Mark scheme

<table>
<tr><th colspan="3">Question</th><th>Answer/Indicative content</th><th>Marks</th><th>Guidance</th></tr>
<tr>
<td>1</td><td></td><td></td>
<td>

Level 3 (5–6 marks)
A comprehensive conclusion using quantitative data from graph to correctly determine
1st order conclusion for CV using half lives/gradients
AND rate at 3 minutes
AND determination of *k*

There is a well-developed line of reasoning which is clear and logically structured.

Level 2 (3–4 marks)
Reaches a conclusion using quantitative data from graph to correctly determine rate at 3 minutes
AND determination of *k*.
OR
Half- lives/gradient with 1st order conclusion for CV
AND determination of *k*
OR
determined rate **AND** half-life/first order for CV
OR
Attempts to determine rate, *k* and order for CV

There is a line of reasoning with some structure and supported by some evidence.

Level 1 (1–2 marks)

Reaches a simple conclusion using at least one piece of quantitative data from the graph, i.e.
Attempts to calculate rate at three minutes **OR** *k* **OR** links half lives to 1st order.3

There is an attempt at a logical structure with a reasoned conclusion from the evidence.

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<td>6</td>
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Indicative scientific points may include:

Care: ALLOW the use of **ECF** for values obtained from a previously, incorrectly, calculated value.

ALLOW minor slips as we are looking for a holistic approach to LoR marking.

<table>
<tr><th></th><th>Minutes</th><th>Seconds</th></tr>
<tr><td>Half life values</td><td>2.4 to 2.6 min</td><td>144 to 156 s</td></tr>
<tr><td>Rate at three minutes</td><td>(-) (1.5 to 1.8) $\times 10^{-8}$ mol dm^{-3} min^{-1}</td><td>(-) (2.5 to 3.0)$\times 10^{-10}$ mol dm^{-3} s^{-1}</td></tr>
<tr><td>Value of *k*</td><td>0.24 to 0.30 min^{-1}</td><td>(4.0 to 5.0) x 10^{-3} s^{-1}</td></tr>
<tr><td>Units of *k*</td><td>min^{-1}</td><td>s^{-1}</td></tr>
</table>

Examples of the communication statement being met would typically include:

- For L1 and L2: full working on the graph and/or appropriate units for calculated values.
- For L3: full working on the graph and appropriate units for calculated values.

If time has been measured in minutes
(see below for values using seconds).

Indicative scientific points may include:

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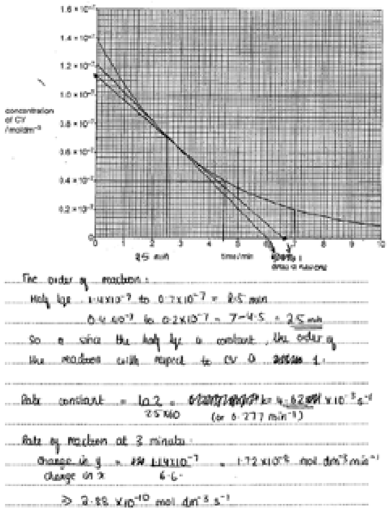
			0 mark *No response worthy of credit*		**Evidence for 1st order** 1st order clearly linked to half-life **OR** 2 gradients: **Half life** Half- life shown on graph Half- life range 2.4 to 2.6 min Two ‘constant’ half lives **OR Two gradients → two rates** 2 tangents shown on graph at *c* and *c*/2 This could include $c = 0.61 \times 10^{-7}$ mol dm^{-3} ($t = 3$ min) Gradient at *c*/2 is half gradient at *c* e.g. $c = 0.8 \times 10^{-7}$ mol dm^{-3}, gradient = 2.2×10^{-8} (mol dm^{-3} min^{-1}) **AND** $c = 0.4 \times 10^{-7}$ mol dm^{-3}, gradient = 1.1×10^{-8} (mol dm^{-3} min^{-1}) For chosen method, conclude that the reaction is 1st order wrt CV. **Rate at three minutes** Tangent shown on graph as line at $t = 3$ min Gradient in range: $(1.5 - 1.8) \times 10^{-8}$ rate as gradient with units: mol dm^{-3} min^{-1} **OR** $k = \frac{\ln 2}{t_{1/2}} = 0.28 \text{min}^{-1}$ And k substituted into rate equation. e.g. Rate = *k* [CV] Rate = $0.277 \times 0.61 \times 10^{-7}$ = 1.7×10^{-8} mol dm^{-3} min^{-1} **Determination of *k*** *k* clearly linked to rate **OR** half-life: e.g. $k = \frac{\text{rate}}{[\text{CV}]} = \frac{1.75 \times 10^{-8}}{0.62 \times 10^{-7}} = 0.28$ *k* in range: 0.24 - 0.30 min^{-1}

