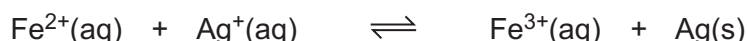


- 1 Aqueous iron(II) ions, $\text{Fe}^{2+}(\text{aq})$, are usually kept in acidic conditions to prevent them readily oxidising to aqueous iron(III) ions, $\text{Fe}^{3+}(\text{aq})$.

$\text{Fe}^{2+}(\text{aq})$ ions react with $\text{Ag}^+(\text{aq})$ ions in a redox reaction. The following equilibrium is established.



The concentration of $\text{Fe}^{2+}(\text{aq})$ at equilibrium can be found by titration with a standard solution of aqueous potassium manganate(VII), $\text{KMnO}_4(\text{aq})$. $\text{KMnO}_4(\text{aq})$ is deep purple in colour. The equilibrium constant for the reaction can be found using the following equation.

$$K_c = \frac{[\text{Fe}^{3+}(\text{aq})]_{\text{eqm}}}{[\text{Fe}^{2+}(\text{aq})]_{\text{eqm}} \times [\text{Ag}^+(\text{aq})]_{\text{eqm}}}$$

A student carries out the experiment using the following instructions.

- step 1** Add 100.0 cm^3 of $0.200 \text{ mol dm}^{-3} \text{ AgNO}_3(\text{aq})$ to 100.0 cm^3 of $0.200 \text{ mol dm}^{-3} \text{ Fe}(\text{NO}_3)_2(\text{aq})$ in a 500 cm^3 conical flask and stopper the flask. Label the conical flask **A**.
- step 2** Leave conical flask **A** for four hours, shaking intermittently. Then leave conical flask **A** untouched for one hour.
- step 3** Use a pipette to transfer 25.00 cm^3 of the solution from conical flask **A** into a clean 250 cm^3 conical flask. Label this conical flask **B**.
- step 4** Add 5 cm^3 of $1.00 \text{ mol dm}^{-3} \text{ NaCl}(\text{aq})$ to the solution in conical flask **B**. A white precipitate of silver chloride forms.
- step 5** Use a measuring cylinder to add 20 cm^3 of 1.00 mol dm^{-3} sulfuric acid to conical flask **B**.
- step 6** Rinse a burette and fill it with a standard solution of $\text{KMnO}_4(\text{aq})$.
- step 7** Add $\text{KMnO}_4(\text{aq})$ to the mixture in conical flask **B** until an end-point is reached.
- step 8** Empty conical flask **B** and rinse it with distilled water ready for the next titration.

The student repeats the titration until concordant readings are achieved.

- (a) The student records their results in Table 1.1.

Table 1.1

	rough	titration 1	titration 2	titration 3
final burette reading / cm^3	10.60	20.35	30.25	9.85
initial burette reading / cm^3	0.10	10.70	20.35	0.10
titre / cm^3				

- (i) Complete Table 1.1. [1]
- (ii) Calculate a suitable mean titre to be used in the student's calculations.

Show clearly how you obtain the mean titre.

mean titre = cm^3 [1]

- (b) State what is meant by a standard solution in **step 6**.

..... [1]

- (c) (i) Suggest why conical flask **A** is left for four hours in **step 2**.

..... [1]

- (ii) Suggest why conical flask **A** is **not** shaken during the final hour in **step 2**.

..... [1]

- (d) Suggest why a measuring cylinder is the most appropriate apparatus to use for measuring sulfuric acid in **step 5**.

..... [1]

- (e) State what the burette should be rinsed with in **step 6**.

..... [1]

- (f) State the change of colour seen in the mixture in conical flask **B** at the end-point in **step 7**.

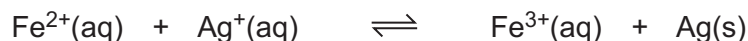
from to [1]

- (g) The student repeats the experiment using $\text{KMnO}_4(\text{aq})$ at a lower concentration. The student obtains a larger mean titre.

Suggest one reason why a larger titre is better than a smaller titre.

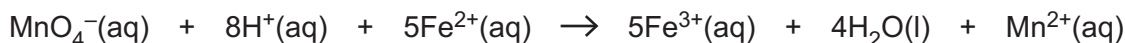
..... [1]

(h) The equilibrium is shown.



When another student carries out the titration with $0.0200 \text{ mol dm}^{-3} \text{ KMnO}_4(\text{aq})$, the mean titre is 21.10 cm^3 .

The ionic equation for the reaction between $\text{MnO}_4^{-}(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$ is shown.



(i) Calculate the concentration of $\text{Fe}^{2+}(\text{aq})$ in the equilibrium mixture.

$$[\text{Fe}^{2+}(\text{aq})]_{\text{eqm}} = \dots\dots\dots \text{mol dm}^{-3} \quad [2]$$

(ii) Suggest why it is **not** necessary to measure the concentration of $\text{Ag}^{+}(\text{aq})$ ions in the equilibrium mixture experimentally.

