26. Reaction kinetics

26.1 Simple rate equations, orders of reaction and rate constants

Paper 4

Marking Scheme

Q1.

(a)(i)	tangent drawn at $t = 0$ **AND** gradient of tangent calculated at $t = 0$ answer between 0.016 to 0.040	**1**
(a)(ii)	$[I^-]$ stays constant / $[I^-]$ does not change **OR** the overall order is one under these conditions	**1**

(c)	the rate constant and rate of reaction 1 will both increase	**1**
(d)	$k = 0.693 \div t_{½}$ $t_{½} = 0.693 \div 0.0158 = 43.9$ s	**1**
(e)	$NO + Br_2 \rightarrow NOBr_2$ **OR** $NO + Br_2 \rightarrow NOBr + Br$ $NOBr_2 + NO \rightarrow 2NOBr$ **OR** $Br + NO \rightarrow NOBr$ **M1** two equations adding up to the overall equation **M2** step 1 has one NO and one Br_2 only and is identified as slow step	**2**

Q2.

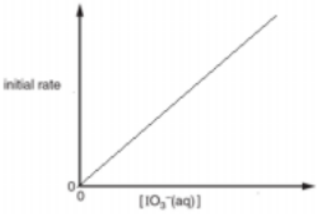
(a)(i)	**M1** (using exp 1 and 2) [NO] × 3, rate × 9 so 2nd order to NO **M2** (using exp 1 and 3) [NO] × 2, $[Cl_2]$ × 4, rate × 16 so 1st order to Cl_2 **OR** (using exp 2 and 3) [NO] × 2 / 3, $[Cl_2]$ × 4, rate × 1.8 so 1st order to Cl_2 **M3** (rate =) $k\,[NO]^2\,[Cl_2]$ ecf	**3**
(a)(ii)	**M1** rate = $k\,[NO]^2[Cl_2]$ $k = (3.68 \times 10^{-2}) \div (0.025^2 \times 0.015) = 3925.33$ ecf (a)(i) min 2sf **M2** $dm^6\ mol^{-2}\ min^{-1}$ ecf (a)(i)	**2**
(b)	initiation $NO_2Cl \rightarrow Cl\bullet + NO_2\bullet$ step 1 $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$ step 2 $ClO\bullet + O_3 \rightarrow Cl\bullet + 2O_2$ Any two [1] all three [2]	**2**
(c)	**M1** $O_3 + NO_2 \rightarrow NO_3 + O_2$ **ALLOW** $O_3 + NO_2 \rightarrow NO_5$ **M2** $NO_3 + NO_2 \rightarrow N_2O_5$ **ALLOW** $NO_5 + NO_2 \rightarrow N_2O_5 + O_2$	**2**

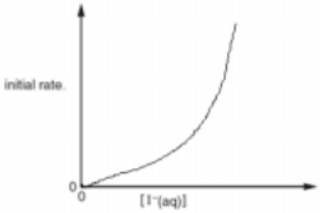
Q3.

(a)(i)	Change in concentration = 0.135 $0.135 / 1800 = 7.5 \times 10^{-5}$	[1] [1]	**2**
(a)(ii)	Rate = k[X]	[1]	**1**
(a)(iii)	$k = 0.693 / t_{½}$ / $k = 0.693 / 900$ / $k = \ln 2 / t_{½}$ / $k = \ln 2 / 900$ / $t_{½} = \ln 2 / k$	[1]	**1**
(a)(iv)	1.16×10^{-4} $mol\ dm^{-3}\ s^{-1}$	[1] [1]	**2**

Q4.

