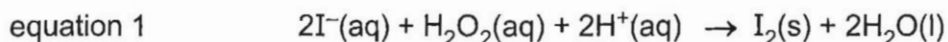




Answer all the questions in the spaces provided.

1 Determination of the kinetics of a redox reaction

Equation 1 represents the reaction between iodide ions and acidified hydrogen peroxide.

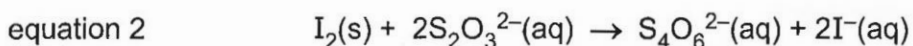


If $[\text{H}^+]$ is kept constant, a simplified rate equation can be used.

$$\text{rate} = k'[\text{I}^-]^a[\text{H}_2\text{O}_2]^b \quad \text{where } k' \text{ is } k[\text{H}^+]$$

When starch is added to the reaction mixture, a blue colour is immediately seen due to the formation of an iodine–starch complex.

If a small amount of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is also present in the reaction mixture, the formation of the blue colour is delayed. The $\text{Na}_2\text{S}_2\text{O}_3$ reacts with I_2 as shown in equation 2.



FA 1 is $0.100 \text{ mol dm}^{-3}$ potassium iodide, KI.

FA 2 is $0.255 \text{ mol dm}^{-3}$ hydrogen peroxide, H_2O_2 .

FA 3 is $2.50 \times 10^{-3} \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

FA 4 is an aqueous mixture of ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, and sodium ethanoate, $\text{CH}_3\text{CO}_2\text{Na}$.

Solution S is starch solution.

You will perform a series of three experiments. You will add a fixed amount of sodium thiosulfate, **FA 3**, to each of your experiments. You will add an amount of deionised water so that the total volume is 100 cm^3 . The time taken for the blue colour to form allows the reaction rate to be determined.

(a) Fill Table 1.1 with the volume of deionised water needed in each experiment.

Table 1.1

experiment	FA 1 / cm^3	FA 2 / cm^3	FA 3 / cm^3	solution S / cm^3	FA 4 / cm^3	deionised water/ cm^3	time, t /s
1	15.0	10.0	10.0	5.0	20.0	40.0	17.0
2	10.0	10.0	10.0	5.0	20.0	45.0	25.8
3	5.0	40.0	10.0	5.0	20.0	20.0	12.9

[4]





Experiment 1

The end-point of the reaction is the **first** appearance of a blue colour.

Note: Insufficient stirring of the reaction mixture may lead to a blue colour appearing before the true end-point is reached.

1. Use an appropriate measuring cylinder to transfer 15.0 cm^3 of **FA 1** into a 250 cm^3 beaker. Place the beaker on the white tile.
2. Using appropriate measuring cylinders, transfer to the beaker
 - 10.0 cm^3 of **FA 3**,
 - 5.0 cm^3 of **solution S**,
 - 20.0 cm^3 of **FA 4**.
3. Use a measuring cylinder to add the appropriate volume of deionised water recorded in Table 1.1.
4. Stir the contents of the beaker using a glass rod.
5. Use the measuring cylinder labelled **FA 2** to transfer 10.0 cm^3 of **FA 2** to the beaker. Start the stopwatch during this addition.
6. Mix the contents in the beaker by **thoroughly** stirring.
7. Stop the stopwatch when the solution **first** turns blue.
8. Record the time taken, t , to the nearest 0.1 s in Table 1.1.
9. Carefully wash out the beaker. Stand it upside down on a paper towel to drain.

Experiments 2 and 3

Repeat experiment 1 using the volumes of **FA 1**, **FA 2**, **FA 3**, **solution S**, **FA 4** and deionised water given in Table 1.1.

You should alternate the use of the two 250 cm^3 beakers.

Record all values of t in Table 1.1.





- (b) Calculate the ratio of the time taken in experiment 2, $t_{\text{expt 2}}$, to the time taken in experiment 1, $t_{\text{expt 1}}$, using the expression shown.

Record your answer to one decimal place.

$$\text{ratio 1} = \frac{t_{\text{expt 2}}}{t_{\text{expt 1}}}$$

.....

Similarly, calculate and record the ratio of reaction time given below.

$$\text{ratio 2} = \frac{t_{\text{expt 2}}}{t_{\text{expt 3}}}$$

.....

