\text{H}_2\text{O}_2]$ changes by $\frac{0.0020}{0.0010} = 2$, rate changes by $\frac{1.14 \times 10^{-5}}{5.70 \times 10^{-6}} = 2$ AND 1st order (Expts 1 & 2) DO NOT ALLOW I₂ for I⁻ IGNORE [H⁺] for Expts 3 & 4

Mark Scheme

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	<i>Calculation of rate constant (3 marks), EITHER</i> $k = \frac{5.70 \times 10^{-6}}{0.0010 \times 0.20}$ OR 2.85×10^{-2} OR 0.0285 OR 0.029 ✓ $k = 2.9 \times 10^{-2}$ ✓ (2 SF in standard form) <i>Subsumes previous mark if no working shown</i> $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ✓	3	IGNORE working DO NOT ALLOW 0.03 ALLOW ECF from error in powers of 10 ONLY e.g. 2.9×10^{-3} by use of 0.010 instead of 0.0010 DO NOT ALLOW 2.90×10^{-2} (3 SF) OR 29×10^{-3} (Not standard form) ALLOW mol^{-1}, dm^3 and s^{-1} in any order, e.g. $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ Examiner's Comments This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions. This part required candidates to show that the experimental results provided evidence for a provided rate equation. Most candidates were able to link concentration changes within the experiments with rate for H_2O_2 and H^+. For I^-, there were two concentration changes but weaker candidates often ignored the H_2O_2 change. The best answers were well-structured and succinct. Many longer, less focussed responses were seen which often omitted important detail. The rate constant was usually calculated correctly but many candidates did not show their calculated answer in standard form or to two significant figures. Candidates are advised to look carefully at the requirements of the question. Answer: $k = 2.9 \times 10^{-2} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

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	b		H^+ ions are consumed / used up OR H^+ ions are in the (overall) equation ✓	1	ALLOW H^+ is not regenerated / reformed ALLOW H^+ is a reactant but not a product ALLOW 'it' for H^+ IGNORE H^+ is not in the rate equation / does not affect rate IGNORE does not take part in rate-determining step Examiner's Comments This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions. This part was answered well, with most candidates recognising that H^+ was used up in the overall equation. Some candidates were distracted by the absence of H^+ in the rate equation.
	c	i	The slowest / slow step ✓	1	ALLOW step that takes the longest time Examiner's Comments This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions. Almost all candidates were aware that the rate-determining step is the slowest step in a multi-step mechanism.
		ii	NO ECF from incorrect rate equation Principles H_2O_2 and I^- must be the reactants in 1st step 2nd mark only to be awarded if 1st mark scored - Step 4 is independent Reactants of Step 1 as $H_2O_2 + I^-$ 1 mark	3	IGNORE state symbols Elements can be in any order in formulae

Mark Scheme

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			Step 1: $\text{H}_2\text{O}_2 + \text{I}^- \checkmark$ Products of Step 1 AND all of Step 2 1 mark Step 1 $\rightarrow \text{IO}^- + \text{H}_2\text{O}$ AND Step 2: $\text{H}^+ + \text{IO}^- \rightarrow \text{HIO} \checkmark$ Step 4 (Independent mark) 1 mark $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \checkmark$		Alternatives for 2nd mark Step 1: $\rightarrow \text{HIO} + \text{OH}^-$ AND Step 2: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \checkmark$ Step 1: $\rightarrow \text{H}_2\text{O}_2\text{I}^-$ AND Step 2: $\text{H}^+ + \text{H}_2\text{O}_2\text{I}^- \rightarrow \text{HIO} + \text{H}_2\text{O} \checkmark$ Other possibilities, contact TL ALLOW $2\text{H}^+ + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O}$ $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$ Examiner's Comments This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions. This part was attempted very well, the majority identifying that the reactants of the rate-determining step (Step 1) are obtained from the rate equation. Various possible equations were allowed for the remaining steps. Some otherwise correct equations could not be credited as charges had been omitted. Candidates are advised to check that charges, as well as species, balance on each side of any equation.
			Total	11	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
33	a	FIRST, CHECK THE ANSWER ON ANSWER LINE IF $K_c = 104 \text{ dm}^3 \text{ mol}^{-1}$ award 4 marks: 3 for calculation of 104 from data, 1 for units ----- Equilibrium concentrations (mol $\times$ 5) (1 mark) $I_2 = 4.00 \times 10^{-5} \times 5 = 2.00 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$ AND $I^- = 9.404 \times 10^{-2} \times 5 = 0.4702 \text{ (mol dm}^{-3}\text{)}$ ✓ AND $I_3^- = 1.96 \times 10^{-3} \times 5 = 9.80 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ Calculation of K_c and units (3 marks) $K_c = \frac{[I_3^-(aq)]}{[I_2(aq)] \times [I^-(aq)]}$ OR $\frac{9.80 \times 10^{-3}}{2.00 \times 10^{-4} \times 0.4702}$ ✓ = 104 ✓ Must be 3 SF $\text{dm}^3 \text{ mol}^{-1}$ OR $\text{mol}^{-1} \text{ dm}^3$ ✓	4	FULL ANNOTATIONS MUST BE USED ----- Throughout, at least 3SF but ALLOW absence of trailing zeroes e.g. for 9.80×10^{-3} ALLOW 9.8×10^{-3} FOR I^- 0.4702, ALLOW 0.47(0) (mol dm⁻³) still → 104 for calc State symbols not required in K_c expression ALLOW ECF from incorrect concentrations Any ECF value MUST be to 3 SF for K_c value ----- COMMON ERRORS 104.2 → 104.2109741 (calc) > 3 SF 2 marks + units 521 no $\times$ 5 for concs 2 marks + units 521.1 → 521.0548703 as above and > 3SF 1 mark + units 2610 $\div$ 5 instead of $\times$ 5 for concs 2 marks + units $9.60 \times 10^{-3} K_c$ upside down, correct concs 2 marks + units $1.92 \times 10^{-3} K_c$ upside down, no $\times$ 5 for concs 1 mark + units

Mark Scheme

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					NOTE: With K_c upside down, units become mol dm^{-3} by ECF Examiner's Comments This question was about equilibrium, set in the context of the solubility of iodine. Most candidates are comfortable with calculations of equilibrium constants. The correct numerical answer of 104 and units of $\text{dm}^3 \text{mol}^{-1}$ were seen often. The commonest calculation error was use of the equilibrium moles, rather than concentrations, giving 521. This question asked for the final value to be expressed to the most appropriate number of significant figures. Candidates should use the least significant number of significant figures in the provided data, in this case 3. Many candidates lost a mark by using more than 3 significant figures (e.g. 104.2 and 104.21). Answer: $K_c = 104 \text{ dm}^3 \text{mol}^{-1}$
	b		Ag^+ / silver nitrate reacts with I^- to form AgI / silver iodide OR $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}$ ✓ yellow precipitate / solid forms ✓ Equilibrium 2 shifts to the left ✓ Equilibrium 1 shifts to left AND I_2 comes out of solution / less I_2 dissolves / I_2 precipitates / black solid / grey solid / violet solid ✓	4	FULL ANNOTATIONS MUST BE USED ----- DO NOT ALLOW cream OR cream73–yellow ALLOW just 'yellow' if supported by AgI(s) somewhere Examiner's Comments This question was about equilibrium, set in the context of the solubility of iodine. This part required candidates to apply their knowledge and understanding of equilibria to a novel situation. Candidates were expected to predict that $\text{Ag}^+(\text{aq})$ and $\text{I}^-(\text{aq})$ ions would react together to form AgI(s), a yellow precipitate, shifting equilibrium 2 to the left. Equilibrium 1 would then shift to the left forming solid iodine. Responses in terms of equilibrium 2 were seen far more often than for Equilibrium 1.

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	c		in all equations ALLOW equilibrium signs IGNORE state symbols ----- Reaction 1: 1 mark $2\text{I}_2 + 5\text{O}_2 \rightarrow 2\text{I}_2\text{O}_5$ ✓ ----- Reaction 2: 2 marks 1st mark: ALL CORRECT species e.g.: $\text{I}_2 + \text{OH}^- \rightarrow \text{I}^- + \text{IO}_3^- + \text{H}_2\text{O}$ 2nd mark for CORRECT balanced equation $3\text{I}_2 + 6\text{OH}^- \rightarrow 5\text{I}^- + \text{IO}_3^- + 3\text{H}_2\text{O}$ ✓✓	3	FULL ANNOTATIONS MUST BE USED ----- ALLOW correct multiples throughout, e.g. $\text{I}_2 + 2\frac{1}{2}\text{O}_2 \rightarrow \text{I}_2\text{O}_5$ ----- For 1st mark, IGNORE e^- present ALLOW species / equation with NaOH or KOH, e.g. $3\text{I}_2 + 6\text{NaOH} \rightarrow 5\text{I}^- + \text{IO}_3^- + 3\text{H}_2\text{O} + 6\text{Na}^+$ $3\text{I}_2 + 6\text{NaOH} \rightarrow 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O}$ ALLOW Species: $\text{I}_2 + \text{OH}^- \rightarrow \text{I}^- + \text{IO}_2^+ + \text{H}_2\text{O}$ ✓ OR Equation: $3\text{I}_2 + 4\text{OH}^- \rightarrow 5\text{I}^- + \text{IO}_2^+ + 2\text{H}_2\text{O}$ ✓✓ Species: $\text{I}_2 + \text{OH}^- \rightarrow \text{I}^- + \text{IO}_3^+ + \text{H}_2\text{O}$ ✓ OR Equation: $3\text{I}_2 + 2\text{OH}^- \rightarrow 5\text{I}^- + \text{IO}_3^+ + \text{H}_2\text{O}$ ✓✓ Examiner's Comments This question was about equilibrium, set in the context of the solubility of iodine. This part required candidates to interpret unfamiliar information to construct reactions for redox reactions of iodine. Candidates were far more successful with the first equation than the more demanding second equation. For the second equation, the key difficulty was the formula of the iodate(V) ion, IO_3^-, with I^{5+} or the formula of I_2O_5 often being shown. The most difficult skill was balancing the second redox equation, suggesting that many candidates need more practice in this area.
			Total	11	

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Question			Answer/Indicative content	Marks	Guidance
34	a		$(K_a =) \frac{[H^+][NO_2^-]}{[HNO_2]} \checkmark$ IGNORE state symbols	1	IGNORE $\frac{[H^+]^2}{[HNO_2]}$ OR $\frac{[H^+][A^-]}{[A]}$ ALLOW H_3O^+ for H^+ Square brackets required Examiner's Comments Almost all candidates successfully wrote the expression for K_a. Responses using $[H^+(aq)]^2$ were not credited. Rarely, the expression was shown inverted or square brackets were omitted from one or more of the terms. For most candidates, this was an easy mark.

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
	b	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.12 award 2 marks ----- $[H^+] = \sqrt{K_a \times [HNO_2]} = 7.502 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} \checkmark$ pH = $-\log 7.502 \times 10^{-3} = 2.12 \checkmark$ pH to 2 DP	2	----- ALLOW intermediate value from 3 SF (7.50 up to calculator value of $7.501999733 \times 10^{-3}$) ALLOW 1 mark for 2.1 OR answer > 2 DP (i.e. not 2 DP) ONLY ALLOW pH mark by ECF if K_a AND 0.120 used and AND pH < 7 ----- COMMON ERRORS (MUST be to 2 DP) pH = 4.25 No square root: 1 mark $[H^+] = (4.69 \times 10^{-4} \times 0.120) = 5.628 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ pH = $-\log 5.628 \times 10^{-5} = 4.25 \checkmark$ pH = 0.92 no K_a used: zero marks pH = $-\log 0.120 = 0.92$ pH = 13.08 K_w / pOH used: zero marks pH = $-\log \frac{1.00 \times 10^{-14}}{0.120}$ OR $14 - \log 0.120 = 13.08$ Examiner's Comments Most candidates calculated $[H^+]$ as the square root of $K_a \times [HNO_2]$, and then the correct pH value. The commonest errors were incorrect rounding of the pH value (e.g. 2.13) and missing out the square root (giving 4.25). Answer: pH = 2.12

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	c	i	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 3.43, AWARD 4 marks ----- Expression: $K_a \times \text{acid} / \text{base ratio}$ Use of $K_a \times \frac{[\text{HNO}_2]}{[\text{NO}_2^-]}$ OR $4.69 \times 10^{-4} \times \frac{[\text{HNO}_2]}{[\text{NO}_2^-]}$ ✓ Using correct concs / mol in expression $[\text{H}^+] = 4.69 \times 10^{-4} \times \frac{0.0400}{0.0500}$ ✓ Subsumes previous mark Calculation of $[\text{H}^+]$ $[\text{H}^+] = 3.752 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ pH to 2 DP (From 3.42573717) $\text{pH} = -\log 3.752 \times 10^{-4} = 3.43 \checkmark$ NO marks are available using K_a square root approach (weak acid pH) $K_w/10^{-14}$ approach (strong base pH) ----- ALLOW alternative approach based on Henderson–Hasselbalch equation (ALLOW $-\log K_a$ for $\text{p}K_a$) $\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$ OR $\text{p}K_a - \log \frac{[\text{HNO}_2]}{[\text{NO}_2^-]}$ ✓ $\text{pH} = \text{p}K_a + \log \frac{0.0500}{0.0400}$ OR $\text{p}K_a - \log \frac{0.0400}{0.0500}$ ✓ $\text{pH} = \text{p}K_a + 0.097 \checkmark$ $\text{pH} = 3.329 + 0.097 = 3.43 \checkmark$	4	FULL ANNOTATIONS MUST BE USED ----- ALLOW just $K_a \times \frac{\text{acid}}{\text{salt}}$ expression Mark by ECF from $4.69 \times 10^{-4} \times \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$ inverted expression Mark by ECF from incorrect $[\text{HNO}_2]$ and $[\text{NO}_2^-]$ ONLY award marks for a pH calculation via K_a AND using concentrations / mol derived from the question DO NOT ALLOW final pH mark by ECF if $\text{pH} > 7$ ----- COMMON ERRORS BUT CHECK WORKING $\text{pH} = 2.82$ 3 marks initial concs: 0.200 and 0.0625 $\text{pH} = 3.23$ 3 marks 0.0400 and 0.0500 acid / base ratio inverted $\text{pH} = 3.83$ 2 marks initial concs: 0.200 and 0.0625 and ratio inverted $\text{pH} = 2.73$ 3 marks Incorrect $[\text{NO}_2^-] = 0.01$ and correct $[\text{HNO}_2] = 0.04$ $\text{pH} = 4.03$ 3 marks correct $[\text{NO}_2^-] = 0.05$ and incorrect $[\text{HNO}_2] = 0.01$ Examiner's Comments This buffer calculation was easier than some on recent papers as the equilibrium moles had been provided. Some candidates tried to mimic the approach for