(a)(i)	the power to which the concentration of a reactant is raised in the rate equation	**1**

<table>
<tr><td>(a)(ii)</td><td><table><tr><td>the order of reaction with respect to [IO₃[−]]</td><td>1</td></tr><tr><td>the order of reaction with respect to [H⁺]</td><td>2</td></tr><tr><td>the order of reaction with respect to [I[−]]</td><td>2</td></tr><tr><td>the overall order of reaction</td><td>5</td></tr></table>All correct for one mark</td><td>1</td></tr>
<tr><td>(a)(iii)</td><td>


</td><td>1</td></tr>
<tr><td>(a)(iv)</td><td>M1 k = rate / $[I^-]^2[IO_3^-][H^+]^2 = (4.20 \times 10^{-2})/(0.025^2 \times 0.04x0.015^2) = 7.47 \times 10^6$
M2 units = $mol^{-4} dm^{12} min^{-1}$</td><td>2</td></tr>
<tr><td>(a)(v)</td><td>$0.0709 = k \times 0.12 \times [H^+]^2 \times 0.0125^2$
$[H^+] = 2.25 \times 10^{-2}$</td><td>1</td></tr>
<tr><td>(a)(vi)</td><td>$x = 10^2 / 1 = 100$</td><td>1</td></tr>
<tr><td>(b)</td><td>M1 step 1 $Fe^{3+} + I^- \rightarrow FeI^{2+}$
M2 step 2 $FeI^{2+} + I^- \rightarrow Fe^{2+} + I_2^-$ OR $FeI^{2+} + I^- \rightarrow FeI_2^+$ AND slowest step = step 2
M3 step 3 $Fe^{3+} + I_2^- \rightarrow Fe^{2+} + I_2$ OR $FeI_2^+ + Fe^{3+} \rightarrow 2Fe^{2+} + I_2$</td><td>3</td></tr>
</table>

Q5.

(a)(i)	the sum/total of the power / exponent to which a concentration of a reactant is raised in the rate equation / law	**1**
(a)(ii)	**M1** (expt 1 and 2) when $[Fe^{3+}] \times 3$, rate × 3 so first order w.r.t. Fe^{3+} **M2** (expt 1 and 3) when $[Fe^{3+}] \times 2$, $[I^-] \times 2$, rate × 8 so second order w.r.t. I^- **OR** (expt 2 and 3) when $[Fe^{3+}] \div 1.5$, $[I^-] \times 2$, rate × 2.7 so second order w.r.t. I^-	**2**
(a)(iii)	(rate =) $k[Fe^{3+}][I^-]^2$ [1] ecf (a)(ii)	**1**
(a)(iv)	k = rate / $[Fe^{3+}][I^-]^2$ = $(2.64 \times 10^{-4}) / (0.04 \times 0.02^2)$ k = 16.5 min 2sf ecf units = $mol^{-2}\,dm^6\,s^{-1}$ ecf	**2**
(a)(v)	(*k* and rate of reaction) both increase	**1**

(b)(i)	step 1 as this has one mole of H_2O_2 and one mole of I^- **OR** step 1 as correct stoichiometry / coefficients of 1 H_2O_2 and 1 I^- **OR** step 1 as number of moles of each reactant are consistent with rate equation / their orders	**1**
(b)(ii)	step 1 I oxid no –1 → +1 **AND** O oxid no –1 → –2 **OR** step 3 I oxid no –1 → 0 **AND** I oxid no +1 → 0	**1**
(b)(iii)	intermediate **AND** formed (in step 2) and used up (in step 3) **ALLOW** oxidising agent (in step 3) **AND** oxidises I^- (to I_2)	**1**

Q6.