[3]

- (c) The simplified rate equation for the reaction shown in equation 1 is

$$\text{rate} = k[\text{I}^-]^a[\text{H}_2\text{O}_2]^b$$

- (i) Deduce the order, a , with respect to $[\text{I}^-]$. Explain your deduction in terms of your experimental results.

$a =$

explanation

.....

.....

[1]





- (ii) Deduce the order, b , with respect to $[\text{H}_2\text{O}_2]$. Explain your deduction in terms of your experimental results.

$b =$

explanation

.....

.....

.....

Hence, complete the expression for the simplified rate equation.

rate = k'

[2]

- (d) Suggest why $[\text{H}^+]$ remains constant in the experiments you performed.

.....

.....

..... [1]

[Total: 11]



2 Determination of the concentrations of two solutions by graphical analysis

Baryta water, $\text{Ba}(\text{OH})_2(\text{aq})$, is a strong base which neutralises both sulfuric acid and hydrochloric acid.

In this question, you will prepare four mixtures, each containing the same volume of baryta water but with different volumes of sulfuric acid added. In each mixture, the solution remains alkaline and is neutralised by titration with hydrochloric acid.

Graphical analysis of your results will enable you to determine the ratio of the acid concentrations. You will also determine the actual concentrations of the baryta water and the sulfuric acid.

Each titration is to be performed **once only**, so great care should be taken that you do not overshoot the end-points.

FA 5 is aqueous barium hydroxide (baryta water), $\text{Ba}(\text{OH})_2$.

FA 6 is dilute sulfuric acid, H_2SO_4 .

FA 7 is $0.150 \text{ mol dm}^{-3}$ hydrochloric acid, HCl .

Solution T is thymolphthalein indicator.

You are also provided with **FA 5 (new)** in a stoppered container. **FA 5 (new)** is a sample of freshly prepared baryta water.

Prepare a table in the space provided on page 8 in which to record, to an appropriate level of precision:

- volume of **FA 6** added in each mixture, $V_{\text{FA 6}}$,
- all burette readings,
- volume of **FA 7** added, $V_{\text{FA 7}}$.

(a) Pour all the **FA 5 (new)** into a 100 cm^3 beaker. Leave the beaker to stand for use in 2(f).

(b) Experiment 1

Note: For all experiments, the containers of **FA 5** and solution **T** should be capped when not in use.

1. Fill the burette labelled **FA 6** with **FA 6**.
2. Fill the other burette with **FA 7**.
3. Pipette 25.0 cm^3 of **FA 5** into a 250 cm^3 conical flask.
4. Add a few drops of **solution T** to the conical flask.
5. Add 5.50 cm^3 of **FA 6** from the burette into the conical flask.
6. Titrate the mixture in the conical flask with **FA 7**. The end-point for this titration is reached when the blue colour **just** disappears.
7. Record $V_{\text{FA 6}}$, all burette readings and $V_{\text{FA 7}}$, to an appropriate level of precision, in your table.





Experiment 2

In this experiment, a very small volume of **FA 7** will be required.

8. Repeat points 3 to 7 but, at point 5, add 21.00 cm^3 of **FA 6**.

Experiments 3 and 4

9. Select **two** other suitable volumes of **FA 6**. Your selected volumes must be **between** 5.50 cm^3 and 21.00 cm^3 .
10. Repeat points 3 to 7 using your selected volumes of **FA 6** at point 5.

Results

Experiment	1	2	3	4
FA6 Final Burette Reading / cm^3	5.50	26.50	36.50	15.00
FA6 Initial Burette Reading / cm^3	0.00	5.50	26.50	0.00
Volume of FA6 used / cm^3	5.50	21.00	10.00	15.00
FA7 Final Burette Reading / cm^3	26.20	40.70	20.20	34.30
FA7 Initial Burette Reading / cm^3	0.00	35.00	0.00	21.00
Volume of FA7 used / cm^3	26.20	5.70	20.20	13.30

[3]



