

Past-paper walk-through

Introduction to Rate Law ■ 5.2

eXercise

Questions in this set

- 2025 Q2
- 2023 Q3
- 2022 Q5
- 2019 Q6
- 2017 Q2
- 2016 Q5
- 2015 Q5
- 2014 Q7

Reading the mark scheme

- **B1** a mark that stands on its own – the point is either made or not.
- **M1** a *method* mark: the right approach, even if the number is wrong.
- **A1** an *answer* mark, and it usually needs its M mark first.
- **C1** a working mark on the way to the answer.
- **//** separates answers the examiner accepts equally.
- **ecf** = error carried forward: a later part is marked on your own earlier answer.
- **owtte** = “or words to that effect” – the wording need not match.

Question 2

2025 ■ Q2

Answer the following questions about ascorbic acid (vitamin C).

(a) A student combusts a sample of ascorbic acid, $C_xH_yO_x$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O .

(a)(i) Calculate the number of moles of H_2O produced.

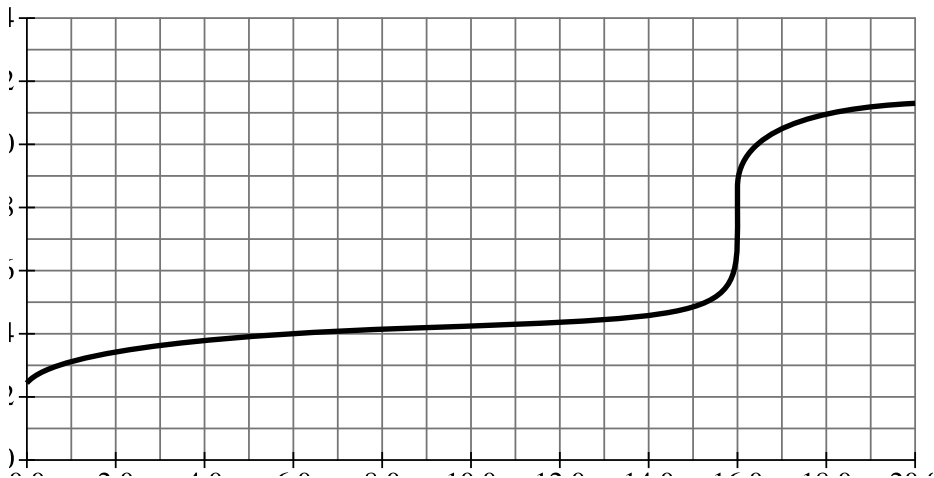
(a)(ii) The mole ratio of carbon (C) to oxygen (O) is 1:1 in ascorbic acid. Based on this information and your answer to part A (i), determine the empirical formula of ascorbic acid.

Question 2

Trial	[HAsc] (M)	$[I_3^-]$ (M)	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

- The rate law for the reaction is $rate = k[HAsc][I_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[HAsc]$.
- Calculate the value of the rate constant k for the reaction. Include units with your

Question 2

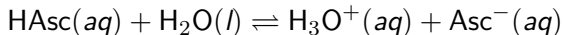


Question 2

2025 ■ Q2

Answer the following questions about ascorbic acid (vitamin C).

(b) Ascorbic acid, $\text{HAsc}(aq)$, acts as a weak acid, as shown in the equation.



The following titration curve was produced when a 10.0 mL sample of $\text{HAsc}(aq)$ was titrated using 0.0550 M $\text{NaOH}(aq)$.

[Titration curve graph: x-axis "Volume of 0.0550 M NaOH Added (mL)" from 0.0 to 20.0 in increments of 2.0; y-axis "pH" from 0 to 14 in increments of 2. The curve starts at about (0.0, 2.6), rises gradually and levels into a broad buffer region around pH 4 from about 2 mL to 14 mL, has a small inflection/bump near (14.0, 4.5)-(15.0,

Question 2

5.2), then rises steeply (equivalence point) through the region 15.0-16.5 mL up to about pH 10.5, then levels off gradually approaching about (20.0, 11.3).]