(a)(i)	M1:$F_2 + ClO_2 \rightarrow FClO_2 + F$ [1] M2:$ClO_2 + F \rightarrow FClO_2$ [1] OR M1: $F_2 + ClO_2 \rightarrow F_2ClO_2$ M2: $F_2ClO_2 + ClO_2 \rightarrow 2FClO_2$ two balanced equations MUST add to give the overall equation	**2**
(a)(ii)	first step AND has one mole / molecule of F_2 and ClO_2 [1] OR same moles of reactants as orders in rate equation	**1**
(b)(i)	rate = $k\,[F_2][ClO_2]$ / rate = $1.22\,[F_2][ClO_2]$ AND second / 2 BOTH[1]	**1**
(b)(ii)	rate = $1.22 \times 2 \times 10^{-3} \times 2 \times 10^{-3} = 4.88 \times 10^{-6}$ [1] min 2sfecf **1(b)(i)**	**1**
(c)(i)	$k_1 = (0.693 / 4) = 0.173$ OR 1.73×10^{-1}[1] MUST BE 3SF s^{-1} [1]	**2**
(c)(ii)	at 4 s = 0.001 at 8 s = 0.0005 at 12 s = 0.00025 smooth curve ALL correct [1]	**1**
(c)(iii)	tangent drawn at 0.00100 $mol\,dm^{-3}$ AND gradient dependent on their rate = Y / X in the range = $1.5–2.0 \times 10^{-4}$ [1] IGNORE sign	**1**

Q7.

(a)	1 0 [1] 1 2 [1]	2
(b)(i)	The line should start at **1×10^{-5}** and decrease to **0.773×10^{-5} / 7.73×10^{-6}** and be **straight** for 10 s [1]	1
(b)(ii)	its not possible **AND** the concentrations in the rate law are not known [1]	1
(c)	9.24×10^{-7} [1]	1
(d)(i)	630 [1]	1
(d)(ii)	Three halvings taking equal times, these times to agree with their answer to di.[1]	1
(e)(i)	$CH_3COH{=}CH_2 + I_2 \rightarrow CH_3C^+(OH)CH_2I + I^-$ [1]	1
(e)(ii)	step 1 **AND** has (both) substances in rate law.[1]	1
(e)(iii)	$CH_3C^+OHCH_3$ and CH_3COCH_3 **OR** $CH_3C^+(OH)CH_3$ and $CH_3C(OH){=}CH_2$ **OR** $CH_3C^+(OH)CH_2I$ and CH_3COCH_2I [1]	1

Q8.

(a)(i)	evidence of tangent drawn at t = 40 s and calculation of gradient = 0.000170 (mol dm^{-3} s^{-1}) min 2sf	1
(a)(ii)	**M1** evidence of construction lines and calculation of two $t_{1/2}$ **OR** evidence of construction lines and times for halving of concentration **M2** deduction: constant half-life / constant time between halving of concentration → 1st order	2
(b)	**M1** two half-lives in 320 s so $t_{1/2}$ = 160 s **M2** k = 0.693 / 160 = 0.00433 s^{-1} ecf min 2sf	2

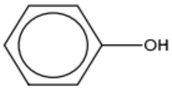
Q9.

(b)(i)	rate = $k[NO]^2[O_2]$ **OR** rate = $8.6 \times 10^6\ [NO]^2[O_2]$	1
(b)(ii)	rate = $8.6 \times 10^6 \times (7.2 \times 10^{-4})^2 \times 1.9 \times 10^{-3}$ rate = 8.47×10^{-3} (mol dm^{-3} s^{-1}) min 2sf	1
(c)(i)	(reaction is) first order wrt cisplatin / overall **OR** rate is directly proportional to concentration of cisplatin	1
(c)(ii)	$0.693 / 2.50 \times 10^{-5} = (2.77 \times 10^4$ s) **OR** $\ln 2 / 2.50 \times 10^{-5} = (2.77 \times 10^4$ s)	1
(c)(iii)	initial concentration is 8.0×10^{-5} mol dm^{-3} – five half-life periods have elapsed [1] time = $5 \times 27720 = 1.39 \times 10^5$ s [1] min 2 sf	2

Q10.

(a)(i)	rate = $k[NO][O_3]$	**1**
(a)(ii)	1.66×10^{-8} [1] mol dm^{-3} s^{-1} [1]	**2**
(a)(iii)	not constant **AND** overall second order / not overall first order	**1**
(b)(i)	graph is straight line clearly parallel to *x*-axis	**1**
(b)(ii)	graph is straight line with negative gradient	**1**
(b)(iii)	adsorption of reactants onto catalyst surface [1] bonds in reactants weaken [1] reaction occurs followed by desorption of products [1]	**3**
(b)(iv)	all active sites on catalyst surface are occupied	**1**

Q11.

