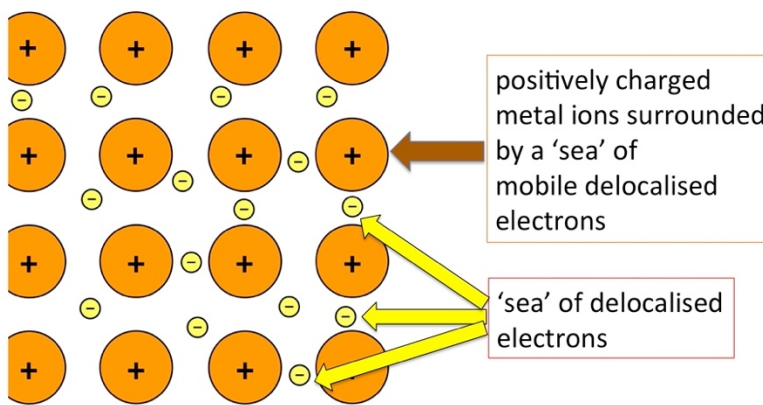
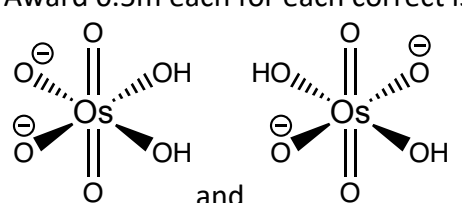


Mark Scheme for Data-based application questions: Physical and Inorganic Chemistry

