Mark schemes

Q1.  
c
(1)
Q2.
(a) Consider experiments 1 and 2: [B constant]
[A] increases 
$$\times$$
 3: rate increases by 3<sup>2</sup> therefore 2nd order with respect to A
(A) increases  $\times$  3: rate increases by 3<sup>2</sup> therefore 2nd order with respect to A
(A) increases  $\times$  2: rate should increase  $\times$  2<sup>2</sup> but only increases  $\times$  2
Therefore, halving [B] halves rate and so 1st order with respect to B
(A) increases  $\times$  2: rate should increase  $\times$  2<sup>2</sup> but only increases  $\times$  2
(B) rate equation: rate =  $k[A]^{2}[B]$ 
(b) rate =  $k[C]^{2}[D]$  therefore  $k = \text{rate } / [C]^{2}[D]$ 
(c) rate =  $k[C]^{2}[D]$  therefore  $k = \text{rate } / [C]^{2}[D]$ 
(c) rate =  $57.0 \times (3.6 \times 10^{-2})^{2} \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3} \pmod{4m^{-3} \text{ s}^{-1}}$ 
(c) rate =  $57.0 \times (3.6 \times 10^{-2})^{2} \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3} \pmod{4m^{-3} \text{ s}^{-1}}$ 
(d) Reaction occurs when molecules have  $E_{2}E_{3}$ 
Doubling T by 10 °C causes many more molecules to have this  $E$ 
Whereas doubling [E] only doubles the number with this  $E$ 

(e	E <sub>a</sub> = <i>RT</i> (InA – In <i>k</i> ) / 1000 Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ	1	
	$E_{a} = 8.31 \times 300 (23.97 - (-5.03)) / 1000 = 72.3 (kJ mol-1)$	1	[12]
Q3. B			[1]
Q4. c			[1]
Q5. B			[1]
Q6.			
<b>d0.</b> (a	The sodium hydrogencarbonate solution neutralises the acid (catalyst)	M1	
	So stops the reaction	M2	
(b	The concentration/amount of propanone is much larger than/200 times larger than the concentration/amount of iodine	M1	
	Concentration of propanone is (almost) constant		
	The change in concentration in propanone is negligible	M2	

(c)



Q7.			
(a)	M1	tangent drawn to the curve at 0,0	
		If tangent not drawn at 0,0 then allow conseq	
		gradient calculation	1
	M2	Evidence of value used in calculation leading to initial rate = $5.5$ Note allow $5 - 7$	
			1
	М3	Cm <sup>3</sup> S <sup>-1</sup>	
		NOT cm <sup>3</sup> / s	1
(b)	M1	$[H_2PO_2^{-}]^2 \alpha 1/t$	
		Accept time argument eg if conc doubled time is quartered	
		Accept suitable words that implies a square or	
		square root relationship	1
			-
	M2	Order = 2 Not simple description of as conc increases time	
		decreases 1	
			1
(c)			
		Gas syringe	
		Conical flask	
	/		
	/		
	881	Reaction mixture	
		母 4 (m) 均 4 (m)	

Either gas syringe or measuring cylinder over water

1

1

1

1

1



Tubing shown should not be closed Syringe should have a plunger shown Allow lack of graduations

(d) Falls by a factor of 8

OR Multiplied by 1/8

OR Divided by 8 Allow halved then quartered / Decreases by 2<sup>3</sup>

(e) **M1**  $[M]^2 = \underline{Rate}$ Re-arrangement

> M2  $[M]^2 = \frac{0.0250}{21.3 \times 0.0155}$  (=7.57 × 10–2) Inserts correct numbers into their rearranged expression

- **M3**  $[M] = \sqrt{7.57 \times 10^{-2}} = 0.275 \text{ mol dm}^{-3} (\text{min 2 sf})$ Takes square root (allow ecf for square root of their M2) Common error is to use 0.25 rather than 0.025. This leads to an answer of 0.870. Scores 2 Upside-down expression leads to an answer of 3.63. Scores 2
- (f) The sum of powers/indices (to which the concentrations are raised in the rate equation)

All the orders added/ sum of the (individual) orders This can be explained using a general rate equation stated as an example

e.g. Rate =  $k[A]^{k}[B]^{j}$  and the overall order is x + y

[11]

1

1

1

#### Q8.

(a)

DNA Replication NOT mitosis NOT DNA synthesis Ignore terms relating to cell division processes Ignore 'damages DNA' Ignore DNA transcription Ignore 'cell replication'

(b) 
$$[Pt(NH_3)_2Cl_2] + H_2O \rightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$
  
*M1* Correct formula **and** charge of B

M2 Correct balancing and charges in equation

Allow **M2** if the **only** error in complex B is the charge (**M1** not awarded) with CF **only** ALLOW complexes without [] and/or () around H<sub>2</sub>O IGNORE () around CI NOT any additional different species (loses **M2**) (allow uncancelled water on both sides)

(C)



M1 Pt in a cis-diammine complex bonded to the correct nitrogen atoms Pt must have the two ammonia ligands shown NOT if drawn as trans IGNORE any charge on Pt Ignore any wedges and dashes (3D representations)

**M2** both lone pairs shown **OR** two arrows indicating co-ordinate bonds

1

1

1

1

2

Allow **M2** if bonds to platinum are from the incorrect nitrogen atoms

- (d) M1 plot concentration (y-axis) against time (x-axis) and take tangents / (calculate the) gradients (to calculate rates)
   Allow concentration-time graph
   NOT time-concentration graph (unless clarified in words or sketch) but mark on
  - M2 Plot rate/gradients against conc
  - M3 straight line through origin / directly proportional confirms first order allow first order if rate halves/doubles when conc halves/doubles