(a)(i)	the power to which a concentration of a reactant is raised in the rate equation / law	**1**
(a)(ii)	**M1:** (using expt 1 and 3) as $[ClO_2] \times 2.5$ rate $\times 6.25$ so 2nd order **M2:** (using expt 1 and 2) as $[OH^-] \times 4$ rate $\times 4$ so 1st order	**2**
(a)(iii)	rate = $k[ClO_2]^2[OH^-]$	**1**
(a)(iv)	**M1:** $k = \text{rate} / [ClO_2]^2[OH^-]$ $k = 7.20 \times 10^{-4} / (0.02)^2(0.03)$ k = 60 **M2:** $mol^{-2}\ dm^6\ min^{-1}$	**2**
(b)(i)	structure of phenol: C_6H_5OH **OR** 	**1**
(b)(ii)	tangent drawn correctly **AND** rate = 0.015 / 260 = 5.8×10^{-5} **ALLOW** values consistent with tangent drawn at 100 sec	**1**
(c)	 **AND** half-life decreases (1st box)	**1**

Q12.

(b)	rate = $2.0 \times 10^{-6} \times 0.75 = \mathbf{1.5 \times 10^{-6}}$	**1**
(c)(i)	slowest step in overall reaction	**1**
(c)(ii)	$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$ **OR** $H_2O_2 + 2HI \rightarrow I_2 + 2H_2O$	**1**
(c)(iii)	$H_2O_2 = 1$ **AND** $I^- = 1$ **AND** $H^+ = 0$	**1**

Q13.

(g)(i)	**M1** Rate = $k[IO_3^-][SO_3^{2-}][H^+]$ **M2** units = $mol^{-2}dm^6s^{-1}$	**2**
(g)(ii)	0.10	**1**

Q14.

<table>
<tr><td>(a)</td><td><table><tr><td>the order of reaction with respect to [NO]</td><td>2</td></tr><tr><td>the order of reaction with respect to [O2]</td><td>1</td></tr><tr><td>the overall order of reaction</td><td>3</td></tr></table>ALL CORRECT [1]</td><td>1</td></tr>
<tr><td>(b)(i)</td><td>$k = (1.51 \times 10^{-4}) / (0.003^2 \times 0.00200)$
$k = \mathbf{8389}$ [1] min 2sf
$mol^{-2}\,dm^6\,s^{-1}$ [1]</td><td>2</td></tr>
<tr><td>(b)(ii)</td><td>$8400 = (6.05 \times 10^{-5}) / (x^2 \times 0.005)$
$x = \sqrt{(6.05 \times 10^{-5}) / (8400 \times 0.005)}$
$x = \mathbf{0.00120 / 1.20 \times 10^{-3}}$ [1] min 2sf ecf from Q1bi</td><td>1</td></tr>
<tr><td>(c)</td><td>slow(est) [1]</td><td>1</td></tr>
<tr><td>(d)(i)</td><td>correct RDS identified as step 1 with only one $S_2O_8^{2-}$ and one I^- [1]
overall mechanism adds up to chemical equation and no cancellable species on LHS / RHS in each of the equations [1]
M2 DEP on one $S_2O_8^{2-}$ and one I^- in step 1
e.g. step 1 $S_2O_8^{2-} + I^- \rightarrow SO_4^{2-} + SO_4I^-$ RDS = step 1
step 2 $SO_4I^- + I^- \rightarrow SO_4^{2-} + I_2$</td><td>2</td></tr>
<tr><td>(d)(ii)</td><td>no. of $t_{1/2} = 192 / 48 = 4$
$[I^-] = 0.0078 / 16 = \mathbf{4.9 \times 10^{-4}}$ [1] min 2sf</td><td>1</td></tr>
</table>

Q15.