1	a	i	<p>H₂ is oxidised, left electrode is anode [0.5] and polarity is negative [0.5] O₂ is reduced to H₂O₂, right electrode is cathode [0.5] and polarity is positive [0.5] Electrons flow FROM the LEFT electrode TO the RIGHT electrode [1]</p>										
		ii	<p>Anode: $\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^-$ Cathode: $\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2$ both for 1m State symbols not mandatory Deduct 0.5m for usage of reversible arrows</p>										
		iii	<p>H₂O [1] $E_{\text{cell}}^\ominus(\text{H}_2\text{O}_2 \text{ production}) = +0.69 \text{ V}$ [1] Since $E_{\text{cell}}^\ominus(\text{H}_2\text{O}_2 \text{ production})$ is less positive than $E_{\text{cell}}^\ominus(\text{H}_2\text{O production}) = +1.23 \text{ V}$, H₂O is preferentially produced. [1, conditional of attainment of previous marking point] OR After H₂O₂ is produced, H₂O₂ can be reduced by hydrogen gas further to water. [1] $E_{\text{cell}}^\ominus = E^\ominus(\text{H}_2\text{O}_2/\text{H}_2\text{O}) - E^\ominus(\text{H}^+/\text{H}_2) = +1.77 \text{ V}$ (positive) (spontaneous process) [1] Hence H₂O will be more likely to be formed.</p>										
	b	i	<p>Step 2: $\text{OH}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{O}^*$ [1] Step 3: $\text{O}^* + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{HOO}^*$ [1] (accept HO₂*, OOH* or O₂H* in place of HOO*) Step 4: $\text{HOO}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{O}_2(\text{g}) + *$ [1] Deduct 1m maximum for missing state symbols and * indicators, deduct 0.5m per missing occurrence No ECF awarded</p>										
		ii	<p>A convincing explanation must be given [1] Candidates are required to present the sum of the left hand and right hand side for full credit</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tbody> <tr> <td style="width: 15%;">Step 1</td> <td>$\text{H}_2\text{O}(\text{l}) + * \rightarrow \text{OH}^* + \text{H}^+(\text{aq}) + \text{e}^-$</td> </tr> <tr> <td>Step 2</td> <td>$\text{OH}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{O}^*$</td> </tr> <tr> <td>Step 3</td> <td>$\text{O}^* + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{HOO}^*$</td> </tr> <tr> <td>Step 4</td> <td>$\text{HOO}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{O}_2(\text{g}) + *$</td> </tr> <tr> <td>Total</td> <td> $\text{H}_2\text{O}(\text{l}) + * + \text{OH}^* + \text{O}^* + \text{H}_2\text{O}(\text{l}) + \text{HOO}^* \rightarrow \text{OH}^* + \text{H}^+(\text{aq}) + \text{e}^- +$ $\text{H}^+(\text{aq}) + \text{e}^- + \text{O}^* + \text{H}^+(\text{aq}) + \text{e}^- + \text{HOO}^* + \text{H}^+(\text{aq}) + \text{e}^- + \text{O}_2(\text{g}) + *$ </td> </tr> </tbody> </table> <p style="color: red;">Cancelling common terms in red gives</p> <p>$2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^-$</p>	Step 1	$\text{H}_2\text{O}(\text{l}) + * \rightarrow \text{OH}^* + \text{H}^+(\text{aq}) + \text{e}^-$	Step 2	$\text{OH}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{O}^*$	Step 3	$\text{O}^* + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{HOO}^*$	Step 4	$\text{HOO}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^- + \text{O}_2(\text{g}) + *$	Total	$\text{H}_2\text{O}(\text{l}) + * + \text{OH}^* + \text{O}^* + \text{H}_2\text{O}(\text{l}) + \text{HOO}^* \rightarrow \text{OH}^* + \text{H}^+(\text{aq}) + \text{e}^- +$ $\text{H}^+(\text{aq}) + \text{e}^- + \text{O}^* + \text{H}^+(\text{aq}) + \text{e}^- + \text{HOO}^* + \text{H}^+(\text{aq}) + \text{e}^- + \text{O}_2(\text{g}) + *$
Step 1	$\text{H}_2\text{O}(\text{l}) + * \rightarrow \text{OH}^* + \text{H}^+(\text{aq}) + \text{e}^-$												
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Total	$\text{H}_2\text{O}(\text{l}) + * + \text{OH}^* + \text{O}^* + \text{H}_2\text{O}(\text{l}) + \text{HOO}^* \rightarrow \text{OH}^* + \text{H}^+(\text{aq}) + \text{e}^- +$ $\text{H}^+(\text{aq}) + \text{e}^- + \text{O}^* + \text{H}^+(\text{aq}) + \text{e}^- + \text{HOO}^* + \text{H}^+(\text{aq}) + \text{e}^- + \text{O}_2(\text{g}) + *$												
		iii	<p>The 2e-WOR is $2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$ Step 2 of 2e-WOR is $\text{OH}^* + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{H}^+(\text{aq}) + \text{e}^- + *$ [1] No penalty for omitting/wrong state symbols</p>										
	c	i	<p>$x < 2.38$ [0.5] This prevents OH* from spontaneously releasing •OH(aq) (since the process has $\Delta G < 0$ otherwise). [1] $y > 3.52$ [0.5] From OH*, either H₂O₂(aq) or O* can be produced. To favour H₂O₂(aq) to be produced, the free energy of formation of H₂O₂ must be less positive than that of O* so that the formation</p>										

Mark Scheme for Data-based application questions: Physical and Inorganic Chemistry