..... [1]

(iii) Determine the decrease in concentration of $\text{Fe}^{2+}(\text{aq})$ from the initial solution. Hence, determine the concentration of $\text{Fe}^{3+}(\text{aq})$ in the equilibrium mixture.

If you were unable to obtain an answer to (h)(i), use $[\text{Fe}^{2+}(\text{aq})]_{\text{eqm}} = 0.0804 \text{ mol dm}^{-3}$. This is **not** the correct answer.

$$[\text{Fe}^{3+}(\text{aq})]_{\text{eqm}} = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

(iv) Determine the value of K_c . Include units in your answer.

$$K_c = \dots\dots\dots$$

$$\text{units} = \dots\dots\dots$$

[2]

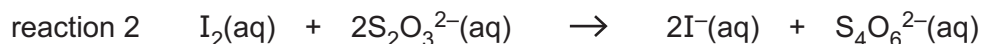
[Total: 15]

- 2 The reaction between iodide ions, $\text{I}^{-}(\text{aq})$, and aqueous hydrogen peroxide, $\text{H}_2\text{O}_2(\text{aq})$, takes place in acidic conditions.



A student carries out a series of experiments to investigate the order of reaction with respect to the concentration of $\text{I}^{-}(\text{aq})$ ions. The student does this by measuring the time taken for a fixed amount of iodine to form.

A known amount of aqueous thiosulfate ions, $\text{S}_2\text{O}_3^{2-}(\text{aq})$, in the reaction mixture react with $\text{I}_2(\text{aq})$ formed in reaction 1.



After all of the $\text{S}_2\text{O}_3^{2-}(\text{aq})$ ions have reacted in reaction 2, any further $\text{I}_2(\text{aq})$ formed is detected using starch indicator.

The following materials are used:

- 50 cm³ beaker containing the correct mass of solid potassium iodide crystals needed to make 250.0 cm³ of 0.100 mol dm⁻³ KI(aq)
- 0.100 mol dm⁻³ Na₂S₂O₃(aq)
- 0.100 mol dm⁻³ H₂O₂(aq)
- 0.200 mol dm⁻³ H₂SO₄(aq)
- starch indicator
- distilled water.

- (a) A second student looked at the equation for reaction 1 and stated the order with respect to the concentration of $\text{I}^{-}(\text{aq})$ ions must be second order because the balanced equation contains $2\text{I}^{-}(\text{aq})$.

Suggest why a balanced equation alone cannot be used to determine the order of a reaction.

..... [1]

- (b) Describe how the student makes 250.0 cm³ of 0.100 mol dm⁻³ KI(aq) starting from the sample of solid potassium iodide in the 50 cm³ beaker.

Give the name and size of any key apparatus used. Describe how the student ensures the volume is exactly 250.0 cm³.

You may wish to write your answer using a series of numbered steps.

.....

.....

.....

.....

.....

.....

.....

(c) The student carries out Experiment 1 using the following steps.

- step 1** Add 25 cm³ of 0.200 mol dm⁻³ H₂SO₄(aq) to a conical flask.
- step 2** Add 20.00 cm³ of distilled water to the conical flask from a burette.
- step 3** Add 5.00 cm³ of 0.100 mol dm⁻³ KI(aq) to the conical flask from a burette.
- step 4** Add 5.00 cm³ of 0.100 mol dm⁻³ Na₂S₂O₃(aq) to the conical flask from a burette.
- step 5** Add 2 cm³ of starch indicator to the conical flask.
- step 6** Use a burette to add 10.00 cm³ of 0.100 mol dm⁻³ H₂O₂(aq) to a small beaker.
- step 7** Add the contents of the beaker to the conical flask and start a timer immediately. Stop the timer when the starch indicates the presence of I₂(aq).

The student carries out a further six experiments by repeating **steps 1 to 7**, using the volumes shown in Table 2.1.

Table 2.1

experiment	volume of H ₂ SO ₄ (aq) / cm ³	volume of distilled water / cm ³	volume of KI(aq), V / cm ³	volume of Na ₂ S ₂ O ₃ (aq) / cm ³	volume of indicator / cm ³	time taken for colour change, t / s
1	25	20.00	5.00	5.00	2	257
2	25	17.50	7.50	5.00	2	120
3	25	15.00	10.00	5.00	2	112
4	25	12.50	12.50	5.00	2	76
5	25	10.00	15.00	5.00	2	1
6	25	5.00	20.00	5.00	2	59
7	25	0.00	25.00	5.00	2	44

- (i) State how the student could improve the reliability of the experiment.

..... [1]

- (ii) State the independent variable in Experiments 1 to 7.

..... [1]

- (iii) In Experiment 5, the starch indicator changed colour immediately on adding H₂O₂(aq). The student realised an error had been made.

