



A-Level Chemistry

Rate Determining Step

Mark Scheme

Time available: 67 minutes

Marks available: 62 marks

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Mark schemes

1.

- (a) H_2O_2 and/or I^- concentration change is negligible /
 H_2O_2 and/or I^- concentration (effectively) constant

Only the concentration of H^+ changes.

so have a constant/no effect on the rate / so is zero order (w.r.t. H_2O_2 and I^-) / a and b are zero

Ignore references to H^+ is limiting reagent / rds / $\text{H}_2\text{O}_2/\text{I}^-$ not in rate equation

Do not allow reference to catalyst.

2

- (b) Stop the reaction / quench

By dilution / cooling / adding a reagent to react with $\text{H}_2\text{O}_2/\text{I}^-$

Allow valid suggestions about how to stop the reaction.

Do not allow reaction with acid/alkali / neutralisation for M2

Do not penalise other named reagents.

Ignore references to measuring volume and adding indicator

2

- (c) M1: constant gradient

OR

change/decrease in concentration is proportional to time

Allow constant rate / rate = k

Ignore reference to straight line

Not increase in concentration / concentration is inversely proportional / concentration (on its own) is proportional

M2: as $[\text{H}^+]$ changes/decreases

M2 dependent on correct M1

*Allow rate v concentration graph would give horizontal straight line
owtte*

Allow so $[\text{H}^+]$ has no effect on the rate

2

- (d) evidence of attempt at calculation of gradient via $\Delta y/\Delta x$
allow construction lines on graph

$$k_1 = 0.0012 / 1.2 \times 10^{-3}$$

At least 2 sf (0.00118 – 0.00122)

Correct answer scores 2/2

No ecf from incorrect or inverted numbers in M1

$k_1 = -0.0012$ scores 1/2

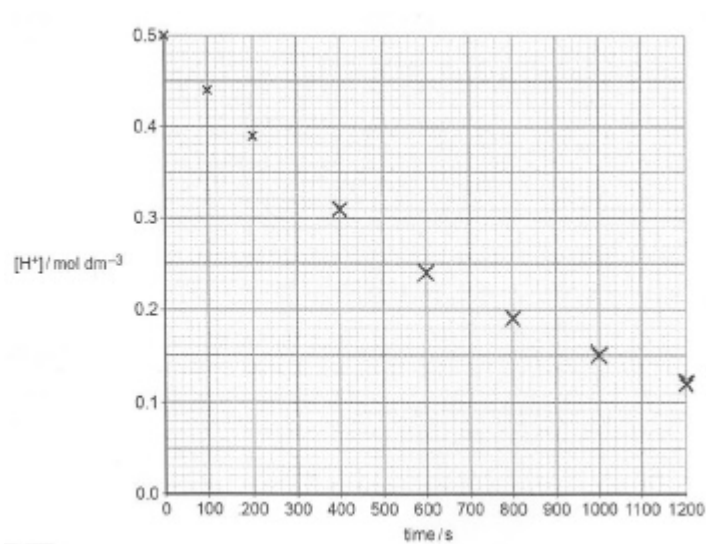
Additional processing of data such as including $[H^+]$ loses M2