(a)(i)	so it won't change / so it stays constant [1]	1
(a)(ii)	constant half-life / both half-lives = 45–55 [1] two half-lives taken (evidence needed) [1]	2
(b)(i)	first order [1] any two rows of data quoted, effect of $[H_2]$ specified [1] effect of $[I_2]$ specified and linked to first order [1]	3
(b)(ii)	rate = $k[H_2][I_2]$ [1]	1
(b)(iii)	2×10^{-13} [1] $mol^{-1}\ dm^3\ s^{-1}$ [1]	2
(c)(i)	forward reaction is faster than backward reaction **and** reaches equilibrium on product side / to the right [1]	1
(c)(ii)	forward reaction is negative **AND** backward reaction is positive [1] equilibrium position further left at higher T [1]	2

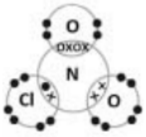
Q16.

(a)(i)	**M1**: using expt 2 and 3, $[NH_3] \times 2$, rate × 4 so order with respect to $[NH_3] = 2$ **M2**: using expt 1 and 2, $[ClO^-] \times 2$ and $[NH_3] \times 2$, as rate × 8 (=2^2 * x) so order with respect to $[ClO^-] = 1$	2
(a)(ii)	rate = $k[NH_3]^2[ClO^-]$	1
(a)(iii)	**M1:** $k = 0.256 / (0.200 \times 0.100^2)$ $k = 128$ **M2:** Units $dm^6\ mol^{-2}\ s^{-1}$	2
(a)(iv)	curve / line showing *k* increasing as temperature increases	1
(b)(i)	**M1:** plot a graph of $[I^-]$ against time **M2:** constant half-lives	2
(b)(ii)	$ClO^- + I^- \rightarrow IO^- + Cl^-$	1
(b)(iii)	step 2 **and** Cl is reduced / oxid no. decreases / oxid no. +1 → –1 ***or*** step 2 **and** I is oxidised / oxid no. increases / oxid no. –1 → +1	1

Q17.

<table>
<tr><td>(a)</td><td>CH_3COCH_3 = 1
I_2 = 0
H^+ = 1
overall order = 2 M1 3 orders [1] M2 overall order based on their M1 [1]</td><td>2</td></tr>
<tr><td>(b)(i)</td><td>k = $5.40 \times 10^{-3} / (1.50 \times 10^{-2} \times 7.75 \times 10^{-1})$
k = 0.46(452) [1] $dm^3\ mol^{-1}\ s^{-1}$ [1] 2sf min</td><td>2</td></tr>
<tr><td>(b)(ii)</td><td><table>
<tr><th></th><th>decreases</th><th>no change</th><th>increases</th></tr>
<tr><td>rate constant</td><td>✓</td><td></td><td></td></tr>
<tr><td>rate of reaction</td><td>✓</td><td></td><td></td></tr>
</table>
both [1]</td><td>1</td></tr>
<tr><td>(c)</td><td>draw a tangent at time, t=0 [1]
measure the gradient / slope of the tangent [1]</td><td>2</td></tr>
<tr><td>(d)</td><td>straight line graph starting at 0,0 and showing rate α [CH_3COCH_3] [1]</td><td>1</td></tr>
<tr><td>(e)(i)</td><td>slowest step / reaction (in the mechanism) [1]</td><td>1</td></tr>
<tr><td>(e)(ii)</td><td>$2Ce^{4+} + Tl^{+} \rightarrow Tl^{3+} + 2Ce^{3+}$ [1]
catalyst and (used in step 1 and) regenerated / reformed in step 3 / end of the reaction [1]</td><td>2</td></tr>
</table>

Q18.