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Question			Answer/Indicative content	Marks	Guidance
					a more complex calculation, introducing errors where there were none. The simpler problem allowed more candidates to obtain the correct value for the pH of the buffer solution than in recent examinations. Answer: pH = 3.43
		ii	Equilibrium: 1 mark $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$ ✓ (ignore state symbols) Control of pH: 2 marks (QWC) <i>Added HCl</i> NO_2^- reacts with added acid / HCl / H^+ OR $\text{NO}_2^- + \text{H}^+ \rightarrow$ OR more HNO_2 forms ✓ <i>Added NaOH</i> HNO_2 reacts with added alkali / NaOH / OH^- OR $\text{HNO}_2 + \text{OH}^- \rightarrow$ OR more NO_2^- forms OR H^+ reacts with added alkali / NaOH OR $\text{H}^+ + \text{OH}^- \rightarrow$ ✓ Equilibrium shift: 1 mark for shifts in $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$ (See 1st mark) Equilibrium for added acid → left AND Equilibrium for added alkali → right ✓ (QWC)	4	FULL ANNOTATIONS MUST BE USED ----- IGNORE $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ Equilibrium sign essential BUT ALLOW small slips in its appearance if it is obviously an attempt to show an equilibrium sign rather than an arrow QWC: Quality of written communication DO NOT ALLOW HA and A^- for HNO_2 and NO_2^- IGNORE just acid reacts with added alkali IGNORE just conjugate base / salt / base reacts with added acid DO NOT ALLOW salt / base reacts with added acid AWARD 'shift mark' ONLY if correct equilibrium equation has been given IGNORE any other equilibria in response Examiner's Comments The role of buffers in controlling pH is a common question and most candidates had prepared their rehearsed answers. Consequently these candidates could obtain the four marks easily. As always, candidates who had not learnt the work produced muddled responses that made little sense and could not be credited.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	d	i	Endothermic AND K_w increases with temperature OR Endothermic AND dissociation increases with temperature OR Endothermic AND (dissociation) involves breaking bonds ✓	1	Endothermic and reason required for the mark ALLOW Endothermic AND increasing temperature shifts equilibrium / reaction to the right / favours forward reaction DO NOT ALLOW breaking hydrogen bonds OR intermolecular bonds / forces Examiner's Comments Candidates were expected to predict the type of energy change using the provided information. Credit was given for responses linking an endothermic change with the increase of K_w with temperature or breaking bonds during dissociation.
		ii	OH^- concentration $[OH^-] = \frac{9.311 \times 10^{-14}}{1.00 \times 10^{-7}} = 9.311 \times 10^{-7} \text{ (mol dm}^{-3}\text{)} \checkmark$ Explanation (dependent on 1st mark) $9.311 \times 10^{-7} > 1.00 \times 10^{-7}$ OR $[OH^-] > [H^+]$ OR OH^- in excess AND Alkaline ✓	2	H^+ OR OH^- concentration (neutral pH) $[H^+] = [OH^-] = \sqrt{9.311 \times 10^{-14}} = 3.05 \times 10^{-7} \text{ (mol dm}^{-3}\text{)} \checkmark$ Explanation (dependent on 1st mark) $pH = -\log(3.05 \times 10^{-7}) = 6.5 \rightarrow 6.515501837 \text{ (calc)}$ AND Alkaline ✓ Examiner's Comments Most candidates calculated a value for $[H^+]$ using the K_w value at 60°C. Many recognised that $[OH^-] > [H^+]$ giving an alkaline solution. An alternative and equally valid method seen was to calculate the pH of a neutral solution at 60°C as 6.52 and then to relate water at a pH of 7 as being alkaline. Many using this approach thought that water would be acidic rather than alkaline, presumably because $6.52 < 7.00$.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iii	$pK_w = 13.03$ ✓	1	ONLY correct answer Examiner's Comments Despite the novel context, almost all candidates obtained the correct pK_w value of 13.03.
		iv	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 10.76, award 3 marks Dilution 1 mark $[OH^-(aq)] = [NaOH(aq)] = \frac{0.0270}{5} = 0.00540 \text{ (mol dm}^{-3}\text{)} \checkmark$ $[H^+]$ 1 mark $[H^+(aq)] = \frac{9.311 \times 10^{-14}}{0.00540} = 1.72 \times 10^{-11} \text{ (mol dm}^{-3}\text{)} \checkmark$ Calculator: $1.724259259 \times 10^{-11}$ pH 1 mark $pH = -\log 1.72 \times 10^{-11} = 10.76 \checkmark$ ALLOW pOH method for 2nd and 3rd mark: $pOH = -\log 0.00540 = 2.27 \checkmark$ (calculator 2.26760624) $pH = 13.03 - 2.27 = 10.76 \checkmark$	3	FULL ANNOTATIONS MUST BE USED ALLOW dilution AFTER calculation of $[H^+(aq)]$ i.e. original $[H^+] = \frac{9.311 \times 10^{-14}}{0.0270} = 3.45 \times 10^{-12} \text{ (mol dm}^{-3}\text{)} \checkmark$ After dilution, $[H^+] = 3.45 \times 10^{-12} \times 5 = 1.72 \times 10^{-11} \text{ (mol dm}^{-3}\text{)} \checkmark$ $pH = -\log 1.72 \times 10^{-11} = 10.76 \checkmark$ ALLOW ECF from incorrect $[H^+(aq)]$ provided that $pH > 7$ COMMON ERRORS (MUST be to 2 DP) $pH = 11.73$ At 25°C (1.00×10^{-14}): 2 marks $pH = -\log 1.85 \times 10^{-12} = 11.73$ $pH = 11.46$ No dilution at 60°C (9.311×10^{-14}) 2 marks $pH = -\log(3.45 \times 10^{-12}) = 11.46$ $pH = 12.43$ No dilution AND 25°C (1.00×10^{-14}) 1 mark $pH = -\log(3.70 \times 10^{-13}) = 12.43$ $pH = 12.16 \times 5$ instead of $\div 5$ at 60°C (9.311×10^{-14}) 2 marks $pH = -\log(6.879 \times 10^{-13}) = 12.16$ $pH = 13.13 \times 5$ instead of $\div 5$ at 25°C (1.00×10^{-14}) 1 mark $pH = -\log(7.407 \times 10^{-14}) = 13.13$ NOTE: Attempts at dilution $\rightarrow 0.0270$ with error in powers of 10 $\rightarrow 12.46$ from 0.00270 , etc may give 2 marks by ECF Examiner's Comments The majority of candidates correctly calculated the pH via K_w but many had

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					problems in initially deriving the concentration of the diluted solution of NaOH. Some candidates did not consider the dilution at all; others produced long calculations of this simple dilution, obtaining an array of concentrations. Provided that this concentration was then converted to a pH by a correct method, credit could still be given for the second part of the problem. Answer: pH = 10.76
			Total	18	
35			B	1	
			Total	1	
36			C	1	
			Total	1	
37			B	1	
			Total	1	
38			B	1	
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
39			FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 5184/5180 atm² award 7 marks IF answer = 5184/5180 with incorrect units award 6 marks Equilibrium amounts in mol 2 MARKS 3 correct ✓✓ 2 correct ✓ $n(\text{H}_2\text{O}) = 0.600 \text{ mol}$ $n(\text{H}_2) = 2.40 \text{ mol}$ $n(\text{CO}) = 0.800 \text{ mol}$ Partial pressures Total moles = 4.00 (mol) ✓ $p(\text{CH}_4) = \frac{0.200}{4.00} \times 30.0 = 1.50 \text{ atm AND}$ $p(\text{H}_2\text{O}) = \frac{0.600}{4.00} \times 30.0 = 4.50 \text{ atm AND}$ $p(\text{H}_2) = \frac{2.40}{4.00} \times 30.0 = 18.0 \text{ atm AND}$ $p(\text{CO}) = \frac{0.800}{4.00} \times 30.0 = 6.00 \text{ atm ✓}$ K_p calculation $k_p = \frac{p(\text{H}_2)^3 \times p(\text{CO})}{p(\text{CH}_4) \times p(\text{H}_2\text{O})} \text{ OR } \frac{18.0^3 \times 6.00}{1.50 \times 4.50}$ ✓ $k_p = 5184 \text{ OR } 5180 \text{ atm}^2 \text{ ✓}$ units = atm² ✓	7	Final answer must be correct and have the correct units to score all seven marks If there is an alternative answer, check to see if there is any ECF credit possible using working below ALLOW ECF from equilibrium amounts OR/AND incorrect total number of moles Correct values substituted into correct expression for K_p gains first five marks. ALLOW ECF with answer 3 or more SF up to calculator value, correctly rounded
			Total	7	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
40	a	i	$(K_a =) \frac{[H^+][C_6H_7O_6^-]}{[C_6H_8O_6]} \checkmark$ ALL species MUST have square brackets State symbols not required TAKE CARE that 'H' is different on top and bottom of expression	1	ALLOW $[H_3O^+]$ for $[H^+]$ IGNORE state symbols, even if wrong IGNORE $\frac{[H^+]^2}{[C_6H_8O_6]}$ OR $\frac{[H^+]^2[A^-]}{[HA]}$
		ii	$pK_a = -\log K_a = -\log (6.76 \times 10^{-5}) = 4.17 \checkmark$	1	Answer required to two DP
		iii	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.82 award 4 marks ----- $n(\text{vitamin C}) = \frac{3 \times 0.500}{176}$ $= 8.52(2) \times 10^{-3} \text{ (mol)} \checkmark$ $[\text{vitamin C}] = 8.52 \times 10^{-3} \times \frac{1000}{250}$ $= 0.0341 \text{ (mol dm}^{-3}\text{)} \checkmark$ $[H^+] = \sqrt{(K_a \times [C_6H_8O_6])} \text{ OR } \sqrt{(6.76 \times 10^{-5} \times 0.0341)} \text{ OR } 1.52 \times 10^{-3} \text{ mol dm}^{-3} \checkmark$ $pH = -\log(1.52 \times 10^{-3}) = 2.82 \checkmark$ Answer required to two DP	4	ALLOW ECF from incorrect $n(\text{vitamin C})$ ALLOW ECF from incorrect $[\text{vitamin C}]$ must be derived from $\sqrt{(K_a \times [C_6H_8O_6])}$ ALLOW ECF from incorrect $[H^+]$ but ONLY if derived from $\sqrt{(K_a \times [C_6H_8O_6])}$

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b	i	FIRST, CHECK THE ANSWER ON ANSWER LINE IF ratio = 0.708 award 3 marks ----- $[H^+] = 10^{-pH} = 10^{-4.02} = 9.55 \times 10^{-5} \text{ (mol dm}^{-3}\text{)} \checkmark$ $\frac{[C_6H_7O_6^-]}{[C_6H_8O_6]} = \frac{K_a}{[H^+]} = \frac{6.76 \times 10^{-5}}{9.55 \times 10^{-5}} \checkmark$ $= \frac{0.708}{1} \checkmark$	3	IF there is an alternative answer, check to see if there is any ECF credit possible using working below ----- ANNOTATIONS MUST BE USED ALLOW ALTERNATIVE using Henderson–Hasselbalch equation ----- ALLOW 9.55×10^{-5} up to calculator value of $9.54992586 \times 10^{-5}$ correctly rounded ALLOW ECF from incorrect $[H^+]$ ALLOW 0.71 (2 SF) up to calculator value correctly rounded
		ii	mass of $C_6H_7O_6Na = 0.708 \times \frac{300}{176} \times 198.0$ $= 239 \text{ OR } 240 \text{ (mg)} \checkmark$	1	ALLOW ECF from answer to (i)
	c		FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = $0.0524 \text{ (mol dm}^{-3}\text{)}$ award 2 marks ----- $[H^+(aq)] = 10^{-pH} = 10^{-12.72}$ $= 1.91/1.9 \times 10^{-13} \text{ (mol dm}^{-3}\text{)} \checkmark$ $[NaOH] / [OH^-(aq)] = \frac{K_w}{[H^+(aq)]}$ $= \frac{1.0 \times 10^{-14}}{1.91 \times 10^{-13}}$ $= 0.0524 \text{ (mol dm}^{-3}\text{)} \checkmark$	2	ALLOW alternative approach via pOH pOH = $14 - 12.72 = 1.28 \checkmark$ $[NaOH] / [OH^-(aq)] = 10^{-pOH}$ $= 0.0524 \text{ (mol dm}^{-3}\text{)} \checkmark$ ALLOW any value between 0.052 and 0.053 answer depends on degree of rounding for H^+ but 2 SF minimum calculator: 0.052480746
			Total	12	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
41	<i>Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i> Level 3 (5–6 marks) A comprehensive conclusion which outlines control of concentrations for each experiment with all volumes shown AND uses quantitative results for determination of orders and rate equation AND calculates a value for the rate constant with units. <i>There is a well-developed conclusion showing a line of reasoning which is clear and logically structured. The working for control of variables, determination of orders/rate equation and rate constant are clearly linked to the experimental evidence.</i> Level 2 (3–4 marks) Reaches a sound, but not comprehensive, conclusion based on the quantitative results AND outlines control of all concentrations, diluting each solution at a time OR correctly identifies the orders supported by results and calculates a value for the rate constant. <i>The conclusion has a line of reasoning with some structure. The working for control of variables OR orders/rate equation AND rate constant are linked to the experimental evidence.</i> Level 1 (1–2 marks) Attempts to controls concentrations by diluting each solution in turn AND reaches a simple conclusion for orders to obtain a rate equation with few errors. <i>The working for orders, and rate equation are linked to the experimental data, but the evidence may not be clearly shown.</i>	6	Indicative scientific points may include: <u>Control of variables</u> <i>Initial concentrations throughout</i> • mix 10 cm³ of Br⁻, BrO₃⁻ and H⁺ • dilute each solution in turn with water • only one solution changed at a time • total volume kept the same NOTE: Volumes of each mixture could be shown and illustrates all points above, e.g. <i>Expt 1: 10 / 10 / 10</i> <i>Expt 2: 2.5 + 7.5 H₂O / 10 / 10</i> <i>Expt 3: 10 / 5 + 5 H₂O / 10</i> <i>Expt 4: 10 / 5 + 5 H₂O / 5 + 5 H₂O</i> ----- <u>Orders/rate equation</u> • Br⁻ 1st order BrO₃⁻ 1st order H⁺ 2nd order OR <i>rate</i> = $k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$ • Supported by reasoning from the experimental results <u>Calculation of k including units</u> • Value of k correctly calculated: $k = 12$ • Units: dm⁹ mol⁻³ s⁻¹ OR mol⁻³ dm⁹ s⁻¹

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			0 marks – No response or no response worthy of credit.		
			Total	6	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance						
42	a		Iodine (solution) has a yellow/orange/brown colour AND Concentration of I ₂ decreases/I ₂ is used up ✓	1	ALLOW products are colourless						
	b		<table border="1"><thead><tr><th>Time/s</th><th>[I₂(aq)]/mol dm⁻³</th></tr></thead><tbody><tr><td>0</td><td>0.0100 ✓</td></tr><tr><td>500</td><td>0.00225 ✓</td></tr></tbody></table>	Time/s	[I ₂ (aq)]/mol dm ⁻³	0	0.0100 ✓	500	0.00225 ✓	2	ALLOW 0.01 and 0.010 ALLOW 0.0023
Time/s	[I ₂ (aq)]/mol dm ⁻³										
0	0.0100 ✓										
500	0.00225 ✓										
	c	i	Axes labelled with units AND linear scales AND at least half of the graph paper used ✓ Points correctly plotted ✓ Best fit straight line ✓	3	Each point must be within one small square on graph paper of value in table						
		ii	Order = 0 ✓ Straight line graph shows rate is constant throughout OR rate does not depend on [I ₂] ✓	2							