$$\text{units} = \underline{\text{mol dm}^{-3} \text{ s}^{-1}}$$

M3 mark independently

3

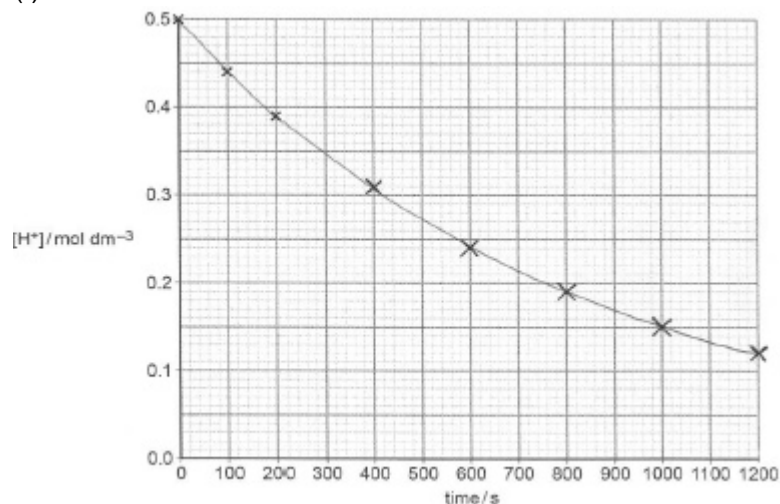
- (e) 5 points correctly plotted



Allow \pm half a small square for each point

1

(f)

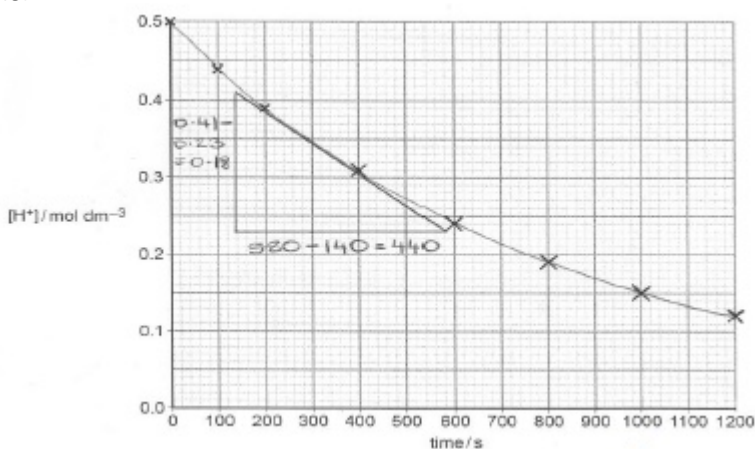


Smooth curve only within one small square of all points
(ecf on part (e))

Not a series of straight lines between points

1

(g)



M1: Tangent to curve drawn at $[H_3O^+] = 0.35 \text{ mol dm}^{-3}$
e.g. 0.18/440

M1 for a tangent / triangle / other suitable working

Allow ECF for both M1 and M2 following on from straight line drawn in 01.6, but must show suitable construction on graph for M1

M2: Rate = $4.09 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1})$

Ignore negative signs

Allow value in range $3.70 \times 10^{-4} - 4.50 \times 10^{-4}$

At least 2sf

ecf from any straight line for correctly calculated gradient

2

- (h) This question is marked using levels of response. Refer to the Mark Scheme Instructions for examiners for guidance on how to mark this question

Level 3 5-6 marks	All stages are covered and the explanation of each stage is correct and virtually complete. Answer is coherent and shows progression through all three stages. A clear explanation of how the order is determined from the results is needed to show coherence.
Level 2 3-4 marks	All stages are covered (NB 'covered' means min 2 from stage 2) but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages covered and the explanations are generally correct and virtually complete Answer is coherent and shows some progression through all three stages. Some steps in each stage may be out of order and incomplete
Level 1 1-2 marks	Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR only one stage is covered but the explanation is generally correct and virtually complete Answer shows some progression between two stages
Level 0 0 marks	Insufficient correct Chemistry to warrant a mark

Indicative Chemistry content Method 1

Stage 1 Preparation

- 1a Measure (suitable/known volumes of) some reagents (ignore quoted values for volume)
- 1b Measure (known amount of) **X** / use a colorimeter
- 1c into separate container(s) – (allow up to two reagents and **X** measured together into one container); reference to **A**, **B** or **C** added last. NOT if **X** added last.