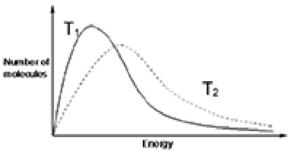
					OR e.g. $k = \frac{\ln 2}{t½} = 0.28\ \text{min}^{-1}$ **Units of *k***: min^{-1} **If time has been measured in seconds:** **Evidence for 1st order** 1st order clearly linked to half-life **OR** 2 gradients: **Half life** Half- life shown on graph Half- life range 144 to 156 s Two 'constant' half lives **OR Two gradients → two rates** 2 tangents shown on graph at *c* and *c*/2 This could include $c = 0.6 \times 10^{-8}$ mol dm^{-3} ($t = 3$ min) Gradient at *c*/2 is half gradient at *c* e.g. $c = 0.8 \times 10^{-7}$ mol dm^{-3}, gradient = 3.7×10^{-10} mol dm^{-3} s^{-1} **AND** $c = 0.4 \times 10^{-7}$ mol dm^{-3}, gradient = 1.8×10^{-10} mol dm^{-3} s^{-1} For chosen method, conclude that the reaction is 1st order wrt CV. **Rate at 180 seconds** Gradient in range (2.5 to 3.0) $\times 10^{-10}$ rate as gradient with units: mol dm^{-3} s^{-1} **OR** $k = \frac{\ln 2}{t½} = 4.6 \times 10^{-3}\ \text{s}^{-1}$ And *k* substituted into rate equation. e.g. Rate = *k* [CV] Rate = $0.00462 \times 0.61 \times 10^{-7}$ = 2.8×10^{-10} mol dm^{-3} s^{-1}

					<u>**Determination of *k***</u> *k* clearly linked to rate **OR** half-life: e.g. $k = \frac{\text{rate}}{[\text{CV}]} = \frac{2.75 \times 10^{-10}}{0.62 \times 10^{-7}} = 4.4 \times 10^{-3}\ \text{s}^{-1}$ *k* in range (4.0 to 4.8) x 10^{-3} s^{-1} **OR** e.g $k = \frac{\ln 2}{t_{½}} = 0.28\ \text{min}^{-1}$ **OR** 4.6 x 10^{-3} s^{-1} **Units of *k*:** s^{-1} <u>**Examiner's Comments**</u> The first Level of Response question in the paper was answered well with the higher-attaining candidates on the paper scoring full marks. These students started with a nice clear analysis of the half-life, referring to labelled sections of the graph, then went on to calculate the rate from a well-drawn tangent with correct indices and were careful to write down the correct units. Then used the rate equation to calculate K and get the correct units. Almost all candidates were able to conclude that it was first order for CV. Most used the half-life approach with others comparing two gradients. Candidates should be advised, especially in LoR questions, that the conclusion needs a clear link to the data. The gradient at 3 minutes was done well and the candidates used the appropriate scale from the graph in their calculations. Clarity of communication does require indication of what is being calculated and how the numbers were obtained. This would allow an initial rate versus a rate at three minutes to be distinguished. Units were particularly important in this question as some candidates used minutes from the graph while others converted time into seconds. A common error was to state the wrong units or leave them out altogether.