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	d		Step 1: $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 + \text{H}^+$ $\longrightarrow \text{H}_3\text{C}-\overset{\text{OH}^+}{\parallel}{\text{C}}-\text{CH}_3 \checkmark$ Step 3: $\text{H}_3\text{C}-\overset{\text{OH}}{\mid}{\text{C}}=\text{CH}_2 + \text{I}_2$ $\longrightarrow \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{I} + \text{HI} \checkmark$	2	ALLOW correct molecular, structural OR skeletal OR displayed formula OR mixture of the above as long as non-ambiguous
			Total	10	
43		i	Complete dissociation would give $[\text{H}^+] = 0.2 \text{ (mol dm}^{-3}\text{)} \checkmark$ pH from complete dissociation = $-\log 0.2 = 0.7$ OR actual $[\text{H}^+] = 10^{-0.96} = 0.11 \text{ (mol dm}^{-3}\text{)} \checkmark$ Stage 1 is complete dissociation AND Stage 2 is partial dissociation $\checkmark$	3	IGNORE Stage 1 is a strong acid AND Stage 2 is a weak acid.
		ii	Observation: fizzing $\checkmark$ H^+ reacts with carbonate AND (Stage 2) equilibrium shifts to the right $\checkmark$	2	ALLOW effervescence/'bubbling'
			Total	5	
44			A	1	
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
45			C	1	ALLOW 4.1 in the box
			Total	1	
46			B	1	ALLOW 0.426 in the box
			Total	1	

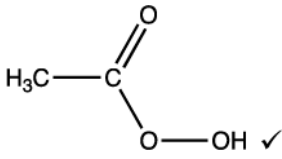
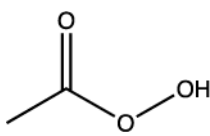
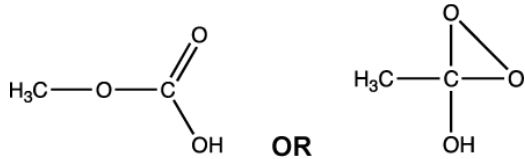
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
47	a	i	(rate =) $k [\text{H}_2\text{O}_2] [\text{I}^-] \checkmark$ $k = \frac{\text{rate}}{[\text{H}_2\text{O}_2] [\text{I}^-]} = \frac{2.00 \times 10^{-6}}{0.0100 \times 0.0100} = 0.02(00) \checkmark$ units: $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \checkmark$	3	Square brackets required IGNORE any state symbols IGNORE $[\text{H}^+]^0$ ALLOW ECF from incorrect rate equation BUT units must fit with rate equation used ALLOW $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ OR in any order NOTE K_c expression with calculation and units 0 marks Examiner's Comments This rates calculation was generally well answered. Surprisingly, some candidates did not write the rate equation, despite being part of the question. A common mistake was omission of $\times 10^{-6}$. Most candidates find determination of orders from initial rates data a straightforward task. Despite this, many obtained an incorrect rate equation, the most common being $\text{rate} = k[\text{I}^-]$. The mark scheme allowed error carried forward from an incorrect rate equation for both the calculated value of k and its units.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	Plot graph using $\ln k$ AND $1/T$ ✓ (Measure) gradient ✓ Independent mark $E_a = (-)R \times \text{gradient}$ OR $(-)8.314 \times \text{gradient}$ ✓ - Independent mark, even if variables for graph are incorrect - Subsumes 'gradient' mark	3	Unless otherwise stated, assume, that $\ln k$ is on y axis and $1/T$ is on x axis IGNORE intercept ALLOW gradient = $(-)\frac{E_a}{R}$ ----- NOTE: ALLOW 'Inverse graph' (special case) Plot graph of $1/T$ against $\ln k$ ✓ (Measure) gradient ✓ Independent mark $E_a = (-)\frac{R}{\text{gradient}}$ OR $(-)\frac{8.314}{\text{gradient}}$ OR gradient = $(-)\frac{R}{E_a}$ ✓ Subsumes 'gradient' mark Examiner's Comment: Most candidates used the logarithmic form of the Arrhenius equation from the Data Sheet and recognised that a graph of $\ln k$ against $1/T$ would produce a gradient of $-E_a/R$. Errors were sometimes made with the graph itself with many opting for $\ln k$ against T or k against T. A significant number of candidates seemed muddled by the term 'against' in describing their graph. A safer option is to state the axes for each variable.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b	i	 ALLOW skeletal OR displayed formula OR mixture of the above as long as non-ambiguous, e.g. 	1	ALLOW  OR Structure must include OH as part of COOOH group ALLOW $\text{O}^- \text{H}^+$ in structure Examiner's Comment: This part was attempted well, with many providing a structure containing the correct COOOH functional group. The mark scheme did allow alternatives provided that the three O atoms were bonded to the C atom, e.g. $\text{H}_3\text{C}-\text{O}-\text{COOH}$

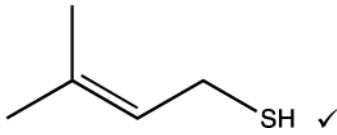
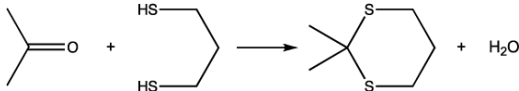
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 0.023(125) (mol) award 3 marks for calculation ----- <i>K_c expression</i> $(K_c =) \frac{[\text{CH}_3\text{COOOH}]}{[\text{H}_2\text{O}_2][\text{CH}_3\text{COOH}]} \checkmark$ [CH₃COOOH] $= 0.37 \times 0.500 \times 0.500 = 0.0925$ (mol dm⁻³) ✓ <i>Subsumes K_c expression</i> n(CH₃COOOH) $= 0.0925 \times \frac{250}{1000} = 0.023(125) \text{ (mol)} \checkmark$	3	If there is an alternative answer, check for any ECF credit ----- ALLOW 0.37 = $\frac{[\text{CH}_3\text{COOOH}]}{0.500 \times 0.500}$ ALLOW ECF but ONLY if 0.37 AND 0.5 × 0.5 have been used Common errors 0.076 2 marks Use of $[\text{CH}_3\text{COOOH}]^2$ 0.675 2 marks Use of 0.5 for $[\text{H}_2\text{O}]$ on K_c 0.169 2 marks Inverted K_c 0.338 1 mark Inverted K_c AND 0.5 for $[\text{H}_2\text{O}]$ 5.78×10^{-3} 2 marks $\times \frac{250}{1000}$ before $[\text{CH}_3\text{COOOH}]$ Examiner's Comment: Many candidates obtained the correct answer but water was often seen in the K_c expression. Candidates then assigned arbitrary values to the concentration of the water, often the same as CH₃COOH, unity, or even 55.6 from 1000/18. The mark scheme allowed some credit by use of error carried forwards. Answer: 0.023 mol
			Total	10	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
48	i $K_a = \frac{[H^+][C_4H_9S^-]}{[C_4H_9SH]} \checkmark$ Square brackets required	1	ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non- ambiguous Examiner's Comment: This part was very well answered. Candidates responded with either near molecular formulae, such as C_4H_9SH, structural formulae or with skeletal formulae. Some candidates made careless errors such as omitting the negative charge or showing $[H^+]^2$ as numerator rather than $[C_4H_9S^-][H^+]$.
	ii $CH_3CH_2CH_2CH_2SH + H_3C-C(=O)OH \longrightarrow H_3C-C(=O)S-CH_2CH_2CH_2CH_3 + H_2O$ Structure of thioester ✓ Complete equation ✓	2	ALLOW correct skeletal OR displayed formula OR mixture of the above as long as non-ambiguous ALLOW C_4H_9SH ALLOW CH_3COOH Thioester functional group must be fully displayed, OR as a skeletal formula but allow SC_4H_9 in thioester Examiner's Comment: In this part, candidates were expected to apply their knowledge and understanding of esterification to thiols and thioesters. Over half the candidates obtained a correct structure of the thioester. Most of these candidates constructed a balanced equation although some omitted the water product. Common errors included formation of a conventional ester and H_2S, and retaining the O atom from the OH in the carboxyl group to form $-COOS-$. As with 4(b)(i), structural and skeletal formulae were used. Candidates are less likely to omit H atoms if the skeletal formula is used.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iii		1	IF correct skeletal formula is shown, IGNORE displayed formula in a second structure Examiner's Comment: Just over half the candidates drew the correct structure, displaying a good understanding of interpreting organic nomenclature when drawing a structure. Common errors included omission of the CH₂ adjacent to the terminal –SH group and placing the branch or double bond in wrong positions. Some candidates spoilt an otherwise good response by showing a structural formula or a mixture of skeletal and structural formulae.
		iv	 Reactants ✓ Products AND balanced equation ✓	2	ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non- ambiguous Examiner's Comment: In this part, candidates were expected to apply their knowledge and understanding of condensation to an entirely new context. One mark was allocated for the reactants and this was usually scored. The second mark for the novel cyclic compound and water was much more difficult, aimed at stretch and challenge. A significant number of candidates interpreted the information to obtain a correct cyclic structure but this mark was the domain of the most able candidates.
			Total	6	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
49		i	(Species have) different states / phases ✓	1	Examiner's Comments All but a few candidates realised that the term heterogeneous equilibrium could be applied because carbon monoxide was in a different physical state to the other reactants and products.
		ii	$(K_p =) p(\text{CO(g)})^4$ ✓	1	Allow species without state symbols and without brackets, e.g. P_{co}^4, $pp\text{CO}^4$, PCO^4, $p(\text{CO}^4)$ etc. DO NOT ALLOW square brackets Examiner's Comments Marks were awarded for less than perfect versions of $K_p = p(\text{CO(g)})^4$. As long as a 'p' or a 'P' was seen and curved, rather than square, brackets, along with the correct power, the mark was awarded. This was to differentiate between the candidates who knew that only the partial pressures of gaseous species should feature in a K_p expression from the candidates who used all four species to write the expression.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iii	ΔG at 25 C $\Delta G = \Delta H - T\Delta S = 676.4 - (298 \times 0.7031)$ $= (+) 467 \text{ (kJ mol}^{-1}\text{) OR (+) 466876}$ $\text{(J mol}^{-1}\text{) } \checkmark$ <i>Non-feasibility statement</i> Non-feasible when $\Delta G > 0$ OR $\Delta G > 0$ OR $\Delta H > T\Delta S \checkmark$ <i>Minimum temperature</i> minimum temperature = $\frac{\Delta H}{\Delta S} = \frac{676.4}{0.7031}$ $= 962(.0) \text{ K } \checkmark$	3	IGNORE units ALLOW (+) 467 up to calculator value of 466.8762 correctly rounded ECF for any positive value determined in M1 ALLOW 962 up to calculator value of 962.0253165 correctly rounded Examiner's Comments Candidates coped well with the calculation and, apart from a significant number of rounding errors, could provide a positive value of ΔG and therefore could show the reaction to not be feasible. Candidates were also able to calculate that the minimum temperature required for the reaction to be feasible was 962.023165 K which was sensibly rounded to 962 K. A significant number of candidates chose to give 963 K as the final answer despite showing a correct value to several decimal places in their working.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iv	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = -110.5, Award 3 marks. ----- Correct expression $-13.5 = (4 \times -393.5) - (-1118.5 + 4 \times \Delta_f H(\text{CO}))$ ✓ Correct subtraction using ΔH and $\Delta_f H(\text{Fe}_3\text{O}_4)$ $4 \times \Delta_f H(\text{CO}) = (4 \times -393.5) - (-1118.5) + 13.5$ $= -442(.0) \text{ (kJ mol}^{-1}\text{)}$ ✓ Calculation of $\Delta_f H(\text{CO})$ formation $\Delta_f H(\text{CO}) = -\frac{442}{4} = -110.5 \text{ (kJ mol}^{-1}\text{)}$ ✓	3	For answer, ALLOW -111 (kJ mol⁻¹) ----- NOTE: IF any values are omitted, DO NOT AWARD any marks. e.g. -393.5 OR -13.5 may be missing ----- Common errors (+)110.5 <i>wrong / omitted sign</i> 2 marks (+)184.625 / 184.63 / 184.6 / 185 <i>No 4CO₂</i> 2 marks (+)738.5 / 739 <i>No 4CO₂ and no CO/4</i> 1 mark -117.25 / -117.3 / -117 <i>Wrong cycle</i> 2 marks -469 <i>Wrong cycle, no CO/4</i> 1 mark (+)177.875 / 177.88 / 177.9 / 178 <i>Wrong cycle, no 4CO₂</i> 1 mark -360.5 <i>Used 118.5</i> 2 marks Any other number: CHECK for ECF from 1st marking point for expressions using ALL values with ONE error only e.g. one transcription error:, e.g.395.3 for 393.5 Examiner's Comments The general method of determining $\Delta_f H(\text{CO})$ was known to most candidates, but many examples of avoidable errors were seen. For example, transcription errors in recording $\Delta_f H$ values (-393 for -393.5 and -118.5 for -1118.5). Candidates should be advised to show every step in their calculation. This would allow method marks to be applied in the absence of a correct final answer.
			Total	8	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
50	a		$n(\text{H}_2\text{O}_2) = 2.30 \times \frac{25.0}{1000} \text{ OR } = 0.0575 \text{ (mol)} \checkmark$ $\text{vol O}_2 = \frac{0.0575}{2} \times 24000 = 690 \text{ cm}^3 \checkmark$ Collect in 1000 cm³/1 dm³ measuring cylinder ✓	3	ALLOW 0.69(0) dm³ 2nd mark subsumes 1st mark ALLOW 1000 cm³/1 dm³ syringe Needs a name of actual apparatus, not just 'container' 'measuring cylinder' without volume is insufficient DO NOT ALLOW burette For other possible apparatus, contact Team Leader ALLOW volumes from 700–1000 cm³ but should be realistic apparatus, e.g. 700, 750, 800, 850, 900, 950. Examiner's Comments The majority of candidates were able to score the two marks for determining the volume of oxygen to be 690 cm³ (or 0.690 dm³). Only a very small proportion of candidates were able to suggest a suitably sized piece of apparatus.
	b		Measure mass (loss) ✓	1	ALLOW weight for mass ALLOW take samples and titrate (remaining H₂O₂) Examiner's Comments The idea of measuring mass loss (over time) was frequently given as a correct response. The idea of titrating samples to determine the concentration of hydrogen peroxide during the course of the reaction was occasionally seen and given credit.