(b)(i) Calculate the molar concentration of the ascorbic acid solution.

(b)(ii) From the titration curve, determine the approximate pK_a of ascorbic acid.

(b)(iii) What is the value of the ratio $\frac{[Asc^-]}{[HAsc]}$ when the pH of the solution is 4.7?

Question 2

Answer the following questions about ascorbic acid (vitamin C).

(c) Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^- , as represented by the following equation.



The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^- , producing the following data.

Trial	[HAsc] (<i>M</i>)	[I ₃ ⁻] (<i>M</i>)	Initial Rate of DHAsc Formation (<i>M/s</i>)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

Question 2

- (c)(i)** The rate law for the reaction is $rate = k[\text{HAsc}][\text{I}_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[\text{HAsc}]$.
- (c)(ii)** Calculate the value of the rate constant, k , for the reaction. Include units with your answer.

Question 2

2025 ■ Q2

Answer the following questions about ascorbic acid (vitamin C).

(d) The triiodide ion, I_3^- , is significantly more soluble in water than elemental iodine, I_2 , is. Identify an intermolecular force between I_3^- and water that is ****not**** present between I_2 and water, which could explain the difference in solubility. Lewis diagrams for I_2 and I_3^- are provided.

[Lewis structures: I_2 shown as two iodine atoms singly bonded together, each with three lone pairs. I_3^- shown in brackets with an overall negative charge, as three iodine atoms in a row connected by single bonds (I—I—I), each terminal iodine with three lone pairs and the central iodine with two lone pairs.]

Solution 2

(a)

Mark scheme

- No separate response required — this is the context/stem describing the combustion of ascorbic acid ($C_xH_yO_x$) producing 0.2400 mol CO_2 and 2.883 g H_2O , which parts (i) and (ii) below use.

(a)(i)

Mark scheme

- moles $H_2O = 2.883 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.1600 \text{ mol } H_2O$.

Solution 2

(a)(ii)

Mark scheme

- moles H = $0.1600 \text{ mol H}_2\text{O} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.3200 \text{ mol H}$ (this step may be left implicit). Using $\text{mol C} = 0.2400 \text{ mol CO}_2 \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.2400 \text{ mol C}$ and the given 1:1 C:O ratio:
 $x : y : z = (\text{mol C}) : (\text{mol H}) : (\text{mol O}) = 0.2400 : 0.3200 : 0.2400 = 3 : 4 : 3$.
Therefore the empirical formula of ascorbic acid is $\text{C}_3\text{H}_4\text{O}_3$.

Solution 2

(b)

Mark scheme

- No separate response required — this is the context/stem describing HAsc(aq) as a weak acid and presenting the titration curve (10.0 mL HAsc titrated with 0.0550 M NaOH) that parts (i)–(iii) below refer to.

Solution 2

(b)(i)

Mark scheme

- Reading the volume of NaOH at the equivalence point (16.0 mL) from the curve:

$$0.0160 \text{ L NaOH} \times \frac{0.0550 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol HAsc}}{1 \text{ mol NaOH}} = 8.80 \times 10^{-4} \text{ mol HAsc.}$$

$$\text{Molarity} = \frac{8.80 \times 10^{-4} \text{ mol HAsc}}{0.0100 \text{ L}} = 0.0880 \text{ M HAsc.}$$

Solution 2

(b)(ii)

Mark scheme

- From the titration curve, the pK_a (the pH at the half-equivalence point) is approximately 4.1 (acceptable range 4.0–4.3).

Solution 2

(b)(iii)

Mark scheme

- Using the Henderson–Hasselbalch equation: $\text{pH} = \text{p}K_a + \log \left(\frac{[\text{Asc}^-]}{[\text{HAsc}]} \right)$.

$$4.7 = 4.1 + \log \left(\frac{[\text{Asc}^-]}{[\text{HAsc}]} \right), \text{ so } \frac{[\text{Asc}^-]}{[\text{HAsc}]} = 10^{0.6} = 4.0.$$

Solution 2

(c)

Mark scheme

- No separate response required — this is the context/stem describing the reaction of ascorbic acid (HAsc) with triiodide (I_3^-) to form DHAsc, and the table of three trials' initial concentrations and rates, that parts (i) and (ii) below use.