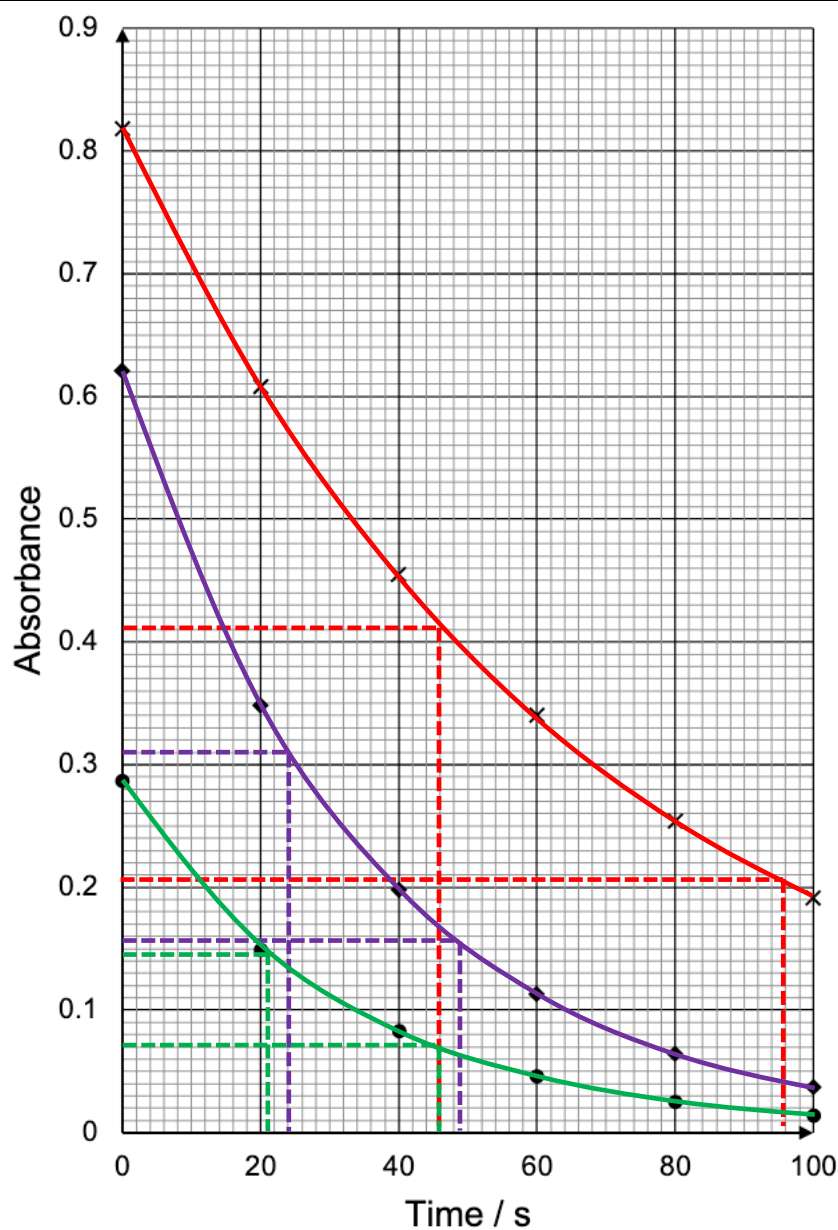
		of H ₂ O ₂ is <u>thermodynamically favoured</u> OR H ₂ O ₂ will be more stable than O* which favours its formation. [1]
	ii	Ticks TiO ₂ only [1] (award 0m for all other combinations)
d		$n(\text{electrons}) = Q/F = It/F = 0.10 \times 10^{-3} \times 20 \times 60 / 96500 = 1.2435 \times 10^{-6} \text{ mol}$ [1] $n(\text{H}_2\text{O}_2)$, maximum = $1.2435 \times 10^{-6} / 2 = 6.2175 \times 10^{-7} \text{ mol}$ [0.5] 2 mol MnO ₄ ⁻ reacts with 5 mol of H ₂ O ₂ [0.5] $n(\text{H}_2\text{O}_2)$, detected in 5.0 cm ³ sample = $4.70 \times 10^{-3} \times 1.00 \times 10^{-5} \times 5 / 2 = 1.175 \times 10^{-7} \text{ mol}$ [0.5] $n(\text{H}_2\text{O}_2)$, detected = $1.175 \times 10^{-7} \times 4 = 4.70 \times 10^{-7} \text{ mol}$ [0.5] FE = $4.70 / 6.2175 \times 100\% = 75.6\%$ [1]
e		Accept any 2 advantages, 1 valid advantage for 1m. <ul style="list-style-type: none"> • 2e-ORR uses 2 raw materials while 2e-WOR uses 1 raw material • 2e-ORR uses flammable hydrogen gas while 2e-WOR uses water which is safe and easily available • 2e-WOR can produce 2 useful products (H₂ and H₂O₂) from H₂O alone, while the 2e-ORR will only produce 1 useful product from 2 raw materials. • 2e-WOR is an electrolytic setup where settings such as voltage, current can be easily adjusted to favour the production of H₂O₂. However, the 2e-ORR doesn't present such an advantage because it's an electrochemical/galvanic cell. • H₂O₂ produced from 2e-WOR can be used immediately for its purposes. However, H₂O₂ produced from 2e-ORR must be isolated first because it's produced in an acidic electrolyte.
f		<u>Low bond energy of O—O</u> at 150 kJ mol ⁻¹ . [1]
2	a	The hydrides of the elements (NH ₃ , CH ₄) in the atmosphere (excluding H ₂) are in its <u>lowest oxidation state</u> , which by extension, will only act as reducing agents. [1]
	b	i $\text{NH}_3 + \text{CH}_4 \rightarrow \text{HCN} + 3 \text{H}_2$ [1] State symbols not mandatory
		ii Glycine can be produced from A because A can be <u>hydrolysed</u> with <u>water vapour being the source of water</u> to form glycine. [1] Candidate must state the source of water and that A can be hydrolysed.
		iii Glycine has a higher solubility in water compared to A. Glycine can form more favourable/stronger ion-dipole interactions [0.5] with water since it exists as a zwitterion and will have a giant ionic structure [0.5, either giant ionic structure or zwitterion]. But A can only form weaker hydrogen bonds with water [0.5] since A has a simple molecular structure [0.5].
c	i	Step 1: $^1\text{H}^+ + ^1\text{H}^+ \rightarrow ^2\text{H}^+ + e^+ + \nu$ Step 2: $^1\text{H}^+ + ^2\text{H}^+ \rightarrow ^3\text{He}^{2+}$ (inclusion of gamma ray is not needed for candidates) Step 3: $2 \ ^3\text{He}^{2+} \rightarrow ^4\text{He}^{2+} + 2 \ ^1\text{H}^+$ Award 1m for each step that is correct Where protons are abbreviated, penalise 0.5m in total Where mass number(s) are omitted, penalise 0.5m in total Where charges are omitted, penalise 0.5m for each mistake up to 1m in total Candidates are reminded to read the question: the words 'nuclei' and 'nucleus' imply that all electrons are stripped off the atom
	ii	High kinetic energy needed to <u>overcome the repulsion</u> between positively charged nuclei [1]
d	i	Minimum ratio = 80.3 (accept 4 s.f.: 80.26) [1] (4 s.f. value is 80.26 not 80.25)