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
	c	<i>Please refer to the marking instructions on page 5 of mark scheme for guidance on marking this question.</i> Level 3 (5–6 marks) A comprehensive conclusion using quantitative data from the graph to correctly determine initial rate AND half lives / gradient with 1st order conclusion for H_2O_2 AND determination of k. <i>There is a well-developed line of reasoning which is clear and logically structured. Clear working for initial rate, half life / gradient and order and k. Units mostly correct throughout.</i> Level 2 (3–4 marks) Attempts to describe all three scientific points but explanations may be incomplete. OR Explains two scientific points thoroughly with few omissions. <i>There is a line of reasoning with some structure and supported by some evidence. The scientific points are supported by evidence from the graph.</i> Level 1 (1–2 marks) Reaches a simple conclusion using at least one piece of quantitative data from the graph. Attempts to calculate initial rate OR half life. <i>There is an attempt at a logical structure with a reasoned conclusion from the evidence.</i> 0 marks No response worthy of credit.	6	Indicative scientific points may include: Initial rate - Tangent shown on graph as line at $t = 0$ s - Gradient determined in range: $1.5 - 2.0 \times 10^{-3}$ e.g. $\frac{2.3}{1300} = 1.77 \times 10^{-3}$ - initial rate as gradient value with units: $\text{mol dm}^{-3} \text{ s}^{-1}$, <i>For other methods contact TL</i> Evidence for 1st order 2 methods 1st order clearly linked to half-life OR 2 gradients: 1. Half life - Half life shown on graph - Half life range 800-1000 s - Two 'constant' half lives ± 50 s 2. Two gradients → two rates 2 tangents shown on graph at c and $c/2$ - Gradient at $c/2$ is half gradient at c e.g. $c = 2.3 \text{ mol dm}^{-3}$, gradient = 1.6×10^{-3} AND $c = 1.15 \text{ mol dm}^{-3}$, gradient = 0.8×10^{-3} - For chosen method, conclusion: H_2O_2 is 1st order Determination of k 2 methods k clearly linked to rate OR half-life:

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					$k = \frac{\text{rate}}{[\text{H}_2\text{O}_2]} \quad \text{s}^{-1} \quad \text{e.g. } k = \frac{1.6 \times 10^{-3}}{2.3} = 7 \times 10^{-4}$ $\text{OR } k = \frac{\ln 2}{t_{1/2}} \quad \text{e.g. } k = \frac{0.693}{950} = 7.3 \times 10^{-4} \text{ s}^{-1}$ Examiner's Comments This was the first of the two extended response questions in which the candidates had to determine three values based initially upon the graph. Some of the workings on the graph were a little hard to follow. Many candidates scored highly on this question, showing a good understanding of the chemistry involved. Weaker candidates sometimes struggled to express the link between the different values being calculated and were awarded a lower level mark.
			Total	10	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
51		i	$(K_c =) \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} \checkmark$ Units: $\text{dm}^3 \text{mol}^{-1} \text{s}$	2	IGNORE state symbols in K_c expression, even if wrong. For units, ALLOW $\text{mol}^{-1} \text{dm}^3$ DO NOT ALLOW dm^3/mol NOTE: If K_c upside down, units become mol dm^{-3} by ECF No other ECF allowed for units. Examiner's Comments The expression and the units were almost universally known by the candidates.
		ii	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.45, Award 4 marks. Equilibrium concentrations 1 MARK (moles x 2.5) $\text{SO}_2 = 0.135 \text{ (mol dm}^{-3}\text{)}$ AND $\text{O}_2 = 0.0675 \text{ (mol dm}^{-3}\text{)}$ ✓ Calculation of $[\text{SO}_3(\text{g})]$ 2 MARKS $[\text{SO}_3] = \sqrt{(K_c \times [\text{SO}_2]^2 \times \text{O}_2)}$ OR $\sqrt{(3.045 \times 10^4) \times 0.135^2 \times 0.0675}$ ✓ $= 6.12039291 \text{ (mol dm}^{-3}\text{)}$ ✓ <i>Answer scores both $[\text{SO}_3]$ marks automatically</i> Calculation of $n(\text{SO}_3)$ in 400 cm^3 1 MARK $n(\text{SO}_3) = 6.12039291/2.5 = 2.45 \text{ (mol)}$ ✓ 3SF required (Appropriate number)	4	FULL ANNOTATIONS NEEDED IF there is an alternative answer, check to see if there is any ECF credit possible using working below ALLOW ECF from incorrect concentrations of SO_2 and / or O_2 ALLOW ECF from incorrect $[\text{SO}_3]$ ALLOW 3 SF, 6.12, up to calculator value of 6.12039291 correctly rounded. Common errors 37.5 1 mark <i>No ✓ for $[\text{SO}_3]^2$ and no scaling by 1/2.5</i> 15.0 2 marks <i>No ✓ for $[\text{SO}_3]^2$</i> 0.619 3 marks <i>Use of mol of SO_2 and O_2</i> 1.55 2 marks <i>No conc used and Use of mol of SO_2 and O_2</i>

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					Examiner's Comments There were three steps to this calculation: • Conversion of molar quantities of SO₂ and O₂ to molar concentrations. • Insertion into the K_c expression and determining of the molar concentration of SO₃. • Conversion of the molar concentration of SO₃ to a molar quantity including an appropriate number of significant figures. Steps 1 and / or 3 of the calculation were occasionally omitted but as long as the calculation was presented in a coherent manner, partial credit was awarded.
			Total	6	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
52	a	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 0.753, award 3 marks $[H^+] = 10^{-pH} = 10^{-2.440} = 3.63 \times 10^{-3}$ (mol dm⁻³) ✓ $[CH_3COOH] = \frac{[H^+]^2}{K_a}$ OR $\frac{(3.63 \times 10^{-3})^2}{1.75 \times 10^{-5}}$ ✓ = 0.753 (mol dm⁻³) ✓	3	ALLOW use of HA and A⁻ ALLOW 3 SF up to calculator value of $3.630780548 \times 10^{-3}$ correctly rounded NOTE: Answer is same from unrounded [H⁺] calculator value and 3 SF [H⁺] value ALLOW 0.749 if [H⁺] has been subtracted from [CH₃COOH] for greater accuracy at end Examiner's Comments Most candidates coped with this commonly seen type of calculation and were able to correctly calculate the concentration of the weak acid

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b		$\text{CH}_3\text{COOH} + \text{FCH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{COOH}_2^+ + \text{FCH}_2\text{COO}^- \checkmark$ B2 A1 A2 B1 OR B1 A2 A1 B2 $\checkmark$ <i>i.e. labels other way round</i>	2	Watch for opposite order on RHS, i.e.: $\text{FCH}_2\text{COO}^- + \text{CH}_3\text{COOH}_2^+$ Take great care matching labels ALLOW ECF for incorrect proton transfer as below. This is the ONLY ECF $\text{CH}_3\text{COOH} + \text{FCH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{FCH}_2\text{COOH}_2^+ \times$ A1 B2 B1 A2 OR A2 B1 B2 A1 $\checkmark$ECF <i>i.e. labels other way round</i> Examiner's Comments For the able candidate, this question was quite straightforward but for the weaker candidate, there were many pitfalls. Candidates struggled with the idea that the equilibrium needed a positive ion and a negative ion on the product side. Others were unable to use K_a values in order to decide which of the two starting acids should become protonated. Finally, the assigning of the conjugate acid-base pairs was also challenging.
	c	i	[CH₃COO⁻] $n(\text{CH}_3\text{COONa}) = \frac{9.08}{82.0} \text{ OR } 0.111 \checkmark \text{ (Calc: } 0.1107317073)$ $[\text{CH}_3\text{COO}^-] = \frac{9.08}{82.0} \times \frac{1000}{250} = 0.443 \text{ (mol dm}^{-3}\text{)}$ OR $n(\text{CH}_3\text{COOH}) = 0.800 \times \frac{250}{1000} = 0.200 \text{ (mol)} \checkmark$ [H⁺] $[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \text{ OR } K_a \times \frac{n(\text{CH}_3\text{COOH})}{n(\text{CH}_3\text{COO}^-)}$ $= 1.75 \times 10^{-5} \times \frac{0.800}{0.443} \text{ OR } 1.75 \times 10^{-5} \times \frac{0.200}{0.111} \checkmark$ $= 3.16 \times 10^{-5} \text{ (mol dm}^{-3}\text{)} \checkmark$	5	ALLOW 2 sig fig ALLOW use of HA and A⁻ Mark by ECF ----- Alternative method (If both methods are attempted, mark the method which produces the higher mark) [H⁺] $[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.50}$ $= 3.16 \times 10^{-5} \text{ (mol dm}^{-3}\text{)} \checkmark$ [CH₃COO⁻]

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			pH (must come from <i>calculated</i> $[H^+]$) $pH = -\log (3.16 \times 10^{-5}) = 4.50 \checkmark$ ----- LAST 3 marks are NOT available using K_a square root approach (weak acid pH) $K_w/10^{-14}$ approach (strong base pH) ----- Henderson-Hasselbalch (HH) alternative $pK_a = -\log 1.75 \times 10^{-5} = 4.757$ (or 4.756961951..) $pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$ OR $pH = pK_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$ OR $pK_a + \log \frac{0.443}{0.800}$ OR $pK_a - \log \frac{0.800}{0.443} \checkmark$ $= pK_a - 0.257 \checkmark$ $= 4.757 - 0.257 = 4.50 \checkmark$		$[CH_3COO^-] = K_a \times \frac{[CH_3COOH]}{[H^+]}$ OR $1.75 \times 10^{-5} \times \frac{0.800}{3.16 \times 10^{-5}} \checkmark$ $= 0.443 \text{ (mol dm}^{-3}\text{)} \checkmark$ mass of CH_3COONa mass $CH_3COONa = 0.443 \times \frac{250}{1000}$ OR 0.111 $\checkmark$ $0.111 \times 82.0 = 9.08 \text{ (g)} \checkmark$ ----- Common errors 4.64 Use of $M(CH_3COONa) = 60$ 4 marks 2.40 Use of K_a of FCH_2COOH 4 marks Examiner's Comments This question caused difficulty for all but the more able. For many weaker candidates getting beyond a concentration of CH_3COONa was a problem. Once again, candidates should be advised to show every step in their calculation. This would allow method marks to be applied in the absence of a correct final answer.
		ii	pH is the same/constant $\checkmark$ ratio/proportion $[HA]/[A^-]$ is the same $\checkmark$	2	M2 is dependent upon M1 ALLOW Change in $[HA]$ and $[A^-]$ is proportional Examiner's Comments Only the very able were able to explain that the ratio of concentrations of acid and salt would remain constant and as K_a is constant, $[H^+]$ and therefore pH would remain constant.
			Total	12	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
53			A	1 (AO 1.1)	<u>Examiner's Comments</u> The vast majority of candidates knew graph A was correct.
			Total	1	
54			B	1 (AO 1.3)	<u>Examiner's Comments</u> This was a very successful multiple choice question for nearly all candidates.
			Total	1	
55			C	1 (AO 2.6)	<u>Examiner's Comments</u> This relatively difficult pH calculation was readily done successfully by higher ability candidates, but lower ability candidates found it difficult, with answer B proving a popular choice.
			Total	1	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
56	a	Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question. Level 3 (5–6 marks) A comprehensive conclusion which uses quantitative results for determination of the reaction orders. AND Determines k from correct rate equation. AND Proposes the two-step mechanism which adds up to overall equation <i>with no intermediate electrons</i>. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated. The working for the scientific content is clearly linked to the experimental evidence.</i> Level 2 (3–4 marks) Reaches a sound, but not comprehensive, conclusion based on the quantitative results. AND Correctly identifies the orders and rate equation. AND Calculates the rate constant OR Proposes the two-step mechanism with reactants of first step matching rate equation or matches orders <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. The working for the scientific content is clearly linked to the experimental evidence.</i> Level 1 (1–2 marks) Attempts to reach a simple conclusion for orders AND Attempts a relevant rate equation.	2	Indicative scientific points may include: Orders and rate equation Fe^{3+} 1st order AND I^- 2nd order OR $\text{rate} = k[\text{Fe}^{3+}][\text{I}^-]^2$ - Supported by experimental results Calculation of k, including units k correctly calculated AND correct units, e.g. $k = \frac{8.10 \times 10^{-4}}{(4.00 \times 10^{-2}) \times (3.00 \times 10^{-2})^2} = 22.5$ $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$ OR $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ Two-step mechanism - Two steps add up to give overall equation - Slow step/ rate-determining step matches stoichiometry of rate equation. - Each step balances by species and charge e.g. $\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow [\text{FeI}_2]^+ \quad \text{SLOW}$ $\text{Fe}^{3+}(\text{aq}) + [\text{FeI}_2]^+ \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq}) \quad \text{FAST}$ $\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{I}_2^-(\text{aq}) \quad \text{SLOW}$ $\text{Fe}^{3+}(\text{aq}) + \text{I}_2^-(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq}) \quad \text{FAST}$ $\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{Fe}^+ + \text{I}_2 \quad \text{SLOW}$ $\text{Fe}^{3+}(\text{aq}) + \text{Fe}^+ \rightarrow 2\text{Fe}^{2+}(\text{aq}) \quad \text{FAST}$ There may be other feasible possibilities <u>Examiner's Comments</u> Most candidates were able to use the information in the table to determine the order of reaction with respect to Fe^{3+} ions and I^- ions, which were 1 and 2 respectively. Most candidates were then able to use this knowledge and further information from the table to determine the rate constant, including units ($22.5 \text{ dm}^6 \text{mol}^{-2} \text{s}^{-1}$).