Solution 2

(c)(i)

Mark scheme

- Comparing trials 1 and 3: $\frac{4.914 \times 10^{-4}}{2.457 \times 10^{-4}} = \left(\frac{0.900}{0.450}\right)^a$, thus $a = 1$. The rate doubles when [HAsc] is doubled while $[I_3^-]$ is held constant, indicating the reaction is first order with respect to [HAsc].

Solution 2

(c)(ii)

Mark scheme

- Using $\text{rate} = k[\text{HAsc}][\text{I}_3^-]$ and trial 1 data:

$$k = \frac{\text{rate}}{[\text{HAsc}][\text{I}_3^-]} = \frac{2.457 \times 10^{-4} \text{ M/s}}{(0.450 \text{ M})(1.200 \text{ M})} = 4.55 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}. \text{ Units: } \text{M}^{-1}\text{s}^{-1}.$$

Solution 2

(d)

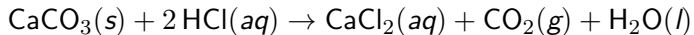
Mark scheme

- Ion-dipole attractions are present between I_3^- ions and water but not between I_2 molecules and water. Because I_3^- is a charged ion, it attracts the polar water molecules via ion-dipole forces, giving it much greater solubility than the neutral, nonpolar I_2 .

Question 3

2023 ■ Q3

Answer the following questions about an experiment in which $\text{CaCO}_3(s)$ is combined with $\text{HCl}(aq)$, represented by the following balanced equation.



(a) Write the balanced net ionic equation for the reaction.

Question 3

2023 ■ Q3

Answer the following questions about an experiment in which $\text{CaCO}_3(s)$ is combined with $\text{HCl}(aq)$, represented by the following balanced equation.



(b) A student performs an investigation to study factors that affect the rate of the reaction. In each trial the student combines 50.0 mL of $\text{HCl}(aq)$ at 21.2°C with 1.00 g of $\text{CaCO}_3(s)$ and measures the time required for the reaction to go to completion. The data are given in the following table.

Trial	Concentration of $\text{HCl}(aq)$ (M)	Particle Size of $\text{CaCO}_3(s)$	Time of Reaction (s)
1	1.00	Fine powder	67
2	1.00	Small chunks	112
3			

Question 3

1.00		Large chunk		342			4		3.00		Fine powder		22			5		3.00		Small chunks		227
		6		3.00		Large chunk		114														

The student correctly identifies that trial 5 is inconsistent with the other trials. Explain why the student's claim is correct using the data in the table.

Question 3

2023 ■ Q3

Answer the following questions about an experiment in which $\text{CaCO}_3(s)$ is combined with $\text{HCl}(aq)$, represented by the following balanced equation.



(c) Based on the reaction conditions and the collisions that occur between particles, explain the reason for the difference in the reaction times for trial 2 and trial 3.

Question 3

2023 ■ Q3

Answer the following questions about an experiment in which $\text{CaCO}_3(s)$ is combined with $\text{HCl}(aq)$, represented by the following balanced equation.



(d) The student claims that the reaction is zero order with respect to $\text{HCl}(aq)$. Do you agree or disagree with the student's claim? Justify your answer using the student's data.

Question 3

2023 ■ Q3

Answer the following questions about an experiment in which $\text{CaCO}_3(s)$ is combined with $\text{HCl}(aq)$, represented by the following balanced equation.



(e) The $\text{HCl}(aq)$ was present in excess in all trials of the experiment. Determine the molarity of the $\text{HCl}(aq)$ in the beaker after the reaction is complete in trial 2. Assume that the volume of the mixture remains constant at 50.0 mL throughout the trial. (The molar mass of CaCO_3 is 100.09 g/mol.)