	ii	<p>Rate constant, $k = \ln 2 / (3.7 \times 10^{-22}) = 1.8734 \times 10^{21} \text{ s}^{-1}$</p> <p>Since the decay has a constant half-life, the decay is first order both points for [1]</p> <p>Rate of depletion (in amount per unit time) = $k \times n = 1.8734 \times 10^{21} \times 2.5 = 4.68 \times 10^{21} \text{ mol s}^{-1}$ [1]</p> <p>Number of half-lives = $\log_{0.5}(10^{-6}/2.5) = 21.2535$ [0.5] Time taken = $21.2535 \times 3.7 \times 10^{-22} = 7.86 \times 10^{-21} \text{ s}$ [0.5]</p>																				
	iii	<p>The angle of deflection is proportional to charge/mass, q/m</p> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th>Nuclei of species</th> <th>Relative charge</th> <th>Relative mass</th> <th>q/m</th> </tr> </thead> <tbody> <tr> <td>^2H</td> <td>+1</td> <td>2</td> <td rowspan="5">+0.5</td> </tr> <tr> <td>^4He</td> <td>+2</td> <td>4</td> </tr> <tr> <td>^8Be</td> <td>+4</td> <td>8</td> </tr> <tr> <td>^{12}C</td> <td>+6</td> <td>12</td> </tr> <tr> <td>^{16}O</td> <td>+8</td> <td>16</td> </tr> </tbody> </table> <p>Since all q/m values are the same, they will deflect at the same angle. Award 1m for calculation of all q/m values Award 1m for convincing explanation</p>	Nuclei of species	Relative charge	Relative mass	q/m	^2H	+1	2	+0.5	^4He	+2	4	^8Be	+4	8	^{12}C	+6	12	^{16}O	+8	16
Nuclei of species	Relative charge	Relative mass	q/m																			
^2H	+1	2	+0.5																			
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^{16}O	+8	16																				
3	a	<p>i</p>  <p>Labelled diagram [1]</p> <p>Os has a giant metallic structure [0.5] where positively charged Os cations are arranged in a lattice [0.5] and a 'sea' of delocalised electrons [0.5] are surrounding the cations. There exists strong electrostatic attraction [0.5] between the electrons and the cations. Metallic bonding is not accepted as candidates are expected to expound on this term (i.e. explain the origin of metallic bonding).</p>																				
	ii	<p>cis-trans [1] Award 0.5m each for each correct isomer</p>  <p><i>Take note that the oxygen atoms that are doubly bonded to Os, and that singly bonded to Os with a negative formal charge, are chemically equivalent due to resonance.</i></p>																				
	iii	<p>Catalyst [1] because OsO_4 is regenerated again. [1]</p>																				
	iv	<p>Reduction in oxidation state of N (from NMO to N-methylmorpholine) is -2.</p>																				