Stage 2 Procedure

- 2a Start clock/timer at the point of mixing (don't allow if only 2 reagents mixed) (allow even if **X** not added or added last)
- 2b Time recorded for appearance of blue colour/specific reading on colorimeter/disappearing cross
- 2c Use of same concentration of **B** and **C** / same total volume / same volume/amount of **X**
- 2d Same temperature/use water bath
- 2e Repeat with different concentrations of A (can be implied through different volumes of A and same total volume)

Stage 3 Use of Results

- 3a 1/time taken is a measure of the rate
- 3b plot of 1/time against volumes/concentrations of **A** or plot $\log(1/\text{time})$ vs $\log(\text{volume or concentration of A})$
- 3c description of interpreting order from shape of 1/time vs volume or concentration graph / gradient of log plot gives order / allow interpretation of time vs concentration graph / ratio between change in concentration and change in rate (e.g, $2x[A] = 2 \times$ rate so 1st order)

Indicative Chemistry content – Alternative Method Using Colorimetry and repeated Continuous Monitoring

Stage 1 Preparation

- 1a Measure (suitable/known volumes of) **A**, **B** and **C** (ignore quoted values for volume)
- 1b Use of colorimeter
- 1c into separate container(s) – (allow up to two reagents measured together into one container) – ignore use of **X**

Stage 2 Procedure

- 2a Start clock/timer at the point of mixing
- 2b Take series of colorimeter readings at regular time intervals
- 2c Use of same concentration of **B** and **C** / same total volume / (same volume/amount of **X**)
- 2d Same temperature
- 2e Repeat with different concentrations of **A** (can be implied through different volumes of **A** and same total volume)

Stage 3 Use of Results

- 3a Plot absorbance vs time and measure/calculate gradient at time=0
- 3b plot of gradient against volumes/concentrations of **A** or plot $\log(1/\text{time})$ vs $\log(\text{volume or concentration of A})$
- 3c description of interpreting order from shape of 1/time vs volume or concentration graph / gradient of log plot gives order

6

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2.

- (a) Amount of propanone = $(25.0 \times 1) / 1000 = 0.025 \text{ mol}$

1

Concentration in mixture **A** = $0.025 / (90.0/1000) = 0.278 \text{ mol dm}^{-3}$

1

- (b) To make volumes constant for all mixtures.

1

So that volume of propanone is proportional to concentration.

1

- (c) Amount of iodine in mixture $E = (40.0 \times 0.02) / 1000 = 8.0 \times 10^{-4}$ mol 1
- Amount of iodine in sample = $8.0 \times 10^{-4} \times (10 / 90) = 8.89 \times 10^{-5}$ mol
As 10 cm³ sample taken from total volume of 90 cm³ 1
- Amount of thio required = $2 \times 8.89 \times 10^{-5} = 1.78 \times 10^{-4}$ mol 1
- Volume of thio = $(1.78 \times 10^{-4} / 0.01) \times 1000 = 17.8$ cm³ 1
- (d) Scale 1
- Graph must cover at least half the grid and axes must be plotted in correct orientation but ignore labeling.*
- Points 1
- Must be correctly plotted to within \pm half a small square.*
- Best-fit straight line 1
- Must be the best-fit line possible if point(s) are plotted incorrectly. Penalise doubled or kinked lines.*
- Gradient = y / x 1
- = -0.060 1
- Allow -0.059 to -0.061
Ignore any units given.*
- (e) Gradients / rates are proportional to volumes / concentrations of propanone **or** B to D show that gradient / rate halves when vol / concentration halves. 1
- So first order with regard to propanone. 1
- (f) To stop / quench the reaction at that time. 1
- Ignore NaHCO₃ reacts with the HI produced.*
- By removing the acid catalyst for the reaction (by neutralisation). 1

[17]

3.

- (a) Power (or index or shown as x in []^x) of concentration term (in rate equation) **(1)**

1

(b) 2 (1)

1

(c) (i) Order with respect to **A**: 2 (1)

Order with respect to **B**: 0 (1)

(ii) Rate equation: (rate =) $k [A]^2$ (1)

Allow conseq on c(i)

Units for rate constant: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (1)

conseq on rate equation

4

[6]