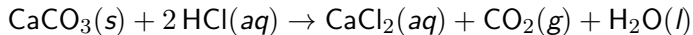
Question 3

2023 ■ Q3

Answer the following questions about an experiment in which $\text{CaCO}_3(s)$ is combined with $\text{HCl}(aq)$, represented by the following balanced equation.



(f)



In order to measure the enthalpy of the reaction shown, the student repeats trial 1 by mixing 50.0 mL of $\text{HCl}(aq)$ with 1.00 g of $\text{CaCO}_3(s)$ using a coffee cup calorimeter. The student records the temperature of the system every 20 seconds. The data are given in the following table.

Question 3

Time (s)	Measured Temperature of Solution ($^{\circ}\text{C}$)	—	—	0	21.20	20	21.51
40	21.70	60	21.85	80	21.90	100	21.90

Is the reaction endothermic or exothermic? Justify your answer using the information in the table.

Question 3

2023 ■ Q3

Answer the following questions about an experiment in which $\text{CaCO}_3(s)$ is combined with $\text{HCl}(aq)$, represented by the following balanced equation.



(g)(i) Based on the experimental data, the mass of the system is 51.0 g, and the specific heat of the reaction mixture is $4.0 \text{ J}/(\text{g} \cdot ^\circ\text{C})$.

Calculate the magnitude of heat transfer, q , in joules.

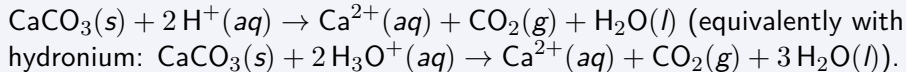
(g)(ii) Calculate the enthalpy of reaction in units of $\text{kJ}/\text{mol}_{\text{rxn}}$. Include the algebraic sign on your answer.

Solution 3

(a)

Mark scheme

- Balanced net ionic equation:



State symbols not required.

Solution 3

(b)

Mark scheme

- Accept either explanation: (1) Even though $[\text{HCl}]$ is greater in trial 5 than trial 2, the reaction time is significantly longer; trials 2 and 5 are otherwise identical, and the trend from trials 1 and 4 shows that a higher $[\text{HCl}]$ gives a shorter reaction time, so concentration alone cannot explain trial 5 — particle size must be the cause. (2) The reaction time in trial 5 (small chunks) is longer than in trial 6 (large chunks), even though trials 5 and 6 are otherwise identical; the trend from trials 1, 2, and 3 shows that larger chunks of solid give a longer reaction time.

Solution 3

(c)

Mark scheme

- The reaction time in trial 2 is shorter than in trial 3 because the calcium carbonate in trial 2 has a larger surface area, meaning more CaCO_3 particles are exposed to H^+ particles in solution (1 point). A larger interface between the two reacting substances means more particle collisions occur per unit time, giving a higher frequency of successful collisions in which particles react to form products, i.e. a higher reaction rate (1 point).

Solution 3

(d)

Mark scheme

- Disagree. Accept either justification: (1) If the reaction were zeroth order with respect to HCl, changing $[\text{HCl}]$ would not affect the reaction rate, so reaction time would be the same for trials differing only in $[\text{HCl}]$ — but the data for trials 1 and 4 (and likewise 3 and 6) show that changing $[\text{HCl}]$ significantly alters the time of reaction. (2) The reaction appears first order, not zeroth order, with respect to $[\text{HCl}]$: tripling $[\text{HCl}]$ results in a reaction time that is $1/3$ of that when $[\text{HCl}] = 1.00 \text{ M}$, meaning the rate has also tripled, indicating a first-order process.