Suggest which step was missed in Experiment 5.

..... [1]

(d) The rate equation is represented as $\text{rate} = k[\text{I}^-]^n$.

- $[\text{I}^-]$ is proportional to the volume of KI(aq)
- n is the order of reaction with respect to I^-
- rate is proportional to $1/t$
- $\log(\text{rate}) = \log k + n\log[\text{I}^-]$

(i) Use the results from the student's experiments in (c) to complete Table 2.2.

V is the volume of KI(aq) and t is the time taken for the colour to change.

Give all values to **three** significant figures.

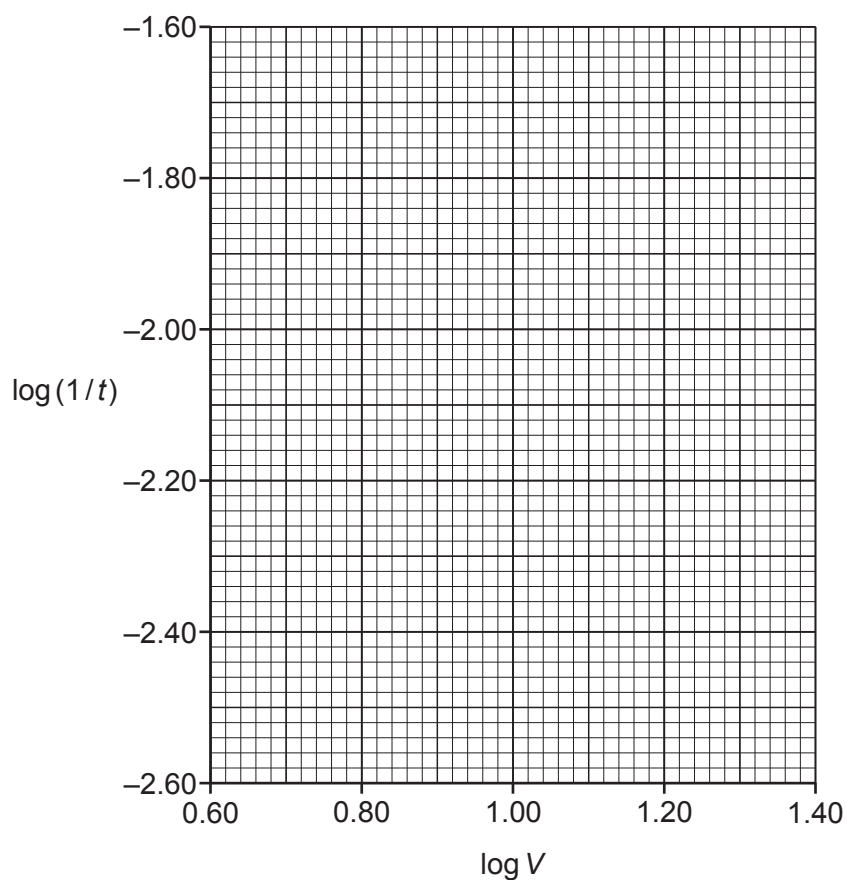
The results for Experiment 5 should **not** be used.

Table 2.2

experiment	V/cm^3	t/s	$\log V$	$\log(1/t)$
1	5.00	257		
2	10.00	120		
3	12.50	112		
4	15.00	76		
5	17.50	1	X	X
6	20.00	56		
7	25.00	44		

[2]

- (ii) Plot a graph on the grid to show the relationship between $\log V$ and $\log(1/t)$. Use a cross (x) to plot each data point. Draw a line of best fit.



[2]

- (iii) A timing error caused the most anomalous point on the graph.

Circle this point and explain the error in timing which led to this point.

..... [1]

- (iv) Use your graph to determine the gradient of the line of best fit.

State the coordinates of both points you used in your calculation. These must be selected from your line of best fit.

Give the gradient to **two** decimal places.

coordinates 1 coordinates 2

gradient =
[2]

- (v) The total percentage error from measurements is determined to be 5.25%.

The true order of reaction is 1. Use this and your gradient from (d)(iv) to determine whether the error in the experiment could be accounted for by error from measurements or is caused by other factors.

Show any working.

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

[Total: 15]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

Group																			
1	2													13	14	15	16	17	18
														1 H hydrogen 1.0					
														2 He helium 4.0					
3 Li lithium 6.9	4 Be beryllium 9.0																		
Key																			
atomic number atomic symbol name relative atomic mass																			
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12								
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4								
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium —	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4								
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids		72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6							
87 Fr francium —	88 Ra radium —	89–103 actinoids		104 Rf rutherfordium —	105 Db dubnium —	106 Sg seaborgium —	107 Bh bohrium —	108 Hs hassium —	109 Mt meitnerium —	110 Ds darmstadtium —	111 Rg roentgenium —	112 Cn copernicium —							