Mark Scheme for Data-based application questions: Physical and Inorganic Chemistry

			Oxidation state of Os in OsO ₄ is +8, so oxidation state of Os in the reduced osmium compound is +6. [1]
		v	Not selective OR other unintended oxidation reactions may occur [1]
	b	i	E(Os ^{x+} /Os) is more positive/less negative than E(Ni ²⁺ /Ni) [1]
		ii	Oxidise Au and Os to their highest oxidation states. Then add <u>excess</u> NaOH(aq). [0.5] Filter and <u>collect the precipitate</u> [0.5] The subsequent treatment of the precipitate (which contains gold) is not required.
		iii	OsO ₄ has a <u>simple molecular structure</u> [0.5] with <u>weak dispersion forces</u> between OsO ₄ molecules [0.5].
	c		A catalyst speeds up the forward and backward reaction to the same extent, so the <u>position of equilibrium does not change</u> with the catalyst used, and the composition of ammonia, by amount, will not change at equilibrium (for the same temperature). [1] Os is a rare metal OR expensive metal while Fe is readily available OR cheap. [1]
4	a	i	IO ₃ ⁻ + 5 I ⁻ + 6 H ⁺ → 3 I ₂ + 3 H ₂ O [1] Ignore state symbols
		ii	I ₂ + 2 Na ₂ S ₂ O ₃ → 2 NaI + Na ₂ S ₄ O ₆ [1] Ignore state symbols Accept ionic equation
		iii	[1] for calculating amount of iodine in salt sample $n_{I_2} = \frac{7.50}{1000} \times 0.00235 \times \frac{1}{2} = 8.8125 \times 10^{-6} \text{ mol}$ $n_I = 8.8125 \times 10^{-6} \times \frac{1}{3} = 2.9375 \times 10^{-6} \text{ mol}$ [1] for mass of iodine in salt sample $\text{mass of iodine} = 2.9375 \times 10^{-6} \times 126.9 = 3.7277 \times 10^{-4} \text{ g}$ [1] for correct conclusion and conversion of concentration of iodine $\text{concentration of iodine in ppm} = \frac{3.7277 \times 10^{-4} \times 10^3 \text{ mg}}{10.000 \times 10^{-3} \text{ kg}} = 37.3 \text{ ppm}$ This sample of salt meets Georgia's regulations for iodised salt.
	b	i	Negatively charged H ₂ AsO ₃ ⁻ ion and [Ce(NO ₃) ₆] ²⁻ ion repel each other causing high activation energy of the reaction. [1]

ii



◆ Run 1 ● Run 2 × Run 3

Let the rate law be

$$\text{Rate} = k [\text{H}_3\text{AsO}_3]^a [\text{KI}]^b [(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]]^c$$

Since H_3AsO_3 is in excess for Runs 1, 2 and 3, and KI is a catalyst, the absorbance measures $[(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]]$.

From Run 3, the 2 half-lives measured are 46s and 50s respectively, which can be taken to be approximately constant. [1] Hence, order of reaction with respect to $[(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]]$ is 1. [1]

Half-life in Run 1 is 48s (on average).