Solution 3

(e) Mark scheme

- Moles of HCl reacted: $1.00 \text{ g CaCO}_3 \times \frac{1 \text{ mol}}{100.09 \text{ g}} = 0.00999 \text{ mol CaCO}_3$;
 $0.00999 \text{ mol CaCO}_3 \times \frac{2 \text{ mol HCl}}{1 \text{ mol CaCO}_3} = 0.0200 \text{ mol HCl reacted (1 point).}$
Remaining [HCl]: initial HCl = $0.0500 \text{ L} \times 1.00 \text{ mol/L} = 0.0500 \text{ mol}$;
 $0.0500 - 0.0200 = 0.0300 \text{ mol remaining}$; $\frac{0.0300 \text{ mol}}{0.0500 \text{ L}} = 0.600 \text{ M HCl remaining}$
(1 point).

Solution 3

(f)

Mark scheme

- Exothermic. The solution temperature increases as the reaction proceeds (per the calorimeter data), indicating heat is released to the surroundings.

Solution 3

(g)(i)

Mark scheme

■ $q_{surr} = mc\Delta T = (51.0 \text{ g}) \left(4.0 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}\right) (21.90^{\circ}\text{C} - 21.20^{\circ}\text{C}) = 140 \text{ J}$ (sign not required).

Solution 3

(g)(ii)

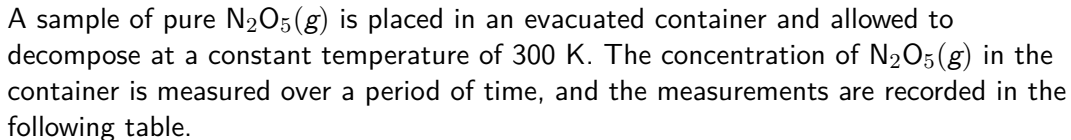
Mark scheme

■ $q_{\text{sys}} = -q_{\text{surr}} = -140 \text{ J} = -0.14 \text{ kJ}$; moles reacted

$$= 1.00 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \times \frac{1 \text{ mol}_{\text{rxn}}}{1 \text{ mol CaCO}_3} = 0.00999 \text{ mol}_{\text{rxn}};$$
$$\Delta H_{\text{rxn}}^{\circ} = \frac{-0.14 \text{ kJ}}{0.00999 \text{ mol}_{\text{rxn}}} = -14 \text{ kJ/mol}_{\text{rxn}} \text{ (include the algebraic sign).}$$

Question 5

The following equation represents the decomposition of N_2O_5 , for which the rate law is $\text{rate} = k[\text{N}_2\text{O}_5]$.

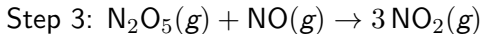
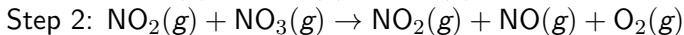
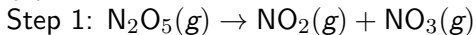


Time (hr)	[N ₂ O ₅] (<i>M</i>)	—	—	0	0.160	1.67	0.0800	3.33	0.0400	5.00
0.0200										

Question 5

(a) Determine the value of the rate constant, k , for the reaction. Include units in your answer.

(b) The following mechanism is proposed for the decomposition of $\text{N}_2\text{O}_5(g)$.



Identify which step of the proposed mechanism (1, 2, or 3) is the rate-determining step. Justify your answer in terms of the rate law given.

(c) If this experiment was repeated at the same temperature but with twice the initial concentration of N_2O_5 , would the value of k increase, decrease, or remain the same? Explain your reasoning.

Solution 5

(a)

Mark scheme

- Calculated value of the rate constant k (1 point), by any valid method: $k = 0.693/t_{1/2} = 0.693/1.67 \text{ hr} = 0.415 \text{ hr}^{-1}$ (or equivalently, using the integrated first-order law $k = (\ln[A]_0 - \ln[A]_t)/t$ with any pair of data points: $\ln(0.160) - \ln(0.0800)$ over $1.67 \text{ hr} = 0.415 \text{ hr}^{-1}$; $\ln(0.160) - \ln(0.0400)$ over $3.33 \text{ hr} = 0.416 \text{ hr}^{-1}$; or $\ln(0.160) - \ln(0.0200)$ over $5.00 \text{ hr} = 0.416 \text{ hr}^{-1}$). Correct units (1 point): hr^{-1} , consistent with the calculated value.