Alternatives to M2 and M3: M2 Plot a graph of log rate vs log conc M3 (Straight) line of gradient = 1 M2 measure (at least) two half-lives (in this case, tangents not required for M1) M3 constant half-life means first order M2 compare rates/gradients at different concentrations M3 first order if rate halves when conc halves

(e)

temperature, <i>T /</i> K	1/K <sup>-1</sup>	rate constant, k / s <sup>-1</sup>	In k
318	0.00314	6.63 x 10 <sup>-7</sup>	-14.2

Allow 3.14 x 10-3

(f)



[15]

#### Q9.

 $A = k / e^{-E_a/RT}$ 

= (3.46 × 10<sup>-8</sup>) / e<sup>-96200/(8.31 × 298)</sup>

$$= 2.57 \times 10^9$$

**S**<sup>-1</sup>

OR using $\ln k = \ln A - E_a/RT$		
$\ln A \rightarrow = \ln k +$	E <sub>2</sub> /RT	
→ = −17.1	79 + 38.847 = 21.667	
A $\rightarrow$ = 2.57	× 10 <sup>9</sup>	
S <sup>−1</sup>		
	M1 Rearrangement (if wrong can only score M2 & M4)	1
	<b>M2</b> Correct conversions of both $E_a$ and T	1
	<b>M3</b> Answer allow 2.45 × 10° to 2.6 × 10°	1
	M4 Units	-
	If use 96.2kJ, A = 3.60 × 10⁻ <sup>8</sup>	1
	If use 96.2kJ and 25°C, A = 5.50 × 10⁻ଃ	

[4]

## Q10.

0.		
(a)	$k = \frac{2.4 \times 10^{-2}}{0.10 \times 0.20 \times (0.30)^2}$	
	Mark is for insertion of numbers into a correctly re-arranged equation.	
	12 (must be 2 of s)	1
	= 13 (must be 2 sfs)	1
	Units mol <sup>-3</sup> dm <sup>+9</sup> s <sup>-1</sup>	
	Can be in any order	1
(b)	Experiment 2 [BrO <sub>3</sub> -] = 0.15	1
	Experiment 3 rate = 0.26 or 0.27	1
	Experiment 4 [H <sup>+</sup> ] = 0.45 or 0.46	
	If k wrong in (a) : allow the expected answer OR values conseq to their k (allow mix & match)	
	$Ex 2 [BrO_3^-] = 2/k$	
	Ext 3 rate = $0.02 \times k$	
	$Ex 4 [H^+] = square root of (2.7/k)$	1
(c)	1/T value 3.31(1) × 10⁻³ or 0.00331(1)	
	Must be 3 sig figs or more	1

(d)

ln(1/t) value -3.30 or -3.297 Not allow -3.29 1 y axis labelled with values (no units) and plotted points use over half M1 of the axis 1 points plotted correctly (see graph below) M2 1 М3 best fit straight line (minimum 3 points plotted) + - one small square for line of best fit 1 M4 gradient =  $-6.64 \times 10^3$  (K) or -6640 (K) Range - 6.5 × 10<sup>3</sup> to - 6.8 × 10<sup>3</sup> or -6500 to -6800 1  $E_{a} = M4 \times 8.31$ M5 If gradient outside range then max 4 for M1, M2, M3 and M5 1 M6 = 55.2 kJ mol<sup>-1</sup> Range 54.0 - 56.5 1



[14]

### Q11.

 (a) H<sub>2</sub>O<sub>2</sub> and/or I<sup>-</sup> <u>concentration</u> change is negligible / H<sub>2</sub>O<sub>2</sub> and/or I<sup>-</sup> <u>concentration</u> (effectively) constant
 <u>Only</u> the <u>concentration</u> of H<sup>+</sup> 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<sup>+</sup> is limiting reagent / rds /  $H_2O_2/F$  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 H<sub>2</sub>O<sub>2</sub>/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 [H+] changes/decreases

M2 dependent on correct M1 Allow rate v concentration graph would give horizontal straight line owtte Allow so [H<sup>+</sup>] 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

1

No ecf from incorrect or inverted numbers in M1  $k_1 = -0.0012$  scores 1/2 Additional processing of data such as including [H<sup>+</sup>] loses M2

units =  $\frac{\text{mol } \text{dm}^{-3} \text{ s}^{-1}}{M3 \text{ mark independently}}$ 

#### (e) 5 points correctly plotted



Allow ±half a small square for each point



Smooth curve only within one small square of all points (ecf on part (e)) Not a series of straight lines between points

1



M1: Tangent to curve drawn at  $[H_3O^+] = 0.35$  mol dm<sup>-3</sup> 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 =  $4.09 \times 10^{-4}$  (mol dm<sup>-3</sup> s<sup>-1</sup>) 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

 (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.
5-0 maiks	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
	<b>OR</b> 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	Two stages are covered but the explanation of each

1-2 marks	stage may be incomplete or may contain inaccuracies
	<b>OR</b> only one stage is covered but the explanation is generally correct and virtually complete
	Answer shows some progression between two stages
Level 0	Insufficient correct Chemistry to warrant a mark
0 marks	

#### 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/time) vs log(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 × rate so 1<sup>st</sup> 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/time) vs log(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