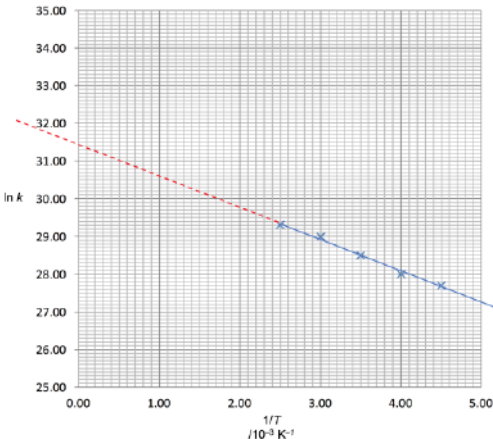
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			<i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant The working for the scientific content is clearly linked to the experimental evidence.</i> 0 marks No response or no response worthy of credit.		Many candidates appreciated that the mechanism involved a stoichiometric ratio of 1 : 2 with respect to Fe³⁺ ions and I⁻ ions, but only the more able were able to suggest a suitable possible two step mechanism. Common errors in proposing a mechanism included equations such as $\text{Fe}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \frac{1}{2}\text{I}_2(\text{aq}) + \text{I}^{-}(\text{aq})$ which gives a net ratio of 1 : 1 for the reactants. or $\text{Fe}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq}) + \text{e}^{-}$ which although introducing a correct ratio of reactants also introduces a ‘floating’ electron which in all reality would have attached itself to one of the product species. In questions such as 17a where the quality of extended responses is assessed candidates need to be aware of the need for explanation of their answers. For instance, just giving a correct order of a species in the rate equation is not as strong an answer as one which explains how altering, say doubling, the concentration of a reactant effects the overall rate of reaction, leading to determination of the order.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
			Exemplar 1 (a)* Determine the rate constant and a possible two-step mechanism for this reaction that are consistent with these results. [6] Experiment 1-2: when $[Fe^{2+}]$ is doubled and $[I^-]$ is constant, rate doubles so reaction is 1st order with respect to $[Fe^{2+}]$. Experiment 1-3: when $[I^-]$ is doubled and $[Fe^{2+}]$ is constant, rate quadruples so reaction is 2nd order with respect to $[I^-]$. $rate = k [Fe^{2+} (aq)] [I^- (aq)]^2$ $k = \frac{rate}{[Fe^{2+}] [I^-]^2}$ $= \frac{4.10 \times 10^{-4}}{4.00 \times 10^{-3} \times (3.00 \times 10^{-3})^2}$ $= 22.5 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ mechanism: slow step: $Fe^{2+} (aq) + 2I^- (aq) \rightarrow Fe^{2+} (aq) + I_2^- (aq)$ fast step: $Fe^{2+} (aq) + I_2^- (aq) \rightarrow Fe^{3+} (aq) + I_2 (aq)$ This exemplifies how a concise response can gain full marks on a Level of Response question. The candidate has clearly identified which data they have referred to in the table, and explained the conclusions that can be drawn. The rate equation is then clearly shown, along with subsequent working to determine the value of the rate constant. Finally, the suggested mechanism is given, along with an indication of which is the slow step. The line breaks clearly identify each stage in the response, and it fully satisfies the level 3 criteria in the mark scheme.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
b i	 Gradient Correct gradient calculated from best-fit straight line drawn within the range $\pm 800 \rightarrow \pm 1040$ ✓ E_a calculation $E_a = (-) \text{ gradient} \times 8.314$ ✓ e.g. from ± 820, $E_a = (+) 6817.48$ (J mol⁻¹) E_a to 3 SF AND use of 10^{-3} for gradient ✓ e.g. from ± 820, $E_a = (+) 6820$ (J mol⁻¹)	3	ALLOW lines which do not intercept y-axis ALLOW mark for gradient if correct working shown within E_a calculation without gradient being calculated separately ALLOW $\pm 0.8(00) \rightarrow \pm 1.04(0)$ (omission of 10^{-3}) ALLOW ECF for calculated gradient $\times 8.314$ If value of gradient not shown separately, ALLOW E_a in range: 6650 $\rightarrow$ 8650 OR 6.65 $\rightarrow$ 8.65 (omission of 10^{-3}) This mark subsumes gradient mark NOTE: Omission of 10^{-3} can get 1st 2 marks <u>Examiner's Comments</u> Higher ability candidates realised that the gradient was equivalent to $-E_a/R$ and determined a gradient within the range ± 800 to ± 1040, depending upon the line drawn. Credit was given to gradients of ± 0.800 to ± 1.040 resulting from calculations which omitted 10^{-3} on the x-axis. The negative gradient was multiplied by R to determine E_a with a value rounded to 3 significant figures. Common errors were omission of 10^{-3} in the calculation which led to E_a values between 6.65 and 8.65 J mol⁻¹, or not rounding to 3 significant figures.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	Intercept shown on graph could be by extrapolation of line, or label on y axis AND $\ln A$ linked to intercept value e.g. $\ln A = 31.4$ ✓ Calculation of $A = e^{\text{intercept}}$ ✓ e.g. $A = e^{31.4} = 4.33 \times 10^{13}$	2	ALLOW $y = 31.4$ ALLOW substitution of correct values of $\ln k$ and $1/T$ into $\ln k = -E_a/R \times 1/T + \ln A$ to give a value of $\ln A$ which approximately matches the intercept if given $\ln A = \ln k + (E_a/R \times 1/T)$ Calculation of $A = e^{\ln A}$ OR $e^{\ln k + (E_a/R \times 1/T)}$ ALLOW ECF from incorrect $\ln A$ $e^{31.2} = 3.55 \times 10^{13}$ $e^{31.3} = 3.92 \times 10^{13}$ $e^{31.35} = 4.12 \times 10^{13}$ $e^{31.45} = 4.56 \times 10^{13}$ $e^{31.5} = 4.79 \times 10^{13}$ $e^{31.6} = 5.29 \times 10^{13}$ $e^{31.7} = 5.85 \times 10^{13}$ $e^{31.8} = 6.46 \times 10^{13}$ $e^{31.9} = 7.14 \times 10^{13}$ $e^{32.0} = 7.9(0) \times 10^{13}$ $e^{32.1} = 8.73 \times 10^{13}$ IF 2 DP answer given, check rounding from calculator value, not 3 DP values given Eg $e^{31.7} = 5.8497 \times 10^{13}$ and = 5.8×10^{13} (2SF) <u>Examiner's Comments</u> Higher ability candidates realised that the y-intercept of $\ln k$ was equivalent to $\ln A$ and A was equivalent to $e^{(\ln A)}$ and were able to process this readily in their calculators. Common errors were to mis-read the intercept. For example, 31.5 was frequently seen as 31.05. Other candidates assumed the y-intercept was $\log A$ and tried to determine A by $10^{(\log A)}$.
			Total	11	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
57	a		$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} \checkmark$ Units = $\text{dm}^3 \text{mol}^{-1} \checkmark$	2	Must be square brackets IGNORE state symbols ALLOW $\text{mol}^{-1} \text{dm}^3$ ALLOW mol dm^{-3} as ECF from inverted K_c expression <u>Examiner's Comments</u> The expression and the units were almost universally known by the candidates.

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
	b	FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 1.2 (mol) award 4 marks Unless otherwise stated, marks are for correctly calculated values. Working shows how values have been derived. $[\text{NO}] = \frac{0.40}{4.0} = 0.1(0) \text{ (mol dm}^{-3}\text{)}$ AND $[\text{O}_2] = \frac{0.80}{4.0} = 0.2(0) \text{ (mol dm}^{-3}\text{)} \checkmark$ $[\text{NO}_2]^2 = 45 \times 0.102 \times 0.20 \text{ OR } = 0.09(0) \checkmark$ $[\text{NO}_2] = \sqrt{(45 \times 0.10^2 \times 0.20)} \text{ OR } = 0.3(0) \text{ (mol dm}^{-3}\text{)} \checkmark$ amount $\text{NO}_2 = 0.30 \times 4 = 1.2 \text{ (mol)} \checkmark$	4	ANNOTATIONS MUST BE USED For all parts, ALLOW numerical answers from 2 significant figures up to the calculator value Ignore rounding errors after second significant figure 1st mark is for realising that concentrations need to be calculated. ALLOW ECF Correct numerical answer with no working would score all previous calculation marks Making point 2 subsumes point 1 Making point 3 subsumes points 2 and 1 Common errors 9.6 = 3 marks mol of NO and O₂ used 0.36 = 3 marks mol of NO₂ calculated from [NO₂]² 2.4 = 2 marks mol of NO and O₂ used and no mol of NO₂ calculated <u>Examiner's Comments</u> There were three steps to this calculation: Conversion of molar quantities of NO and O₂ to molar concentrations. Insertion into the K_c expression and determination (via a square root calculation) of the molar concentration of NO₂. Conversion of the molar concentration of NO₂ to a molar quantity. Steps 1 and/or 3 of the calculation were occasionally omitted but if the calculation was presented in a coherent manner, even here, partial credit was awarded.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c	i	Exothermic AND K_p decreases as temperature increases ✓	1	ALLOW K_c for K_p ALLOW Equilibrium shifts to left hand side as temperature increases <u>Examiner's Comments</u> Most candidates knew the forward reaction was exothermic due to K_p decreasing as temperature increased. A common error was to write vague responses such as 'K_p decreases with temperature'.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	Equilibrium shift (Equilibrium position) shifts to right / forward / towards products ✓ Effect of increased pressure on K_p expression Ratio (in K_p expression) decreases OR Denominator/bottom of K_p expression increases more (than numerator/top) ✓ Equilibrium shift (K_p expression) Ratio (in K_p expression) increases to restore K_p OR Numerator/top of K_p expression increases to restore K_p ✓	3	FULL ANNOTATIONS NEEDED ALLOW K_c for K_p throughout the response. ALLOW K_p (initially) decreases for second marking point IF K_p is seen to be restored later in the process. ALLOW more NO_2 / product formed to restore K_p ALLOW ratio adjusts to restore K_p <u>Examiner's Comments</u> Candidates almost universally secured the first mark for equilibrium shifting to the right. Many scored this by simple application of Le Chatelier's principle, and then went on to incorrectly explain K_p increased because of this shift. Very few realised that (a constant) K_p drives Le Chatelier's principle (and not the other way around). An increase of pressure will increase the value of the partial pressures in the bottom half of the K_p expression more than the top half, thus (initially) decreasing the K_p ratio. Therefore, to restore K_p, the amount of NO_2 present must increase; consequently, the equilibrium shifts to the right.
			Total	10	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
58	a	i	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \checkmark$	1	IGNORE state symbols Must be square brackets IGNORE expressions with HA or with $[H^+]^2$ <u>Examiner's Comments</u> Almost universally known. Common errors were the use of [HA], $[A^-]$ or $[H^+]^2$.
		ii	FIRST, CHECK ANSWER ON ANSWER LINE IF answer = 4.76 award 3 marks $[H^+] = 10^{-pH}$ $= 10^{-2.41} = 3.89 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} \checkmark$ $K_a = \frac{[H^+]^2}{[CH_3COOH]} = \frac{(3.89 \times 10^{-3})^2}{0.870}$ $= 1.74 \times 10^{-5} \text{ (mol dm}^{-3}\text{)} \checkmark$ $pK_a = -\log K_a = -\log 1.74 \times 10^{-5} = 4.76 \checkmark$	3	ALLOW use of HA and A^- ALLOW 3 SF up to calculator value of: $3.89045145 \times 10^{-3}$ correctly rounded K_a $1.739725573 \times 10^{-5}$ NOTE: 1.74×10^{-5} is same from unrounded $[H^+]$ calculator value and 3 SF $[H^+]$ value 2 DP required <u>Examiner's Comments</u> This three-step calculation was successfully completed by almost all candidates. The common errors were to omit giving the final answer to 2 decimal places or to use $[H^+]$ rather than $[H^+]^2$ in the calculation, leading to a pK_a of 2.35.
		iii	$\% \text{ dissociation} = \frac{[H^+]}{[CH_3COOH]} \times 100$ $= \frac{3.89 \times 10^{-3}}{0.870} \times 100 = 0.447(\%) \checkmark$	1	3 SF required <u>Examiner's Comments</u> This proved a more difficult calculation than expected, but higher ability candidates realised that $[H^+]$ (determined from the pH) divided by the given concentration of CH_3COOH was required. Answers had to be expressed to three significant figures in order to receive credit.

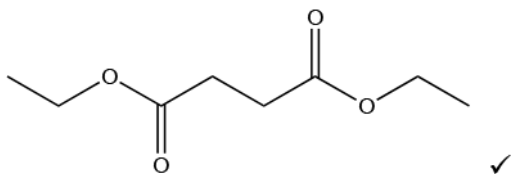
Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
	b	FIRST, CHECK ANSWER ON ANSWER LINE IF answer = 95.9(%) award 4 marks $[H^+] = 10^{-pH}$ $= 10^{-13.48} = 3.31 \times 10^{-14} \text{ (mol dm}^{-3}\text{)} \checkmark$ $[OH^-]$ from K_w $= \frac{1.00 \times 10^{-14}}{3.31 \times 10^{-14}} = 0.302 \text{ (mol dm}^{-3}\text{)} \checkmark$ Mass of (NaOH) $= 0.302 \times \frac{100}{1000} \times 40.0 = 1.21 \text{ (g)} \checkmark$ % of NaOH to 3 SF $= \frac{1.21}{1.26} \times 100 = 95.9 \text{ (}\%\text{)} \checkmark$	2	ALLOW ECF throughout IGNORE rounding errors beyond 3rd SF throughout ALLOW $3.3 \times 10^{-14} \text{ (mol dm}^{-3}\text{)}$ ALLOW 0.30 ALLOW 0.303 if 3.3×10^{-14} used in the first marking point ALLOW pOH method: $pOH = 14 - 13.48 = 0.52$ $[OH^-] = 10^{-0.52} = 0.302 \text{ (mol dm}^{-3}\text{)}$ ALLOW $[OH^-] \times 0.1 \times 40$ Rounding $[OH^-]$ to 0.3(0) gives $1.2/1.26 = 95.2\%$ Award 4 marks Rounding $[OH^-]$ to 0.303 gives $1.212/1.26 = 96.2\%$ Award 4 marks <u>Examiner's Comments</u> To help candidates, on this occasion early rounding was ignored and consequently most candidates scored full marks in this multi-step calculation. However, candidates should be advised not to round in the early stages of calculations such as this, as this introduces rounding errors into the final answer. Candidates should be encouraged to indicate what they are attempting to calculate in unstructured calculations such as this. The first step was frequently seen as $10^{-13.48} = 3.31... \times 10^{-14}$ which most examiners could take to be $[H^+]$. However, it is clearer to write $[H^+] = 10^{-13.48} = 3.31... \times 10^{-14} \text{ mol dm}^{-3}$. Even inclusion of units

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					would help some candidates achieve partial credit as this might allow examiners to determine what a candidate is attempting to do.
			Total	9	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
59		i	Titration ✓	1	IGNORE type of titration <u>Examiner's Comments</u> Candidates found this part difficult and only higher ability candidates identified that a titration could easily determine the concentration of succinic acid. The answers seen covered most of the techniques encountered in the course. Candidates should consider the information provided in a practical context to arrive at an informed response rather than what sometimes seemed to be a guess.
		ii	$(\text{CH}_2\text{COOH})_2 + 2\text{C}_2\text{H}_5\text{OH} \rightleftharpoons (\text{CH}_2\text{COOC}_2\text{H}_5)_2 + 2\text{H}_2\text{O} \checkmark$	1	ALLOW → instead of $\rightleftharpoons$ sign ALLOW molecular formulae or hybrid formulae <i>Structures provided on QP</i> e.g. $\text{C}_4\text{H}_6\text{O}_4 + 2\text{C}_2\text{H}_6\text{O} \rightleftharpoons \text{C}_8\text{H}_{14}\text{O}_4 + 2\text{H}_2\text{O}$ <u>Examiner's Comments</u> Candidates were required to derive the equation from which the supplied K_c expression had been written. Overall, this part was answered well but some candidates struggled with the brackets or used CH_2COOH_2 for succinic acid.
		iii		1	IGNORE displayed formulae <u>Examiner's Comments</u> This part discriminated extremely well with many candidates finding it difficult to convert the bracketed structural formula into a skeletal formula. Common errors were drawing of the mono-ester or omitting a carbon atom in the centre of the structure. Even when incorrect, most attempted answers were skeletal formulae.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iv	Volume cancels OR Same number of moles on each side of equation ✓	1	ALLOW units cancel ALLOW (sum of) balancing numbers/coefficients on each side of equation are the same OR same number of (moles of) reactants and products IGNORE volume is the same; K_c has no units <u>Examiner's Comments</u> Many candidates did not seem to realise that the supplied equation used moles, not concentrations. Those who did often stated that the mole representation could be used because the volume was the same for all. Of those who went on to state that the volume would cancel, only a few explained why that was true in this particular case. This challenging part discriminated very well. The best responses showed the units as n/V in the expression and showed that the volumes cancel.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		v	Moles of equilibrium products 1 mark $n(\text{CH}_2\text{COOC}_2\text{H}_5)_2 = 0.0300 \text{ (mol)}$ AND $n(\text{H}_2\text{O}) = 0.0600 \text{ (mol) } \checkmark$ Moles of $\text{C}_2\text{H}_5\text{OH}$ 1 mark $n(\text{C}_2\text{H}_5\text{OH}) = 0.150 - 0.060 = 0.0900 \text{ (mol) } \checkmark$ K_c calculated 1 mark $= \frac{0.03 \times 0.06^2}{0.02 \times 0.09^2} = 0.667 \text{ OR } 0.67 \checkmark$ NOTE: 0.02 must be used for $n(\text{succinic acid})$	3	ALLOW ECF ALLOW 0.66, 0.666, etc. (2 SF and more) <i>Treated as meaning 0.6 recurring</i> ALLOW 2/3 IGNORE any units <u>Examiner's Comments</u> Overall, this part discriminated well with many candidates obtaining the correct answer of 0.67. Common errors included a one significant figure answer of 0.6 or 0.7 and 0.375, by using 0.12 mol instead of 0.09 mol for the moles of ethanol. Many successful answers were well-presented and included a table of initial and final values. This gave a systematic way of deriving the equilibrium moles.
			Total	7	

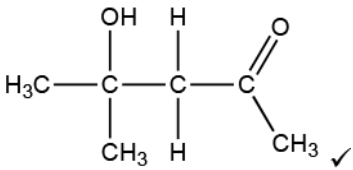
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
60		i	3-hydroxybutanal ✓	1	ALLOW 3-hydroxybutan-1-al IGNORE lack of hyphens or addition of commas ALLOW 4-oxobutan-2-ol OR 1-oxobutan-3-ol DO NOT ALLOW • 3-hydroxybutal • 3-hydroxybutanal <u>Examiner's Comments</u> Most candidates made good attempts at the name, the difficulty being that hydroxyl group needed to be shown as a hydroxy-prefix, rather than the suffix -ol. Common errors included 2-hydroxybutanal (counting the carbon chain from the wrong end) and 2- or 3-hydroxybutanoic acid (reading the aldehyde group as a carboxylic acid).
		ii	Addition ✓	1	IGNORE nucleophilic OR electrophilic OR radical DO NOT ALLOW addition–elimination, condensation, polymerisation <u>Examiner's Comments</u> This part was answered well with most choosing nucleophilic addition. Credit was given just for 'addition'.