					Most candidates used the rate equation to calculate K and get the correct units. A few approached the value by using $k = \frac{\ln 2}{t_{½}}$. Error carried forward was given for those with incorrect half-lives or rate value. Candidate errors arose from graph readings that caused rate to be wrong, errors in concentrations used in rate or K calculation, and badly drawn tangents causing the rate to be out of tolerance. Some candidates tried to adjust the concentrations as if conducting mole calculations or take the rate from two points on the graph. Exemplar 2  The order of reaction : Half life 1.4×10^{-7} to 0.7×10^{-7} = 2.5 min 0.4×10^{-7} to 0.2×10^{-7} = 7 − 4.5 = 2.5 min So as since the half life is constant, the order of the reaction with respect to CY is ~~[illegible]~~ 1. Rate constant = $\frac{\ln 2}{2.5 \times 60}$ = ~~[illegible]~~ k = 4.62×10^{-3} s⁻¹ (or 0.277 min⁻¹) Rate of reaction at 3 minutes: $\frac{\text{change in } y}{\text{change in } x} = \frac{1.14 \times 10^{-7}}{6.6}$ = 1.72×10^{-8} mol dm⁻³ min⁻¹ ⇒ 2.88×10^{-10} mol dm⁻³ s⁻¹ The candidate scored Level 3. The graph was clearly used to obtain half-lives and gradients. This was communicated on the answer lines, showing calculations and units. **OCR support** M3 section of the Maths Skills handbook contains useful information on use of graphs in chemistry, including M3.5 on drawing and using the slope of the tangent to a curve as a measure of a rate of change: Teach Cambridge (ocr.org.uk)
			Total	**6**	

2			Equation for Step 1 $F_2 + NO_2 \rightarrow F + NO_2F$ ✓ Rate Equation Rate = k $[F_2][NO_2]$ ✓	2	Mark independently **ALLOW** rate = k $[NO_2][F_2]$ Care – k must be included. **Examiner's Comments** Candidates found this question more challenging. Many candidates deduced Step 1 and then went on to state the rate equation. A few candidates incorrectly deduced F rather than F_2 and/or obtained a second order for NO_2
			Total	**2**	
3			**B**	1	**ALLOW** +133 (correct numerical answer) **Examiner's Comments** The correct answer was B. Candidates generally find the use and manipulation of the Arrhenius equation challenging. Focus was need on the unit conversion when using R (**J**mol^{-1}K^{-1}) for the gradient and activation energy (**kJ** mol^{-1}). This led to a few candidates selecting D. It is worth reminding candidates that the two forms of this equation are given on the data sheet.
			Total	**1**	
4			**D**	1	**Examiner's Comments** The correct answer was D. Candidates performed well on this question with incorrect answers rarely seen. A minority of candidates confused rate-concentration graphs with concentration-time graphs.
			Total	**1**	
5			**FIRST CHECK THE ANSWER ON ANSWER LINE** **If range = 4.4×10^{-5} – 4.5×10^{-5} (kJ mol^{-1}) award 3 marks** ---	3 (AO 3.1 ×3)	Calculator: 0.0316227766 **ALLOW** $10^{-1.5}$

			$[H+] = 10^{-1.50}$ **OR** 0.0316 … **OR** 0.032 mol dm^{-3} ✓ **1 mark** ***THEN 2 APPROACHES: EITHER:*** **Factor that concentration changes by 1 mark** Factor = $\frac{0.0316.....}{0.680}$ = 0.0465… times **OR** $\frac{0.680}{0.0316.....}$ = 21.5..... times ✓ **Initial rate with diluted acid 1 mark** = 0.0465… × 9.52 × 10^{-4} **OR** $\frac{9.52 \times 10^{-4}}{21.5.....}$ = 4.43 × 10–5 (mol dm^{-3} s^{-1}) ✓ ***OR:*** **Rate α concentration (1st order) 1 mark** $k = \frac{rate}{[HCl]} = \frac{9.52 \times 10^{-4}}{0.680} = 1.4(0) \times 10^{-3}$ **OR** Constant = $\frac{0.680}{9.52 \times 10^{-4}}$ = 714.2857… ✓ **Initial rate with diluted acid** = 1.4(0) × 10^{-3} × 0.0316 … **OR** $\frac{0.0316...}{714.2857...}$ = 4.43 × 10^{-5} (mol dm^{-3} s^{-1}) ✓		**ECF** possible from incorrect $[H^+]$ From unrounded [H+], Calculator: 0.04650408324 **From $[H^+]$ = 0.032**, Factor = 21.25 From unrounded $[H^+]$, Calculator = 4.427188724 × 10^{-5} **From $[H^+]$ = 0.032**, rate = 4.48 × 10^{-5} --- **ECF** possible from incorrect $[H^+]$ **DO NOT ALLOW ECF** unless derived from concentration and rate **SUMMARY** **M1 $[H^+]$ 0.0316…. OR 0.032 1 mark** **M2 Working 0.0465 OR 21.5 OR 1.4 × 10^{-3} OR 714 1 mark** **M3 Initial rate Range: 4.4 × 10^{-5} – 4.5 × 10^{-5} 2 SF or more** *depends on intermediate rounding* ***CHECK*** **1 mark** **<u>Examiner's Comments</u>** The marks for this calculation were much more polarised than the calculation in Question 2 (a). Many candidates worked through the problem methodically to get an answer for the initial rate between 4.4 × 10^{-5} and 4.5 × 10^{-5} mol dm^{-3} s^{-1}. A substantial number of candidates worked out $[H^+]$ using 10^{-pH} for 1 mark but were then unable to progress any further. This was a novel calculation, requiring candidates to develop their own strategy for its solution. Candidates who found this question difficult often attempted a solution based on stock weak acid calculation, using $[H^+]^2/[HA]$.
			Total	**3**	