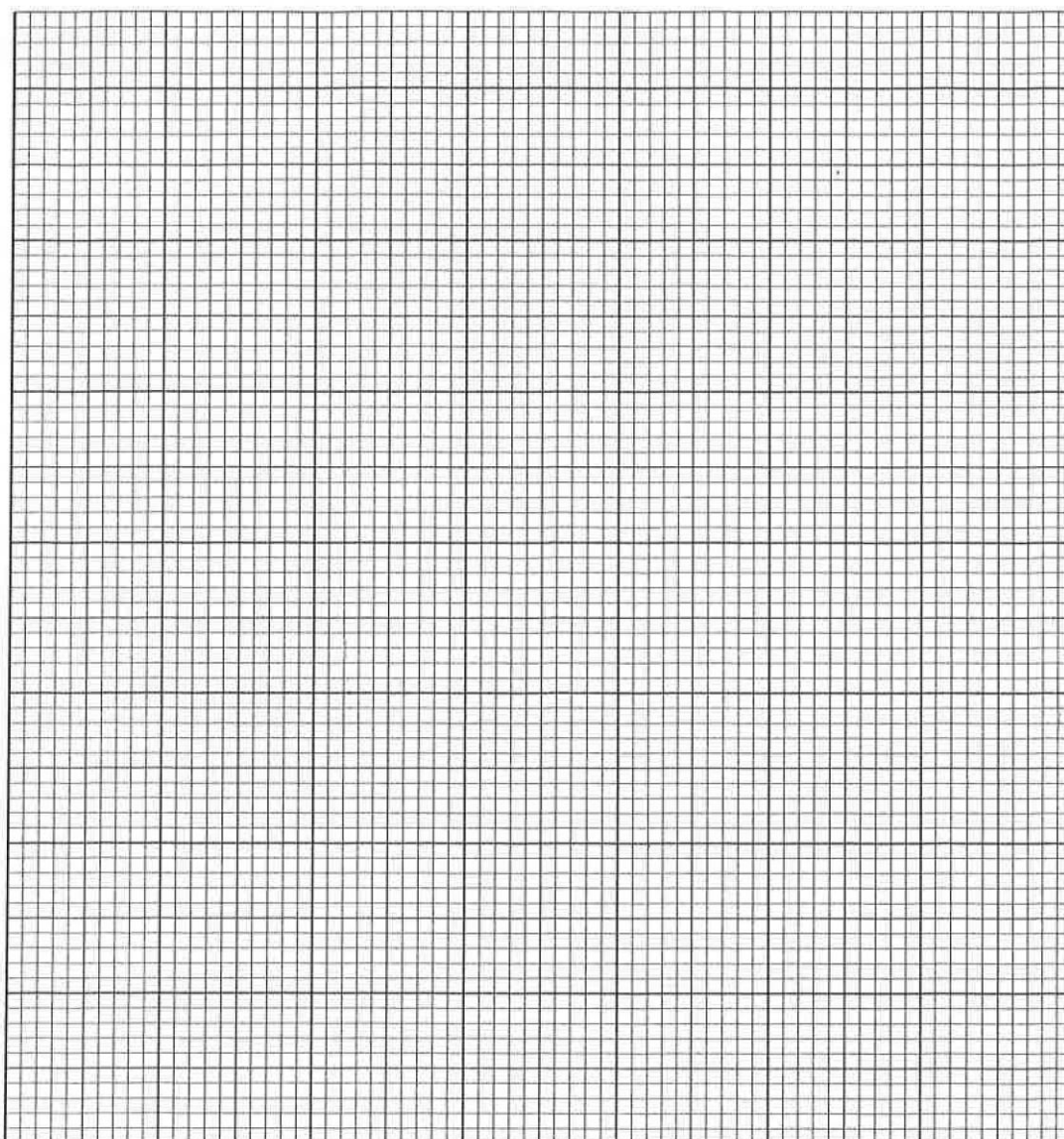


- (c) (i) Plot a graph of V_{FA7} on the y-axis against V_{FA6} on the x-axis.

The scales for both axes must be chosen to provide an origin and to allow the graph line to be extrapolated (extended) to both axes.

Draw the best-fit straight line taking into account all of your plotted points.

Extrapolate (extend) your line until it touches **both** axes.