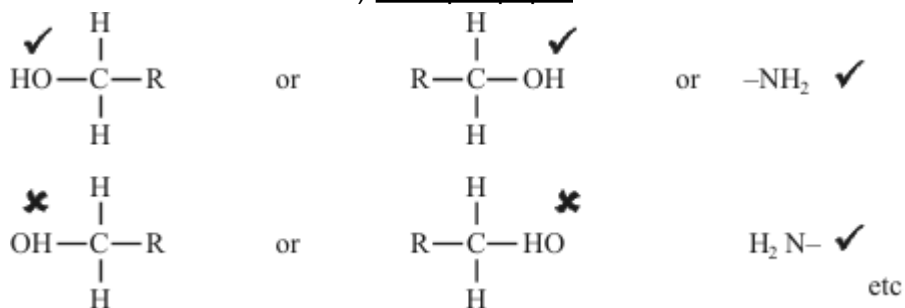
Organic points

- (1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space e.g.



- (2) Structures

penalise sticks (i.e. $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$) once per paper



Penalise once per paper

allow CH_3- or $-\text{CH}_3$ or $\begin{array}{c} \text{CH}_3 \\ | \end{array}$ or CH_3
or $\text{H}_3\text{C}-$ or CH

4.

(a) (i) $k = \frac{8.4 \times 10^{-5}}{(4.2 \times 10^{-2})^2 \times 2.6 \times 10^{-2}}$ **OR** $\frac{8.4 \times 10^{-5}}{(1.76 \times 10^{-3}) \times 2.6 \times 10^{-2}}$

Mark is for insertion of numbers into a correctly rearranged rate equation, $k = \text{etc.}$

If upside down, score only units mark from their k

AE (-1) for copying numbers wrongly or swapping two numbers

1

= 1.8(3)

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

If k calculation wrong, allow units consequential to their $k = \text{expression}$

1

(ii) $5.67 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1})$ **OR** their $k \times 3.1 \times 10^{-4}$

Allow 5.57×10^{-4} to 5.7×10^{-4}

1

(b) (i) 2 or second or $[\text{D}]^2$

1

(ii) 0 or zero or $[\text{E}]^0$

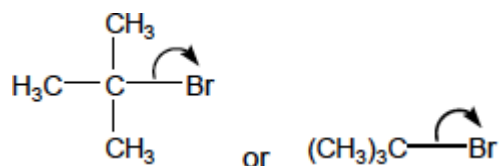
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(c) (i) Step 1 or equation as shown

Penalise Step 2 but mark on

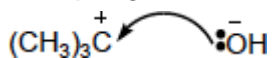
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(ii)



Ignore correct partial charges, penalise full / incorrect partial charges

If Step 2 given above, can score the mark here for



allow: OH^- (must show lp)

If $\text{S}_{\text{N}}2$ mechanism shown then no mark (penalise involvement of $:\text{OH}^-$ in step 1)

Ignore anything after correct step 1

1

[8]

5.

- (a) Consider experiments 1 and 2: [B constant]

[A] increases $\times 3$: rate increases by 3^2 therefore 2nd order with respect to A

1

Consider experiments 2 and 3:

[A] increases $\times 2$: rate should increase $\times 2^2$ but only increases $\times 2$

Therefore, halving [B] halves rate and so 1st order with respect to B

1

Rate equation: rate = $k[A]^2[B]$

1

- (b) rate = $k[C]^2[D]$ therefore $k = \text{rate} / [C]^2[D]$

1

$$k = \frac{7.2 \times 10^{-4}}{(1.9 \times 10^{-2})^2 \times (3.5 \times 10^{-2})} = 57.0$$

Allow consequential marking on incorrect transcription

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

1

- (c) rate = $57.0 \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3} (\text{mol dm}^{-3} \text{s}^{-1})$

OR

Their $k \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2}$

1

- (d) Reaction occurs when molecules have $E \geq E_a$

1

Doubling T by 10 °C causes many more molecules to have this E

1

Whereas doubling [E] only doubles the number with this E

1

- (e) $E_a = RT(\ln A - \ln k) / 1000$

Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ

1

$$E_a = 8.31 \times 300 (23.97 - (-5.03)) / 1000 = 72.3 (\text{kJ mol}^{-1})$$

1

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