6			**A**	1(AO1.2)	**Examiner's Comments** This question was quite well answered with many candidates realising that for a first order reaction, determination of the rate constant, k, from the constant half-life, $t^{1/2}$, they should use the relationship: k = ln $2/t^{1/2}$. A common error was option B, as many used 1/t used for ln $2/t^{1/2}$.
			Total	**1**	
7	a	i	 Axes labelled (number of) molecules **AND** (kinetic) energy **AND** correct drawing of a Boltzmann distribution i.e. curve must start within the first small square nearest to the origin **AND** must not touch the x-axis at high energy ✓ Drawing of correct Boltzmann distributions at **two** different temperatures with one termperature identified. ✓ (At higher temperature) **more** molecules/particles have energy above activation energy ✓	3 (AO1.1×3)	**ALLOW** particles on the y-axis **DO NOT ALLOW** atoms on y-axis **DO NOT ALLOW** enthalpy on x-axis **DO NOT ALLOW** an increase of more than one small square at the high energy end of the curve i.e. allow a small inflection **ALLOW** T2 as 'higher termperature' Maximum of curve for higher temperature must be to the right **AND** lower than the maximum of the curve for lower temperature Lines can only cross once **ALLOW ORA** if states the effect when the temperature is lower **ALLOW** has enough energy to react **ALLOW** E_a shown on graph **AND** greater area under the curve to the right of E_a

					DO NOT ALLOW lowers E_a **DO NOT ALLOW** atoms for molecules **IGNORE** (more) successful collisions **<u>Examiner's Comments</u>** Almost all candidates produced a graph which showed the correct shape curve, although they sometimes incorrectly identified the quantities on the axes, e.g. rate versus time. Those who produced an incorrect diagram were able to discuss 'more' particles reaching the activation energy threshold. A few limited their answer to discussing successful collisions. Candidates needed to identify which curve was the higher temperature and to make sure that the curves did intersect more than once.
		ii	**Orders** **(Expt 1+2)** When [NO] × 2, rate × 4 **AND** 2nd order with respect to NO ✓ **(Expt 2+3)** When [NO] × 2 **AND** [CO] × 4, rate × 16 **AND** 1st order with respect to CO ✓ **Rate Equation** rate = k $[NO]^2[CO]$ ✓	5 (AO3.1) (AO3.2) (AO2.6) (AO1.2×2)	**ALLOW ORA** throughout e.g. expt 2+1 [NO] halves, rate quarters etc. **IGNORE** [CO] constant **ALLOW** if working shown with the table. **ALLOW** if seen in 2 steps i.e. When [NO] × 2, rate x 4 AND [CO] × 4, intermediate rate × 4. **ALLOW** comparing **Expt 1+3** When [NO] × 4 AND [CO] × 4, rate × 64 **AND** 1st order with respect to CO **ALLOW ECF** from incorrect orders **ALLOW** rate = k $[NO]^2[CO]^1$ **ALLOW** rate equation with correct