Solution 5

(b)

Mark scheme

- Step 1 is the rate-determining step. The rate law of elementary step 1 is rate = $k[\text{N}_2\text{O}_5]$, which is consistent with the first-order kinetics of the given overall rate law.

Solution 5

(c)

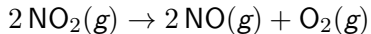
Mark scheme

- The rate constant k would remain the same. k is independent of concentration and will remain the same at constant temperature.

Question 6

2019 ■ Q6

Nitrogen dioxide, $\text{NO}_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $\text{NO}_2(g)$ decomposes according to the equation below.



The concentration of a sample of $\text{NO}_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.

[Graph 1: $[\text{NO}_2]$ (mol/L, y-axis 0.00 to 0.08) vs. Time (s, x-axis 0 to 300); data points approximately: (0, 0.075), (60, 0.018), (120, 0.010), (180, 0.008), (240, 0.007), (300, 0.005) — a decaying curve]

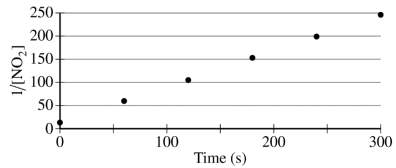
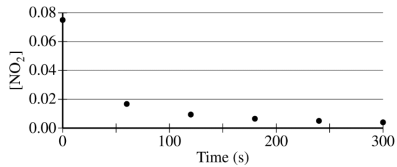
Question 6

[Graph 2: $1/[\text{NO}_2]$ (y-axis 0 to 250) vs. Time (s, x-axis 0 to 300); data points approximately: (0, 13), (60, 58), (120, 105), (180, 152), (240, 200), (300, 245) — an approximately straight increasing line]

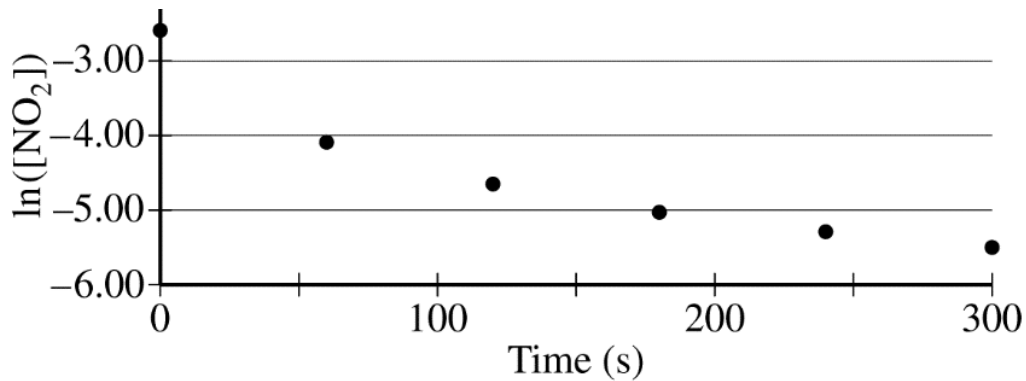
[Graph 3: $\ln([\text{NO}_2])$ (y-axis -6.00 to -2.00) vs. Time (s, x-axis 0 to 300); data points approximately: (0, -2.6), (60, -4.1), (120, -4.6), (180, -5.05), (240, -5.2), (300, -5.4) — a curved, decreasing, concave-up trend]

(a) Explain how the graphs indicate that the reaction is second order.

Question 6



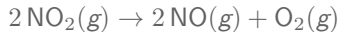
Question 6



Question 6

2019 ■ Q6

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Question 6

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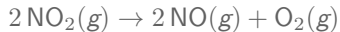
(b) Write the rate law for the decomposition of $\text{NO}_2(g)$.

Consider two possible mechanisms for the decomposition reaction.