[3]





- (ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this.

gradient = [2]

- (iii) Use your answer from **2(c)(ii)** to deduce a value for the ratio of the concentration of hydrochloric acid in **FA 7** to the concentration of sulfuric acid in **FA 6**.

$\frac{[\text{FA 7}]}{[\text{FA 6}]} = \dots\dots\dots$ [1]

- (d) (i) Read from your graph, and record, the volume of **FA 6**, $V_{\text{FA 6}}(\text{max})$, required to exactly neutralise 25.0 cm^3 of **FA 5**.

$V_{\text{FA 6}}(\text{max}) = \dots\dots\dots$

Read from your graph, and record, the volume of **FA 7**, $V_{\text{FA 7}}(\text{max})$, required to exactly neutralise 25.0 cm^3 of **FA 5**.

$V_{\text{FA 7}}(\text{max}) = \dots\dots\dots$ [2]





(ii) Calculate the concentration of barium hydroxide in **FA 5**.

concentration of barium hydroxide in **FA 5** = [2]

(iii) Using your answer in **2(c)(iii)** or otherwise, calculate the concentration of sulfuric acid in **FA 6**.

concentration of sulfuric acid in **FA 6** = [4]

(e) Explain, in terms of the chemistry involved, the direction of the slope of your graph.

.....
.....
..... [1]

(f) (i) Record your observations of the solution of **FA 5 (new)** in the beaker prepared in **2(a)**.

White ppt formed in colourless solution

.....
..... [1]

(ii) Write an equation, including state symbols, to explain your observation in (f)(i).

..... [1]





- (g) A student poured a 2 cm depth of **FA 5** into two test-tubes and left them open to the air for several days. The student carried out the following experiments and recorded the observations in Table 2.1.

Consider the observations in Table 2.1. There is no need to perform these experiments, the tests have been carried out for you and the observations recorded.

Table 2.1

test	observations
To the 2 cm depth of FA 5 in a test-tube add FA 7 , slowly with shaking, until no further change is seen.	Bubbles are seen, and the gas gives a positive test with limewater. The white precipitate dissolves.
To the 2 cm depth of FA 5 in a test-tube add FA 6 , slowly with shaking, until no further change is seen.	Bubbles are seen, and the gas gives a positive test with limewater. The white precipitate does not dissolve.

- (i) Write **two** equations, including state symbols, that explain the student's observations recorded in Table 2.1.

.....

 [2]

- (ii) A student performed **Experiment 1** in 2(b) but left the open conical flask containing the **FA 5** to stand for some time before titrating with **FA 7**.

Suggest what effect, if any, leaving the flask to stand would have on the volume of **FA 7** required to neutralise the mixture. Explain your answer.

effect

explanation

..... [1]

[Total: 23]





3 Organic Analysis

In this question you will deduce the identities of four organic compounds.

FA 8, **FA 9**, **FA 10** and **FA 11** have the molecular formulae shown.

FA 8	$\text{C}_2\text{H}_4\text{O}_2$
FA 9	$\text{C}_3\text{H}_8\text{O}$
FA 10	$\text{C}_3\text{H}_6\text{O}$
FA 11	$\text{C}_3\text{H}_6\text{O}$

- (a) You are provided with aqueous samples of three of these compounds, **FA 8**, **FA 9** and **FA 10**.

You will perform some of the tests described in Table 3.1.

Using the observations in Table 3.1, and the given molecular formulae, you will then deduce the identities of **FA 8**, **FA 9**, **FA 10** and **FA 11**.

In addition to having access to the usual bench reagents, you are also provided with the following:

- magnesium turnings,
- iodine solution.

Perform the tests described in Table 3.1. Some of the observations have been completed for you. There is no need to carry out those tests. Record your observations in Table 3.1.

Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Use a fresh sample of each solution in each test.