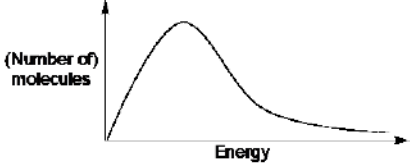
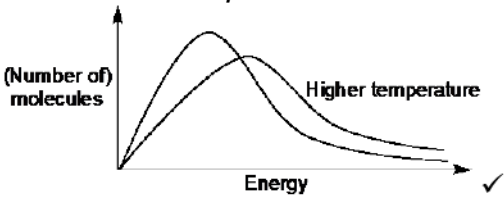
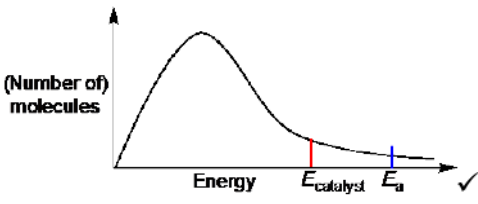
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	iii ALLOW any formula provided that number and type of atoms and charge are correct, e.g. For CH₃CHO, ALLOW CH₃COH, C₂H₄O, etc. Step 1: • Correct equation ✓ • One correct acid–base pair ✓ i.e. A1 and B1 OR A2 and B2 CH₃CHO + OH[−] ⇌ [−]CH₂CHO + H₂O OR CH₃CHO + OH[−] ⇌ CH₃CO[−] + H₂O ✓ A1 B2 B1 A2 OR A2 B1 B2 A1 Step 2: CH₃CHO + [−]CH₂CHO + H₂O → CH₃CHOHCH₂CHO + OH[−] ✓ For [−]CH₂CHO: ALLOW CH₂CHO[−]; CH₃CO[−]; C₂H₃O[−] For CH₃CHOHCH₂CHO, ALLOW C₄H₈O₂	3	Throughout, IGNORE ‘connectivity in any formula or structures shown. Examples in Answer column and in 6a(iv) guidance below Step 1: ALLOW H⁺ transfer from OH[−], i.e. CH₃CHO + OH[−] ⇌ CH₃CH₂O⁺ + O^{2−} ✓ B2 A1 A2 B1 OR B1 A2 A1 B2 Step 2: CH₃CHO + CH₃CH₂O⁺ + O^{2−} → CH₃CHOHCH₂CHO + OH[−] ✓ For CH₃CH₂O⁺: ALLOW CH₃CHOH⁺, C₂H₅O⁺ Examiner’s Comments This novel question linked together acid–base equilibria with a multi-step process. Many candidates completed an equation to generate acid–base pairs, which were then usually assigned correctly. The final equation was challenging but the highest ability candidates were able to combine together all the information with their earlier responses to arrive at the correct equation. See Exemplar 15. Exemplar 15 CH₃CHO + OH[−] ⇌ ..CH₃CO[−]..... + ...H₂O..... ✓ acid.1..... base.2..... base.1..... acid.2..... ✓ • Suggest the equation for step 2. CH₃CHO + ~~CH₃CO[−]~~ + H₂O → $\begin{array}{c} \text{H} & \text{OH} & \text{H} & \text{O} \\ & & & // \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \end{array}$ + OH[−] ✓ [3]

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iv		1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous For connectivity, ALLOW $\begin{array}{c} \\ \text{OH} \end{array}$ $\begin{array}{c} \\ \text{CH}_3 \end{array}$ CH₃– C₃H– OH– (Connectivity not being assessed) Examiner's Comments This part was one of the most challenging on the paper. Candidates needed to link the earlier information for combining two ethanal molecules to derive the product for combining two propanone molecules. Despite the challenge, the highest ability candidates were able to come up with the correct structure.
			Total	6	
61			D	1 (AO 1.2)	
			Total	1	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
62	Boltzmann distribution (seen anywhere) 2 marks  Curve Curve starts close to origin (ALLOW flexibility) AND curve does not touch x axis at high energy ✓ Labels (Number of) molecules/particles AND Energy ✓ Curves for two temperatures 1 mark  Catalyst and activation energy 1 mark  Molecules and activation energy, E_a 1 mark Explanation At higher temperature OR in presence of catalyst More molecules/particles/collisions • have energy above activation energy OR have enough energy to overcome E_a ✓ <i>Could be shown on diagram(s) using shaded area with annotations</i>	5	FULL ANNOTATIONS THROUGHOUT NOTE: Look for marking criteria within annotations on Boltzmann distribution diagram IGNORE slight inflexion on the curve IGNORE small increase at end of curve For labels, ALLOW kinetic energy IGNORE number of atoms IGNORE enthalpy for energy Temperature Drawing of two labelled curves AND higher temperature peak at higher energy AND lower on molecules IGNORE curves meeting at higher energy Higher temperature curve must cross over ASSUME that T_2 is higher temperature than T_1 Catalyst E_c shown at lower energy than E_a on Boltzmann distribution IGNORE catalyst provides a lower activation energy <i>Boltzmann distribution not used</i> ALLOW more molecules have energy to react ALLOW E_a for activation energy ALLOW E_c for activation energy with catalyst IGNORE more successful collisions OR collide more frequently Examiner's Comments This question was well-answered showing that most candidates were well-acquainted with the Boltzmann distribution. Some candidates used one diagram to show the effect of increasing the temperature and of

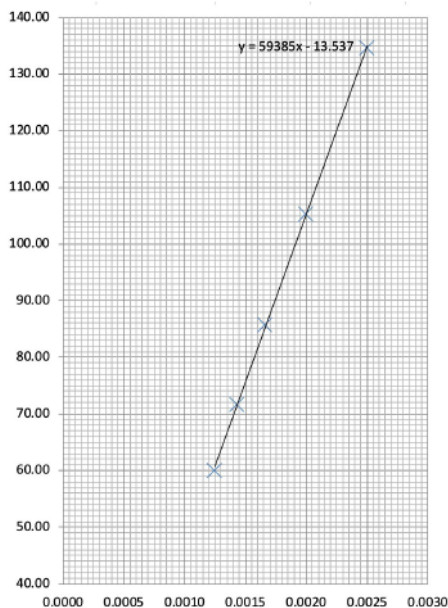
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					using a catalyst. Other candidates showed two curves, one for temperature, the other for the presence of a catalyst. Either approach could produce a clear response. Most candidates knew that the activation energy was lower with a catalyst that without. A significant number of candidates limited their explanations to 'successful collisions' without referring to more molecules exceeding the lower activation energy in the presence of catalyst or at a higher temperature. The best responses secured all five marks from a well-drawn and annotated graph supported by a brief explanation. Candidate should make full use of annotated diagrams to communicate their answers.
			Total	5	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance																																								
63	a	<table border="1"> <tr> <td>T/K</td><td>500</td><td>600</td><td>700</td><td>800</td></tr> <tr> <td>K_p</td><td>5.86×10^{45}</td><td>1.83×10^{37}</td><td>1.46×10^{31}</td><td>1.14×10^{26}</td></tr> <tr> <td>$\frac{1}{T}/K^{-1}$</td><td>2.00×10^{-3}</td><td>1.67×10^{-3}</td><td>1.43×10^{-3}</td><td>1.25×10^{-3}</td></tr> <tr> <td>$\ln K_p$</td><td>105</td><td>86</td><td>72</td><td>60</td></tr> </table> ✓ ✓ <i>Calculator values</i> <table> <tr> <td>$1/T$</td><td>2.00</td><td>1.66</td><td>1.42857</td><td>1.25</td></tr> <tr> <td>$/10^{-3}$</td><td></td><td>recurring</td><td>1429</td><td></td></tr> <tr> <td>$\ln K_p$</td><td>105.384</td><td>85.7999</td><td>71.7585</td><td>59.9982</td></tr> <tr> <td></td><td>4788</td><td>6441</td><td>7432</td><td>4068</td></tr> </table>	T/K	500	600	700	800	K_p	5.86×10^{45}	1.83×10^{37}	1.46×10^{31}	1.14×10^{26}	$\frac{1}{T}/K^{-1}$	2.00×10^{-3}	1.67×10^{-3}	1.43×10^{-3}	1.25×10^{-3}	$\ln K_p$	105	86	72	60	$1/T$	2.00	1.66	1.42857	1.25	$/10^{-3}$		recurring	1429		$\ln K_p$	105.384	85.7999	71.7585	59.9982		4788	6441	7432	4068	2 (AO 1.2×2)	Mark by row ALLOW 2 SF or more for $1/T$ but ignore trailing zeroes ALLOW whole numbers (± 1) for $\ln K_p$ ALLOW 1 small slip in each row. e.g. 1.66 for 1.67; 71.7 for 71.8 <i>Check with calculator values below table</i> BUT DO NOT ALLOW whole number errors, e.g. 85 for 86 <u>Examiner's Comments</u> Candidates were expected to complete values for $1/T$ and $\ln K_p$ from supplied T and K_p values. Candidates were supplied with an example and this enabled most candidates to obtain both available marks.
T/K	500	600	700	800																																								
K_p	5.86×10^{45}	1.83×10^{37}	1.46×10^{31}	1.14×10^{26}																																								
$\frac{1}{T}/K^{-1}$	2.00×10^{-3}	1.67×10^{-3}	1.43×10^{-3}	1.25×10^{-3}																																								
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	4788	6441	7432	4068																																								
	b	Equilibrium (position) shifts to the left AND (forward) reaction is exothermic ✓	1 (AO 2.2)	ALLOW 'favours reverse reaction' <i>Implies shift to left</i> ALLOW 'shifts in endothermic direction' BUT only if (forward) reaction stated as exothermic <u>Examiner's Comments</u> Most candidates were aware that a decrease in K_p with increasing temperature signals that the forward reaction is exothermic. The question also asked for the effect on the equilibrium position. A significant number of candidates omitted this part of the question. Candidates are advised to check back to all the requirements in a question.																																								

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
	c	Plotting of graph <u>All</u> points correctly plotted AND best-fit straight line ✓ Gradient Correct gradient of best-fit straight line within the range $\pm 57000 \rightarrow \pm 63000$ ✓ ΔH calculation (subsumes mark for gradient) $\Delta H = (-)$ gradient $\times 8.31(4)$ OR calculated value ✓ <i>e.g. from ± 60000, $\Delta H = (+)498840$ (J)</i> OR ± 498.840 (kJ) ΔH in kJ mol^{-1} ΔH correct in kJ mol^{-1} AND 3SF AND – sign ✓ <i>e.g. from ± 498840, $\Delta H = -499$ (kJ mol^{-1})</i>	4 (AO 3.1) (AO 3.1) (AO 3.2) (AO 3.2)	 ALLOW 4 points on graph Tolerance 1 small square ALLOW ΔH in range: $-480 \rightarrow -530$ (kJ mol^{-1}) This mark subsumes gradient mark <u>Examiner's Comments</u> Candidates were required to plot a graph using their calculated values from the above part. The axes for the graph had been provided. It was expected that the plotting of 5 points, with a best-fit straight line, would be straightforward. Many candidates plotted one or more points incorrectly, particularly the point at $1/T = 1.25 \times 10^{-3}$. Candidates then needed to recognise that the gradient is equal to $-\Delta H/R$ from Equation 5.1, to measure the gradient, and then to determine ΔH. Most candidates recognised that the gradient needed to be measured but its value was then not taken any further. The higher-attaining candidates correctly multiplied the gradient by R but did not always convert the calculated J mol^{-1} value into kJ mol^{-1}, or to express their value to 3 significant figures,

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					as required in the question. Significantly, nearly a third of candidates did not collect any of the four available marks. The question was an excellent discriminator.
	d		Extrapolate line to (y) intercept OR Measure/Use (y) intercept ✓ Intercept = $\frac{\Delta S}{R}$ OR $\Delta S = R \times (y) \text{ intercept}$ ✓ <i>This statement automatically subsumes 1st mark</i> NOTE: If 'x' intercept, DO NOT ALLOW 1st mark but 2nd mark available for $\times R$ as BOD	2 (AO 3.1x2)	ALLOW substitute values of $\ln K_p$, $1/T$ and gradient into Equation 5.1 ✓ From provided values and gradient = 60000: $= \frac{\Delta S}{R} = \ln K_p - \text{gradient} \times 1/T$ OR $135 - 60000 \times 2.50 \times 10^{-3} = -15$ ✓ Examiner's Comments Mathematically able candidates used the $y = mx + c$ equation for a straight line with the supplied mathematical relationship (Equation 5.1) to identify the y intercept as $\Delta S/R$. They then stated that ΔS could be determined by multiplying the value of the y intercept by R. Many candidates found the mathematical requirements of the above parts difficult. Responses for this part were often in terms of the gradient instead of 'intercept'.
			Total	9	
64			C	1 (AO 1.2)	ALLOW 2 in the answer box
			Total	1	
65			B	1 (AO 1.1)	
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
66			$\text{HCOOH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{HCOO}^- + \text{CH}_3\text{COOH}^{2+} \checkmark$ A1 B2 B1 A2 OR A2 B1 B2 A1 $\checkmark$ CARE: Both + and – charges required for products in equilibrium DO NOT AWARD the 2nd mark from an equilibrium expression that omits either charge	2 (AO 1.2×2)	IGNORE state symbols (even if wrong) IF proton transfer is wrong way around ALLOW 2nd mark for idea of acid–base pairs, <i>i.e.</i> $\text{HCOOH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{HCOOH}_2^+ + \text{CH}_3\text{COO}^-$ B2 A1 A2 B1 NOTE For the 2nd marking point (acid–base pairs), this is the ONLY acceptable ECF <i>i.e. NO ECF from impossible chemistry</i>
			Total	2	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
67	a		$p(\text{O}_2) = 0.21 \times 1.00 \times 10^5$ $= 21,000 / 2.1 \times 10^4 \text{ (Pa)} \checkmark$	1 AO 2.2	Examiner's Comments This question tested an understanding of 'partial pressure' as a concept. Most candidates obtained the correct response of 21,000 Pa or 2.1×10^4 Pa. Scaling proved to be a common error with 2.1×10^{-4} Pa being seen, presumably from dividing, instead of multiplying, 0.21 by 1×10^4. In calculations, candidates are advised to think about whether their answer is sensible, rather than relying just on the answer displayed on the calculator.
	b		$\text{Initial rate} = 10^{-2} \times 2.4 \times 10^{-3} \text{ s}^{-1}$ $= 2.4 \times 10^{-5} \text{ (mol dm}^{-3} \text{ s}^{-1}) \checkmark$	1 AO 2.2	Examiner's Comments This part tested an understanding of pH as a logarithmic scale and the relationship between rates and order. This part discriminated extremely well. A pH of 3 meant that the H^+ concentration would be 100 times less than at a pH of 1. Being a first order reaction with respect to H^+, the initial rate is simply 100 times less than at a pH of 1: $2.4 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$. The higher-ability candidates identified the relationships and often wrote the correct answer on the answer line with no visible working (presumably doing the calculation in their head). Others used their well-learned equations to calculate the same correct answer. Many candidates found the calculation difficult and 7.2×10^{-3} ($3 \times (2.4 \times 10^{-3})$) was a very common incorrect answer. If candidates had fully scrutinised this answer, they may have realised that a more dilute solution cannot produce a faster rate.
			Total	2	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
68	a		$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{HCO}_3^-$ OR $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^- + \text{CO}_2 \checkmark$	1 AO 1.2	ALLOW $\text{CO}_3^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{OH}^- + \text{H}_2\text{CO}_3$ IGNORE state symbols ALLOW inclusion of Na^+ as spectator ion, e.g. $2\text{Na}^+ + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^- + 2\text{Na}^+ + \text{CO}_2$ IGNORE $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2$ <i>Ionic equation required</i> IGNORE equation with H^+ or H_3O^+ e.g. $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{OH}^- + \text{CO}_2$ <i>Question asks for reaction with H_2O</i> <u>Examiner's Comments</u> This equation presented problems for many candidates, despite the question asking for an equation between carbonate ions and water. An acceptable equation had to be ionic and needed to produce OH^- (for the alkaline solution) and either HCO_3^- or CO_2. Many candidates wrote an equation with H^+ instead of H_2O, with lower ability candidates showing the carbonate ion with the wrong charge as CO_3^-. Many candidates wrote full equations despite the question asking for an ionic equation. Candidates do need to read the instructions in the question.