			Value of *k* $(k = \frac{1.85 \times 10^{-4}}{(2.75 \times 10^{-4})^2 \times 7.25 \times 10^{-4}})$ **= 3.37 × 10^6** ✓ **Units of *k*** $dm^6\ mol^{-2}\ s^{-1}$ ✓		numbers substituted **ALLOW** 3.36 x 10^6 from the use of Expt 3 **IGNORE** errors in working out –the mark is for the value **ALLOW** 3 SF upto the calculator value 3374180.678 OR 3.374180678 x10^6 **IGNORE** rounding errors past **3SF** **ALLOW** units in any order e.g. $mol^{-2}\ dm^6\ s^{-1}$ **ALLOW ECF** from incorrect rate equation. **Common errors** **4 marks (including units)** 4.65 x 10^9 $mol^{-3}\ dm^9\ s^{-1}$ (use of 2nd order with respect to CO) 2446 $mol^{-1}\ dm^3\ s^{-1}$ (use of zero order wrt CO) **<u>Examiner's Comments</u>** Many candidates were able to explain clearly the second order dependence on [NO] but many found it more challenging to identify and explain the first order relationship for [CO], where the candidate had to consider the second order dependence on [NO] to work out the effect on rate for the change in [CO]. Most gave a rate equation of the correct format based on the orders they had stated, and worked out a value for k. Although some did not determine the correct units, there was an encouraging number who managed this either from memory or by cancelling. The most common error was not including s^{-1}
	b		$2NO_2$ **<u>only</u>** on LHS of step 1 ✓ Rest of mechanism ✓	2(AO3.1×2)	M2 dependent on M1 ***Examples:***

					Step 1 : $2NO_2 \rightarrow NO + NO_3$ *Step 2* : $NO_3 + CO \rightarrow NO_2 + CO_2$ **OR** *Step 1* : $2NO_2 \rightarrow N_2O_4$ *Step 2* : $N_2O_4 + CO \rightarrow NO + NO_2 + CO_2$ **OR** *Step 1* : $2NO_2 \rightarrow N_2 + 2O_2$ *Step 2* : $N_2 + 2O_2 + CO \rightarrow NO + NO_2 + CO_2$ **OR** *Step 1* : $2NO_2 \rightarrow 2NO + O_2$ *Step 2* : $NO + O_2 + CO \rightarrow NO_2 + CO_2$ **Examiner's Comments** Many candidates recognised the need for $2NO_2$ in the first step, with slightly less then adding an appropriate second step. Errors included unbalanced species and unbalanced charges. A wide range of suggested possible mechanisms were seen, including several which led to multiple correct versions of the overall equation. Both balanced equations needed to combine to form the overall equation. However, a few inventive candidates gave a first step of $NO_2 + NO_2 \rightarrow 2NO_2$, followed by the full balanced equation for the second step – this was not given marks.
			Total	**10**	
8			**At 90 °C**/higher temperature • Faster rate **AND** more frequent collisions ✓ • More particles have the activation energy/E_a or greater ✓ • $[Co(H_2O)_6]^{2+}$ is lower ✓ • (forward reaction) ΔH -ve **OR** exothermic ✓	4 (1 ×AO2.7) (1 ×AO1.2) (1 ×AO2.3) (1 ×AO1.2)	**ORA for 50 °C** **IGNORE** more successful collisions **ALLOW** more molecules have enough energy to react **ALLOW** atoms/molecules/ions **ALLOW** decreases **Examiner's Comments** This question asked candidates to explain the different rates from a novel experiment carried out at 50°C and 90°C, and to predict the ΔH sign for the forward reaction. Candidate explanations for the rates were often

					superficial, solely in terms of greater energy at 90°C. Many responses referred neither to the different frequency of collisions nor the greater number of particles exceeding the activation energy at 90°C. Most candidates predicted that Δ*H* would have a negative sign. Candidates were expected to link the evidence from the absorbance data in the graph to less $[Co(H_2O)_6]^{2+}$ being present at 90°C. When experimental information has been presented, candidates are advised to look for the evidence responsible in their explanations.
			Total	**4**	