Table 3.1

	observations with FA 8 , $\text{C}_2\text{H}_4\text{O}_2$	observations with FA 9 , $\text{C}_3\text{H}_8\text{O}$	observations with FA 10 , $\text{C}_3\text{H}_6\text{O}$	observations with FA 11 , $\text{C}_3\text{H}_6\text{O}$
1. Add 1 cm depth of the FA solution to a test-tube. Add 5 cm depth of 2,4-dinitrophenylhydrazine solution to the test-tube.	no observable change	no observable change	yellow precipitate formed	yellow precipitate formed
2. Add about 1 cm depth of FA 8 in a test-tube. Add, using the tip of a spatula, a small portion of magnesium turnings to this test-tube. Repeat using FA 10 instead of FA 8.	Effervescence of colourless, odourless gas that 'pop' with a lighted splint. $\text{H}_2(\text{g})$ evolved. $\text{Mg}(\text{s})$ dissolves	no observable change	No observable change	no observable change
3. Add about 1 cm depth of FA 8 in a test-tube. To this test-tube add 8 drops of sodium hydroxide solution followed by iodine solution, dropwise, until a permanent orange/red colour is present. Warm the mixture in a beaker of hot water for two minutes.	After warming, the solution remains orange.	After warming, yellow ppt formed in brown solution.	After warming, yellow ppt formed in brown solution.	solution FA 11 turns orange
Add sodium hydroxide solution using a teat pipette until no further change is seen. Repeat using FA 9 and then using FA 10 instead of FA 8.	Orange solution turns pale yellow	Brown solution turns pale yellow. Yellow ppt remains	Brown solution turns pale yellow. Yellow ppt remains	solution FA 11 turns colourless
4. Add 1 cm depth of aqueous silver nitrate to a test-tube. Then slowly add 1 cm depth of aqueous sodium hydroxide. Add aqueous ammonia slowly, with shaking, until the precipitate just dissolves. You may use a clean glass rod to stir the mixture and help dissolve the precipitate. Add 1 cm depth of FA 10 to this mixture, shake the tube and place it in the test-tube rack to stand.	no observable change	no observable change	Brown ppt on addition of $\text{NaOH}(\text{aq})$. Brown ppt dissolves in $\text{NH}_3(\text{aq})$ to give colourless solution. No silver mirror upon standing	silver mirror formed



(b) Complete Table 3.2 with the identities of **FA 8**, **FA 9**, **FA 10** and **FA 11**.

Give evidence from the observations in Table 3.1 to support your conclusions.

Table 3.2

	identity	evidence
FA 8		
FA 9		
FA 10		
FA 11		

[4]

[Total: 9]



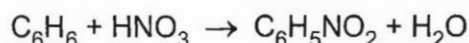


4 Planning

Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, is a yellow liquid at room temperature. Both nitrobenzene and benzene are almost insoluble in water.

Nitrobenzene is manufactured in large quantities by nitration of benzene. This reaction is highly exothermic.

A teacher prepared nitrobenzene as a class demonstration. The equation for this reaction is shown.



A nitrating mixture containing 8.0 cm^3 of concentrated nitric acid and 8.0 cm^3 of concentrated sulfuric acid was prepared.

A total of 8.0 cm^3 of benzene was then added to the mixture, with stirring, in four separate 2.0 cm^3 portions. The teacher ensured that the temperature of the mixture did not rise above 50°C during this addition.

The temperature of the reaction mixture was then kept at 60°C for 30 minutes.

The reaction mixture was then poured into 75 cm^3 of deionised water and thoroughly stirred. The upper water layer was poured away. The remaining oily layer was washed with 75 cm^3 of aqueous sodium carbonate, which was then poured away. The oily layer was then washed with a further 75 cm^3 of deionised water, which was also poured away.

The impure nitrobenzene was dried by adding anhydrous calcium chloride and leaving it for 20 minutes.

The nitrobenzene was then purified.

As with most organic reactions, the yield of this reaction is less than 100%. Using the procedure described, a yield of 70% can be expected.

Table 4.1 gives information about properties of benzene and nitrobenzene.

Table 4.1

chemical	M_r	density $/\text{g cm}^{-3}$	boiling point $/^\circ\text{C}$	other properties
benzene	78	0.8765	80.1	flammable, toxic, carcinogenic
nitrobenzene	123	1.199	211	flammable, toxic, causes respiratory problems, eye irritant



- mass of benzene = g [2]

- an estimate of the quantities of the acids to be used to ensure a yield of **10.0 g** of nitrobenzene,
- the apparatus you would use,
- the procedure you would follow to obtain pure and dry nitrobenzene.

[illegible]

[7]

..... [1]

[2]

[Total: 12]