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
	b	Acid/H⁺/HCl reacts with OR protonates - benzoate / C₆H₅COO⁻ - carboxylate / salt (to form benzoic acid) ✓	1 AO 2.3	ALLOW suitable equation, e.g. C₆H₅COO⁻ + H⁺ → C₆H₅COOH IGNORE responses purely in terms of neutralisation of alkali, e.g. Acid/H⁺/HCl neutralises / reacts with/removes alkali / OH⁻ / CO₃²⁻ / Na₂CO₃ <u>Examiner's Comments</u> Candidates found this part extremely difficult. The question was aimed to stretch and challenge. Many candidates followed on directly from part (a), stating in simple terms that the alkaline solution needed to be neutralised to remove hydroxide ions. However, candidates were expected to recognise that the alkaline conditions would lead to benzoate ions rather than benzoic acid being present in the mixture. The mixture is acidified to protonate the benzoate. The hint in the question was about making the benzoic acid appearing when acid is added.
	c	C₆H₅CH₂OH + 2[O] → C₆H₅COOH + H₂O ✓	1 AO 2.6	ALLOW molecular, structural, displayed formulae, etc e.g. molecular: C₇H₈O + 2[O] → C₇H₆O₂ + H₂O <u>Examiner's Comments</u> This part discriminated well with many candidates being able to write a correct equation using their knowledge of the oxidation of alcohols. Mistakes usually resulted in the balancing with either [O] instead of 2[O] or 2H₂O instead of H₂O. Written equations always need to be checked for the atoms balancing.
	d	FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 33.8 OR 33.9 (%) award 3 marks ----- Theoretical moles	3 AO2.8×1	ALLOW ECF for each step Calculator = 0.03851851852

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Question			Answer/Indicative content	Marks	Guidance
			AND Filter AND (leave to) dry ✓ <i>All three needed</i>		DO NOT ALLOW use of drying agent (e.g. MgSO_4) IGNORE - Initial filtering - hot filtration to remove insoluble impurities <u>Examiner's Comments</u> Many candidates produced thorough responses, showing that they had encountered recrystallisation as a technique in their practical work. Most candidates were aware that the impure product is dissolved in a minimum volume of hot solvent, although 'minimum' was sometimes omitted. The subsequent stages were sometimes incomplete or in the wrong order. Many were aware that the hot solution can be passed through fluted filter paper to remove solid impurities. (This is beyond the specification requirements for A Level but good practice). Most candidates were aware of the need to filter (usually under reduced pressure) but the necessary cooling stage to form the crystals was sometimes omitted. Finally, many responses omitted the need to dry the crystals. Candidates did sometimes dry the crystals by adding an anhydrous salt (e.g. CaCl_2 or MgSO_4), a clear confusion with drying an organic liquid. Others described the purification of an organic liquid for their response, including use of a separating funnel, drying and distillation.
			Total	8	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
69			C	1 (AO 2.6)	<u>Examiner's Comments</u> This was well answered, with many candidates understanding that the activation energy in kJmol^{-1} is equal to (- gradient x R) divided by 1000, leading to C as the correct answer. Common errors included dividing the gradient by R, giving option A. or forgetting the minus sign and opting for B.
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
70	a		FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 2.98 award 2 marks ----- $[H^+] = \sqrt{(K_a \times [C_2H_5COOH])} = 1.039 \times 10^{-3}$ (mol dm⁻³) ✓ pH = $-\log 1.039 \times 10^{-3} = 2.98$ (Must be to 2 DP) ✓	2 (AO 2.2 ×2)	ALLOW ECF throughout ONLY ALLOW pH mark by ECF if K_a AND 0.080 used and AND pH <7 Common errors (Must be to 2 DP) One mark for pH = 5.97 (No square root): One mark for pH = 0.92 OR pH = 5.15 (Using incorrect K_a values) Examiner's Comments Most candidates could calculate the pH of a weak acid although a significant number gave the answer as 3.0, presumably confusing the demand for two decimal points with two significant figures.
	b	i	$n(C_2H_5COOH) = (0.0800 \times \frac{25.0}{1000}) = 0.002$ (mol) AND $V(NaOH) = \frac{0.002}{0.100} \times 1000 = (= 20(.0)$ cm³) ✓	1 (AO 2.5)	ALLOW 0.02 dm³ if unit given Mark is for WORKING which could all be shown as 1 step ALLOW method showing 20cm³ NaOH contains the same moles as acid $n(C_2H_5COOH) = 0.08(00) \times 0.025(0) = 0.002$ (mol) and $n(NaOH) = 0.02(00) \times 0.1 = 0.002(00)$ (mol) Examiner's Comments Showing by calculation something already known is a skill that some candidates find challenging. Many responses included rows of figures with '20 cm³' appearing at the end. Clarity of working is essential and in questions such as this, candidates are advised to include word descriptions of what they are calculating, even if it is abbreviations such as 'n' for number of moles.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	ii FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 12.55 award 4 marks ----- Excess mol of NaOH: $n(\text{OH}^-)_{\text{excess}} = n(\text{OH}^-) - n(\text{C}_2\text{H}_5\text{COOH})$ $= (0.100 \times \frac{45.0}{1000}) - (0.0800 \times \frac{25.0}{1000})$ $= 0.0045 - 0.002 = 0.0025 \text{ (mol)} \checkmark$ Concentration of OH⁻: $[\text{OH}^-] = (\frac{0.0025}{70.0 \times 10^{-3}}) = 0.0357 \text{ (mol dm}^{-3}\text{)} \checkmark$ Concentration of H⁺: $[\text{H}^+] = (\frac{1.00 \times 10^{-14}}{0.0357}) = 2.8 \times 10^{-13} \text{ (mol dm}^{-3}\text{)} \checkmark$ Conversion to pH: $\text{pH} = (-\log 2.8 \times 10^{-13}) = 12.55 \checkmark$	4 (AO 1.2 ×1) (AO 2.6 ×3)	ALLOW ECF throughout For first mark ALLOW (Excess volume of NaOH = 25(.0) cm³) $n(\text{OH}^-)_{\text{excess}} = 0.100 \times \frac{25.0}{1000} = 0.0025 \text{ (mol)}$ Common errors If initial V(NaOH) = 45 cm³ [OH⁻] = 0.0643 (mol) [H⁺] = 1.56 × 10⁻¹³ (mol dm⁻³) pH = 12.81 award three marks (no 1st mark) If $n(\text{OH}^-)_{\text{excess}}$ is used in [H⁺] calculation $n(\text{OH}^-)_{\text{excess}} = 0.0025 \text{ (mol)}$ $[\text{H}^+] = \frac{1.00 \times 10^{-14}}{0.0025} = 4.00 \times 10^{-12} \text{ (mol dm}^{-3}\text{)}$ pH = 11.40 award three marks (no 2nd mark) ALLOW pOH method for last two marks pOH = -log[OH⁻] = 1.447 pH = 14 - 1.447 = 12.55 ALLOW ECF for conversion from [H⁺] to pH provided value calculated is above 7 and from derived [H⁺] Examiner's Comments This calculation proved difficult with once again, many figures and sums appearing with little indication as to their relevance. Responses to 20bi/ii often featured rows of figures and random sums without a single word about what the figures were or sums were set to calculate. Candidates should remember to provide written indications of what it is they're working out – presenting the calculations without any annotations can make it harder for error carried forward marks to be given if there is an error in their calculation.

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		iii	Shape Slight rise/flat, AND (near) vertical, AND then slight rise/flat ✓ pH Vertical section within the extremes of pH 5 to 12 and a minimum range of three pH units AND middle of vertical section (equivalence point) needs to be above pH 7 ✓ End point Vertical section at ~ 20 cm³ NaOH ✓	3 (AO 2.3 ×1) (AO 2.4 ×2)	If pH curves wrong way round (i.e. adding acid to alkali), ONLY award mark for End point (~ 20 cm³) <u>Examiner's Comments</u> This weak acid / strong alkali titration curve required candidates to apply their knowledge. Some candidates found it difficult to draw an adequate titration curve. The key points to titration curves are: • A 'vertical' section at the end point • The vertical section with pH range correct to relative to the strength of acid/alkali • A correct equivalence point relative to pH 7 with respect to the strength of acid/alkali • A 'shallow curve' leading from 0 cm³ to vertical section • A 'shallow curve' leading from the vertical section to the total volume added For this reaction: • The vertical section was at 20 cm³ (given in 20bi) • As it was a weak acid and strong alkali reacting, the vertical section should start above pH 5 and finish around pH 11 • The equivalence point (half-way up the vertical section) for a weak acid / strong alkali titration should be above pH 7 • The starting pH should be that of the weak acid, C₂H₅COOH (answer to 20(a)) • The final pH should be that of the final solution (answer to 20(b)(ii))

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Question			Answer/Indicative content	Marks	Guidance
		iv	cresol purple AND pH range matches vertical section/rapid pH change OR end point/colour change matches vertical section/rapid pH change ✓	1 (AO 3.3)	ALLOW pH range (of the indicator) matches equivalence point ALLOW end point/colour change matches equivalence point IGNORE colour change matches end point <i>Colour change is the same as end point</i> <u>Examiner's Comments</u> Some candidates realised that the most suitable indicator for a weak acid / strong alkali titration would be cresol purple. For incorrect responses, other indicators appeared to be selected at random, suggesting that candidates were unclear on the criteria for selected a suitable indicator.
		v	similarity: end point / volume (20 cm^3) of NaOH needed to neutralise OR final pH / shape of curve after end point ✓ difference: HCN higher starting pH OR HCN shorter vertical section ✓	2 (AO 3.2 ×2)	End point must not refer to same pH ALLOW different equivalence point IGNORE different starting pH <u>Examiner's Comments</u> When identifying a similarity, many candidates confused the term 'equivalence point' with the term 'end point'. For differences, many candidates realised that HCN had a different K_a to $\text{C}_2\text{H}_5\text{COOH}$ but often did not appreciate that this would lead to a starting point with a higher pH.

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Question			Answer/Indicative content	Marks	Guidance
	c		HIO_3 dissociation is not negligible / dissociates to a significant extent OR Large K_a and HIO_3 is 'stronger' (weak) acid OR $[\text{HIO}_3]_{\text{eqm}}$ is significantly lower than $[\text{HIO}_3]_{\text{initial/undissociated}}$ ✓	1 (AO 3.3)	ALLOW use of HA Ignore $[\text{HIO}_3]_{\text{equilibrium}} < [\text{HIO}_3]_{\text{initial/undissociated}}$ ALLOW $[\text{HIO}_3]_{\text{equilibrium}} \sim [\text{HIO}_3]_{\text{undissociated}}$ is no longer a valid assumption ALLOW $[\text{HIO}_3]$ has a larger K_a so the assumption that $[\text{HIO}_3]$ at equilibrium = $[\text{HIO}_3]$ initially so assumption is not valid Examiner's Comments Very few candidates scored the mark for this question. The most common error was to write 'HIO_3 dissociates'. While correct, this is true of all weak acids. The subtlety in this question was to realise that because K_a was relatively high, the resultant acid strength would mean that the degree of dissociating was significant enough so initial $[\text{HIO}_3]$ was significantly less than $[\text{HIO}_3]$ at equilibrium. In other words, the assumption $[\text{HIO}_3]_{\text{initial}} = [\text{HIO}_3]_{\text{equilibrium}}$ is not valid in this case.
			Total	14	
71			C	1 (AO 2.2)	
			Total	1	
72			D	1 (AO 2.6)	
			Total	1	
73			B	1 (AO 2.6)	
			Total	1	
74			D	1 (AO 2.2)	
			Total	1	