<table>
<tr><td>(a)</td><td>
M1: eight electrons around N atom [N=O, N-O, N-Cl with N-O as dative]
M2: all other electrons correct</td><td>2</td></tr>
<tr><td>(b)(i)</td><td>(rate =) k[$ClNO_2$][NO]</td><td>1</td></tr>
<tr><td>(b)(ii)</td><td>$mol^{-1}\ dm^3\ s^{-1}$</td><td>1</td></tr>
<tr><td>(b)(iii)</td><td>Yes AND number of moles of reactants in overall equation is the same as order in rate equation</td><td>1</td></tr>
<tr><td>(c)(i)</td><td>• straight line with a negative gradient
• starting at 2.0×10^{-4}
• reaches at 1.8×10^{-4} at 0.2 seconds
Award 1 mark for two points, award 2 marks for all three points</td><td>2</td></tr>
<tr><td>(c)(ii)</td><td>2×10^{-5} ($mol\ dm^{-3}$)</td><td>1</td></tr>
<tr><td>(c)(iii)</td><td>The reaction has reached equilibrium</td><td>1</td></tr>
</table>

Q19.

(a)	**M1:** the time taken for the amount/concentration or a reactant to halve **M2:** the slowest step	**2**
(b)	- Use an excess of CH_3Br - (Several experiments with) different initial [OH] - control / equilibrate temperatures - measure time - find $[OH^-]$ by sample and titrate or use of pH probe **or** find $[Br^-]$ by sample and reference to use of Ag^+. - processing of results – plot graph of $[OH^-]$ vs rate or evaluate rate is proportional to $[OH^-]$ numerically Alternative approach: - Use an excess of CH_3Br - One experiment with known initial $[OH^-]$ - control / equilibrate temperatures - measure time - find $[OH^-]$ by sample and titrate or use of pH probe **or** find $[Br^-]$ by sample and reference to use of Ag^+ and describes how to calculate $[OH^-]$. - processing of results – plot graph of $[OH^-]$ vs time and look for constant half-life Award 1 mark for each correctly identified point.	**4**

(c)	**M1:** rate = k[ester]$[OH^-]$ **M2:** value of k = 0.206 **M3:** units $mol^{-1}dm^3s^{-1}$	**3**

Q20.

(a)	change in amount / mass / concentration of reactant / product per time	**1**
(b)	decrease in volume or pressure	**1**
(c)	8.13×10^4 / 81280 / 81300	**1**
	$mol^{-2}\ dm^6\ s^{-1}$	**1**
(d)	$\sqrt{}(0.00231 / (0.0046 \times 81280)) = 2.49 \times 10^{-3}$	**1**
(e)	2, 1, 3	**1**
(f)(i)	2	**1**
(f)(ii)	the total of steps 1 and 2 / the components of 2 are two NO and one H_2	**1**
(g)(i)	time for amount or mass or concentration to halve	**1**
(g)(ii)	0.02 at start and 0.01 after 2 seconds	**1**
	0.005 after 4 seconds and 0.0025 after 6 seconds	**1**
(h)(i)	$NO + ½ O_2 \rightarrow NO_2$ **or** $NO + O_2 \rightarrow NO_2 + ½ O_2$ **AND** $NO_2 + SO_2 \rightarrow NO + SO_3$	**1**
(h)(ii)	(NO is) regenerated / reformed	**1**
(h)(iii)	$SO_3 + H_2O \rightarrow H_2SO_4$ **AND** acid rain or consequence of this described	**1**

Q21.

(a)	change in amount / mass / concentration of reactant / product per time	**1**
(b)	decrease in volume or pressure	**1**
(c)	8.13×10^4 / 81280 / 81300	**1**
	$mol^{-2}\ dm^6\ s^{-1}$	**1**
(d)	$\sqrt{(0.00231 / (0.0046 \times 81280))} = 2.49 \times 10^{-3}$	**1**
(e)	2, 1, 3	**1**
(f)(i)	2	**1**
(f)(ii)	the total of steps 1 and 2 / the components of 2 are two NO and one H_2	**1**
(g)(i)	time for amount or mass or concentration to halve	**1**
(g)(ii)	0.02 at start and 0.01 after 2 seconds	**1**
	0.005 after 4 seconds and 0.0025 after 6 seconds	**1**