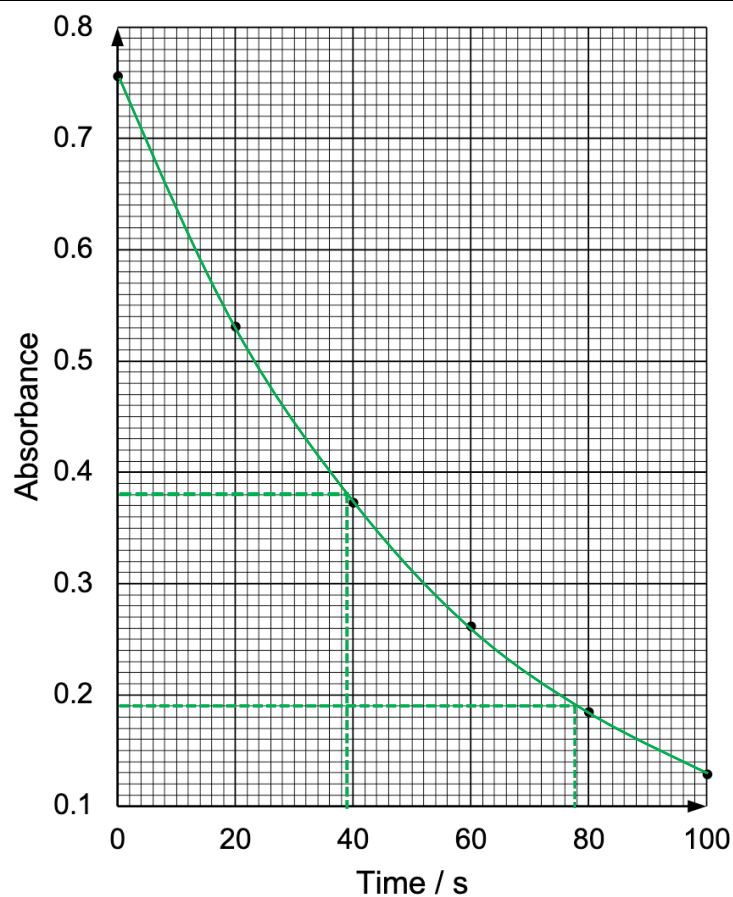
$$c = 1$$

Compare Runs 1 and 3. The half-life for Run 1 is measured to be 24s and 25s respectively. Half-life in Run 2 is 24.5s (on average). [1]

Since starting $[\text{H}_3\text{AsO}_3]$ is the same, the rate can be taken to be

	<p style="text-align: center;">$\text{Rate} = k' [\text{KI}]^b [(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]]$</p> $t_{\frac{1}{2}} = \frac{\ln 2}{k' [\text{KI}]^b}$ <p>Since half-life in run 1 is half of that of run 3 when $[\text{KI}]$ in run 1 is double of that in run 3, $b = 1$. Reaction is first order with respect to KI. [1]</p> <p style="text-align: center;">$\text{Rate} = k' [\text{KI}] [(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]]$</p> <p>Half-lives of run 2 are measured to be 21s and 25s. Half-life of run 2 is 23s (on average), which is no different from run 1. [1] Hence, changing $[\text{H}_3\text{AsO}_3]$ has no effect on the rate/k'. [1] Order of reaction with respect to H_3AsO_3 is 0. [1]</p> <p style="background-color: yellow;">Candidates should not take the "initial" rate of each experiment because the question states that "The first reading of the absorbance of the reaction mixture is recorded at time = 0 s. This is not the time when the reaction first starts."</p>
iii	<p>Half-life in Run 1 is 48s (on average).</p> <p>[1] for both expressions (award ecf)</p> <p style="text-align: center;">$\text{Rate} = k [\text{KI}] [(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]]$</p> $t_{\frac{1}{2}} = \frac{\ln 2}{k [\text{KI}]}$ <p>Substituting the values and solving for k, [1] for k and correct units $k = 1.01 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$</p>

iv



The half-life of this reaction is 39s.

Using

$$t_{\frac{1}{2}} = \frac{\ln 2}{k [\text{KI}]}$$

We have

$$[\text{KI}] = 1.76 \times 10^{-6} \text{ mol dm}^{-3} \text{ [1]}$$

$$\text{Amount of iodine} = 1.76 \times 10^{-6} \times (0.0500 + 1.000 + 0.800 + 0.200) \div 1000 \div 0.0500 \times 10.0$$

$$= 7.216 \times 10^{-7} \text{ mol [1]}$$

$$\text{Mass of iodine} = 9.157 \times 10^{-5} \text{ g}$$

$$\text{Iodine content in ppm} = 9.157 \times 10^{-5} \times 10^6 = 91.6 \text{ ppm [1]}$$

The skill in (b) is to use the half-life to find the rate constant. This is also less prone to error compared to if you were to find the initial rate.