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Question	Answer/Indicative content	Marks	Guidance
75	FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 7.4 award 4 marks ----- Initial moles of reactants 1 mark $n(\text{CH}_3\text{OH})_{\text{initial}} = \frac{9.6}{32} = 0.3 \text{ (mol)}$ AND $n(\text{CH}_3\text{COOH})_{\text{initial}} = \frac{12}{60} = 0.2 \text{ (mol)} \checkmark$ Equilibrium moles 2 marks $n(\text{CH}_3\text{COOH})_{\text{reacted}} = 0.2 - 0.03 = 0.17 \text{ (mol)}$ AND $n(\text{CH}_3\text{OH})_{\text{equil}} = 0.3 - 0.17 = 0.13 \text{ (mol)} \checkmark$ $n(\text{CH}_3\text{COOCH}_3)_{\text{equil}} = 0.17 \text{ (mol)}$ AND $n(\text{H}_2\text{O})_{\text{equil}} = 0.17 \text{ (mol)} \checkmark$ K_c calculation 1 marks $K_c = \frac{0.17/V \times 0.17/V}{0.13/V \times 0.03/V} = 7.4 \checkmark$	4 (AO 1.2×1) (AO 2.8×3)	ALLOW minimum of 2SF throughout ALLOW ECF from initial moles ALLOW ECF from equilibrium moles Use of V not required but Kc expression must be correct ALLOW up to calculator answer of 7.41025641 <u>Examiner's Comments</u> This question asked the candidate to calculate K_c. Higher-attaining students tended to gain full marks. Some candidates made full use of tables (e.g. RICE: Reaction, Initial concentration, Change in concentration, Equilibrium concentration) which allowed for credit to be given through error carried forward. Some candidates did not use 0.03 as the change, and lower-attaining candidates did not use water in the K_c expression. Candidates should remember to provide written indications of what it is they are working out – presenting the calculations without any annotations can make it harder for error carried forward marks to be given if there is an error in their calculation.
	Total	4	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
76	<i>Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i> Level 3 (5–6 mark) Detailed explanation of equilibrium, the action of the buffer and correct calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3–4 marks) Detailed explanation of equilibrium and the action of the buffer. OR Detailed explanation of equilibrium and correct calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio. OR Detailed explanation of the action of the buffer and correct calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio. OR Partial explanations of equilibrium, and the action of the buffer and attempt calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio. <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1–2 marks) Detailed explanation of equilibrium. OR Correct calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio. OR Detailed explanation of the action of the buffer. OR Partial explanations of equilibrium and the action of the buffer. OR Partial explanation of equilibrium and	6 (AO1.1 ×2) (AO1.2 ×2) (AO3.1 ×1) (AO3.2 ×1)	Indicative scientific points may include: (State symbols not required in equations) Equilibrium and equilibrium shifts $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$ - Addition of H^+ causes $\rightleftharpoons$ to shift to left - Addition of OH^- causes $\rightleftharpoons$ to shift to right Action of buffer - Increase in H^+ / addition of acid leads to: $\text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$ OR HCO_3^- reacts with added acid - Increase in OH^- / addition of alkali leads to: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ OR $\text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$ OR H_2CO_3 reacts with added alkali Calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio $K_a = 10^{-6.38}$ OR $4.17 \times 10^{-7} \text{ (mol dm}^{-3}\text{)}$ $[\text{H}^+] = 10^{-7.40}$ OR $3.98 \times 10^{-8} \text{ (mol dm}^{-3}\text{)}$ $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$ OR $\frac{4.17 \times 10^{-7}}{3.98 \times 10^{-8}}$ - ratio = 10.47(:1) OR 10.48(:1) ALLOW 10.5 OR 10(:1) (after working shown) ALLOW $\frac{4.2 \times 10^{-7}}{4.0 \times 10^{-8}}$ And ratio = 10.5 OR 11 (after working shown) ALLOW $\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]}$ OR $\frac{3.98 \times 10^{-8}}{4.17 \times 10^{-7}}$ And ratio = 1 : 0.095 .. <u>Examiner's Comments</u>

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Question	Answer/Indicative content	Marks	Guidance
	attempt at calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio.' OR Partial explanation of the action of the buffer and attempt at calculation of $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio. <i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks <i>No response or no response worthy of credit.</i>		This Level of Response question was generally well answered with many candidates achieving maximum marks by simply considering what was required in the question. The calculation of the $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio was well described although sometimes the final expression of the ratio left ambiguity as it was hard to tell whether the ratio given referred to the $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio or the $[\text{H}_2\text{CO}_3] : [\text{HCO}_3^-]$ ratio The buffer reactions on separate addition of acid (H^+ ions) and alkali (OH^- ions) were explained and, better still, shown in equation form. The direction of shift on the $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ equilibrium was invariably correct, but many candidates did not achieve credit for responses such as 'Addition of H^+ ions shifts the equilibrium to the left' because they did not give the equilibrium which was undergoing shift. An example of a complete answer gaining L3 (6 marks) is given. Exemplar 5 the equilibrium is... $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ hydrogencarbonate ion ° if acid is added into the blood then ~~this reacts with~~ the excess H^+ ions react with HCO_3^- and shift the position of equilibrium to the LHS in order to replace the concentration of H^+ $\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$ ° if alkali is added into the blood then the OH^- ions react with the H^+ ions forming water. The position of equilibrium shifts to the RHS to replace the lost H^+ ions $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ ⇒ in this way when small amounts of acid or alkali are added to the blood the concentration of H^+ ions remains approximately constant and therefore so does the pH $K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$ Additional answer space provided $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{K_a}{[\text{H}^+]} = \frac{10^{-6.38}}{10^{-7.40}} = 10.47128548$ ∴ $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ 10.5 : 1 21 : 2 The candidate clearly writes the equilibrium at the top.

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					The first bullet point gives a chemical equation for the reaction occurring when H^+ ions are added as well as the shift in equilibrium. The second bullet point gives a chemical equation for the reaction occurring when OH^- ions are added as well as the shift in equilibrium. The steps in the calculation are clearly shown and the ratio is clear.
			Total	6	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
77	<i>Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i> Level 3 (5–6 marks) Most evidence used to determine the correct orders AND rate equation AND rate constant. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3–4 marks) Some evidence used to determine two orders correctly AND rate equation AND rate constant consistent with orders. OR Little evidence used to determine all three orders correctly AND rate equation AND rate constant. <i>There is a line of reasoning presented with some structure. The information presented is in the most part relevant and supported by some evidence.</i> Level 1 (1–2 marks) Little evidence used to determine two orders correctly OR One order correct, with attempt to determine the rate equation AND rate constant. <i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks <i>No response or no response worthy of credit.</i>	6 (AO 3.1 ×4) (AO 3.2 ×2)	Indicative scientific points may include: <u>Orders</u> Student 1 • zero order wrt Br₂ Student 2 • 1st order wrt CH₃COCH₃ Student 3 • 1st order wrt H⁺ <u>Explanation</u> Student 1 • constant gradient OR linear negative gradient OR constant rate OR rate independent of concentration OR decreasing half-life Student 2 • straight line through 0,0 • OR rate directly proportional to [CH₃COCH₃] OR [CH₃COCH₃] × 2, rate × 2 Student 3 • [H⁺] × 2, rate × 2 <u>Rate equation, rate constant and units</u> Student 1 • rate = k [CH₃COCH₃] [H⁺] ALLOW rate = k [Br₂]⁰ [CH₃COCH₃]¹ [H⁺]¹ $k = \frac{\text{rate}}{[\text{CH}_3\text{COCH}_3][\text{H}^+]}$ OR $\frac{1.25 \times 10^{-5}}{1.6 \times 0.2}$ • k = 3.9... × 10⁻⁵ • units: dm³ mol⁻¹ s⁻¹ (Any order, e.g. mol⁻¹ dm³ s⁻¹) <u>Examiner's Comments</u> The second Level of Response question in

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Question	Answer/Indicative content	Marks	Guidance
			the paper was also answered very well. Almost all candidates determined the order with respect to H^+ to be first order and gave suitable explanations. A very high proportion of candidates determined the order with respect to CH_3COCH_3 to be first order and related this to the direct proportionality shown on the graph. The zero order with respect to Br_2 proved a little more problematic with many candidates just giving an order with no attempted explanation. Having determined orders, nearly all candidates were able to give a corresponding rate equation and could calculate a value for the rate constant, albeit with frequent omission of units and forgetting that the initial rates given were in terms of 10^{-5}. An example of a complete answer achieving L3 (6 marks) is given. Exemplar 8 > studying the graph of the results of student 1 we can determine that the rate of reaction in respect to $[Br_2]$ is zero order $\Rightarrow$ because the gradient of the concentration-time graph is constant (it is a straight line of negative gradient) $\Rightarrow$ since the gradient of a concentration-time graph equals the rate this shows that $[Br_2]$ has no effect on the rate of reaction > looking at the results of student 2 we can work out that the reaction is first order with respect to $[CH_3COCH_3]$ because the graph is a straight line through the origin $\Rightarrow$ this shows that $[CH_3COCH_3] \propto$ rate of reaction > studying the results of student 3 where $[H^+]$ is doubled while $[Br_2]$ and $[CH_3COCH_3]$ are both kept constant between the 2 experiments we can see that the initial rate has doubled $\Rightarrow$ therefore the rate of reaction is also first order with respect to $[H^+]$ Additional answer space if required $\text{rate} = k[CH_3COCH_3][H^+]$ $k = \frac{\text{rate}}{[CH_3COCH_3][H^+]} = \frac{1.25 \times 10^{-5}}{1.60 \times 0.20}$ $k = 3.90625 \times 10^{-5}$ $= 3.91 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ This candidate gave each order clearly followed by a concise explanation of each choice.

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Question			Answer/Indicative content	Marks	Guidance
					The rate equation (based on the orders given) is clearly stated, the calculation clearly shows working and correct units are given.
			Total	6	

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Question	Answer/Indicative content	Marks	Guidance
78	$\text{CH}_3\text{SO}_2\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{SO}_2\text{O}^- + \text{H}_3\text{O}^+$ ✓ A1 B2 B1 A2 ✓ For an equilibrium shown using CH_3COOH instead of H_2O, mark acid–base pairs by ECF, i.e. $\text{CH}_3\text{SO}_2\text{OH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{SO}_2\text{O}^- + \text{CH}_3\text{COOH}_2^+$ ☒ A1 B2 B1 A2 ECF ✓ $\text{CH}_3\text{SO}_2\text{OH}$ dissociates more (than CH_3COOH) OR $\text{CH}_3\text{SO}_2\text{OH}$ is a stronger acid ✓ <i>ORA in terms of CH_3COOH being a weaker acid</i> Student is correct AND (sulfonic acid has) lower $\text{p}K_a$/higher K_a OR greater $[\text{H}^+]$ ORA ✓	4 (AO 2.1×2) (AO 3.1) (AO 3.2)	ALLOW → for ⇌ ALLOW acid–base pairs labelled other way round. i.e. $\text{CH}_3\text{SO}_2\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{SO}_2\text{O}^- + \text{H}_3\text{O}^+$ A2 B1 B2 A1 ALLOW small slip If ONE charge is missing from equilibrium. ALLOW ECF for acid–base pairs mark IGNORE ‘more acidic’ <i>Response needs strength/dissociation</i> ALLOW maths explanation for final 2 marks, e.g. $K_a(\text{CH}_3\text{COOH}) = 10^{-(4.76)} = 1.74 \times 10^{-5}$ $[\text{H}^+] = \sqrt{(1.74 \times 10^{-5}) \times 1} = 4.17 \times 10^{-3}$ $\text{pH} = -\log 4.17 \times 10^{-3} = 2.38$ ✓ $K_a(\text{CH}_3\text{SO}_2\text{OH}) = 10^{-(1.90)} = 79.4$ $[\text{H}^+] = \sqrt{(79.4) \times 1} = 8.91$ $\text{pH} = -\log 8.91 = -0.95$ ✓ BOTH pH calcs subsumes ‘Student is correct’ Examiner’s Comments Most candidates completed a correct equilibrium equation and assigned the correct acid–base pairs. A significant number of candidates used ethanoic acid instead of water in the equation. The examiners allowed error carried forward in this case for the acid–base pairs. Candidates found it much more difficult to explain whether the sulfonic acid had a lower pH value. The higher-attaining candidates answered concisely. They usually identifying that the sulfonic acid would have a lower pH as the $\text{p}K_a$ value was lower (or the K_a value greater), leading to more dissociation than ethanoic acid. Lower-attaining candidates often produced unfocussed and lengthy responses,

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Question			Answer/Indicative content	Marks	Guidance
					sometimes relating increased dissociation in an acid to a higher, rather than a lower, pH. Some candidates approached their explanation mathematically, calculating pH values for ethanoic acid and sulfonic acid from their concentrations and pKa values. If correct, this approach was fully credited.
			Total	4	
79			FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 2.22×10^4 award first 2 marks ----- $\ln K_p = -\Delta G/RT = \frac{2.48 \times 10^4}{8.314 \times 298} = 10.01 \checkmark$ (AO 3.1×2) $K_p = 2.22 \times 10^4 \text{ (3SF required)} \checkmark$ (AO 1.2×1) Units = $\text{atm}^{-2} \checkmark$	3	ALLOW ECF for transcription errors in first sum ALLOW 10 up to calculator value of 10.00979992 ALLOW 22200 ALLOW 2.20×10^4 OR 22000 (use of 10) ALLOW alternatives (k)Pa⁻² OR N⁻² m⁴ OR mmHg⁻² OR PSI⁻² OR bar⁻² Common errors for 1 mark: 22400 (use of 8.31) 4.50×10^{-5} (use of -10.01) <u>Examiner's Comments</u> <i>This was an unfamiliar expression linking ΔG and K_p. Many candidates correctly calculated this number. Some candidates calculated ln K_p as 10.0 but then put a – in front for the e calculation. The question required the answer to 3 significant figures. Higher-attaining candidates were able to work out the units as any pressure unit⁻².</i>
			Total	3	

Mark Scheme

[illegible]

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			$4 = 4.75 + \log \frac{8.16 \times 10^{-2}}{[\text{CH}_3\text{COO}^-]}$ OR $4.75 - \log \frac{[\text{CH}_3\text{COO}^-]}{8.16 \times 10^{-2}}$ ✓ $\log[\text{CH}_3\text{COO}^-] = 4 - 4.75 - 1.09 = -1.84$ ✓ $[\text{CH}_3\text{COO}^-]_{\text{buffer}} = 1.5 \times 10^{-2}$ ✓ $[\text{CH}_3\text{COO}^-]_{\text{initial}} = 2.4 \times 10^{-2}$ ✓		calculate the original concentration of ethanoate ions in the buffer. Higher-attaining students gained full credit. Most students calculated the concentration in the buffer solution but did not factor for the original solution. Lower-attaining candidates often scored the first two marking points but did not use the buffer equation.
			Total	6	

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81		i	To keep $[\text{CH}_3\text{OH}]$ (effectively) constant OR Zero order with respect to CH_3OH OR To ensure equilibrium is far to the right ✓	1 (AO 3.3)	ALLOW Change in $[\text{CH}_3\text{OH}]$ is negligible ALLOW rate is independent of $[\text{CH}_3\text{OH}]$ IGNORE Methanol doesn't run out/is not limiting reagent. <u>Examiner's Comments</u> Most candidates used incorrect ideas about reaction going to completion or the methanol not being limiting.
		ii	One half-life $t_{1/2}$ between 102 and 110 (mins) Two half-lives calculated OR evidence on the graph of two half-lives AND constant half-life/values (means first order) ✓	2 (AO 3.1) (AO 3.1)	ALLOW any two combinations of positions, e.g. 5 and 2.5 AND 4 and 2 AND 3 and 1.5 <u>Examiner's Comments</u> Very few candidates were given full marks. Higher-attaining students calculated one half life in range but very few could come up with a second half life as the graph did not allow another successive half life to be obtained. Higher-attaining candidates chose alternative half lives from the data given.  Misconception Candidates are advised that half lives can be calculated from any numerical values on the graph. Further guidance on rates of reaction can be found at: https://www.ocr.org.uk/Images/371956-experiments-on-rates-of-reaction.doc

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		iii	Using gradients Evidence of tangent at $t = 0$ and intercept between 100 -140 (min) ✓ Correctly calculated gradient in the range of 2.9×10^{-5} to 4.0×10^{-5} (mol dm⁻³ min⁻¹) ✓ OR Using half-life <i>For $t_{1/2} = 106$ min,</i> $k = \frac{\ln 2}{t_{1/2}} = 0.00654 \text{ (min}^{-1}\text{)} \checkmark$ $\text{rate} = 0.00654 \times 5 \times 10^{-3} = 3.27 \times 10^{-5} \text{ (mol dm}^{-3} \text{ min}^{-1}\text{)} \checkmark$	2 (AO 3.1×1) (AO 3.2×1)	ALLOW ECF from value of $t_{1/2}$ in (ii) <u>Examiner's Comments</u> This question required the candidate to draw a line of best fit and then draw a tangent at $t=0$. Many candidates did not draw a line of best fit, and many did not get a tangent in the acceptable range. Very few candidates processed the gradient by using the correct subtraction on the y axis (scale was from 1 to 5) or by using the 10^{-3} on the axis label.
			Total	5	