Question 6

2019 ■ Q6

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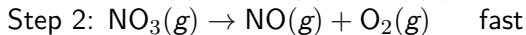
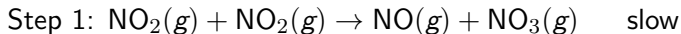
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Question 6

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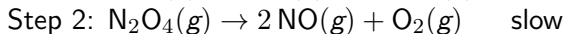
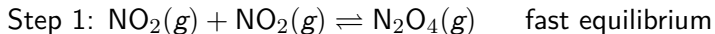
(c)(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I



(c)(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism II



Solution 6

(a)

Mark scheme

- The graph of $1/[\text{NO}_2]$ vs. time is linear, which is the diagnostic signature of a second-order reaction (integrated second-order rate law: $1/[A] = kt + 1/[A]_0$). 1 point for this correct explanation.

Solution 6

(b)

Mark scheme

- $\text{rate} = k[\text{NO}_2]^2$. 1 point for the correct second-order rate law, consistent with part (a).

Solution 6

(c)(i)

Mark scheme

- Yes, mechanism I is consistent. Step 1 ($\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$) is the slow step, so it is rate-determining. The rate law for this elementary step is $\text{rate} = k[\text{NO}_2][\text{NO}_2] = k[\text{NO}_2]^2$, which matches the second-order rate law from part (b). 1 point for the correct answer (yes) with this justification.

Solution 6

(c)(ii)

Mark scheme

- Yes, mechanism II is also consistent. Step 2 ($\text{N}_2\text{O}_4 \rightarrow 2\text{NO} + \text{O}_2$) is slow and rate-determining, giving rate $= k[\text{N}_2\text{O}_4]$. Since N_2O_4 is a reaction intermediate, it must be eliminated using the fast pre-equilibrium of step 1: $K_{\text{eq}} = [\text{N}_2\text{O}_4]/[\text{NO}_2]^2$, so $[\text{N}_2\text{O}_4] = K_{\text{eq}}[\text{NO}_2]^2$. Substituting into the rate law gives rate $= (k \cdot K_{\text{eq}})[\text{NO}_2]^2$, which is second order in $[\text{NO}_2]$ and consistent with part (b). 1 point for the correct answer (yes) with this justification.

Question 2

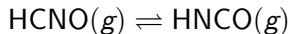
2017 ■ Q2

Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

[Two Lewis structures side by side: Left: $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (H bonded to C by a single bond, C triple-bonded to N, N bonded to O by a single bond, O has two lone pairs) Right: $\text{H}-\text{C}=\text{N}=\ddot{\text{O}}:$ (H bonded to C by a single bond, C double-bonded to N, N double-bonded to O, C has one lone pair, O has two lone pairs)]

Fulminic acid can convert to isocyanic acid according to the equation below.



fulminic acid

isocyanic acid

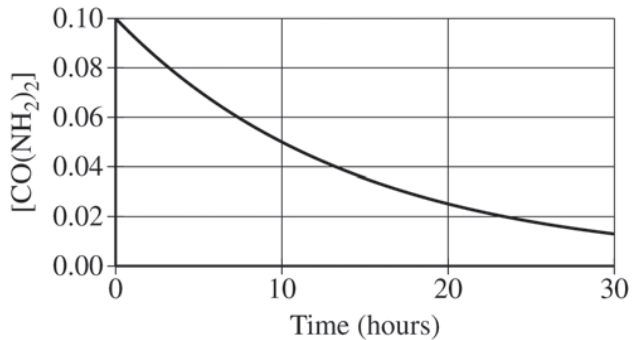
Question 2

| Fulminic Acid | Isocyanic Acid | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) |
 $\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Question 2

Time (hours)	$[\text{CO}(\text{NH}_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



Question 2

Fulminic Acid	Isocyanic Acid
$\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$	$\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$

Question 2

Bond	Enthalpy (kJ/mol)		Bond	Enthalpy (kJ/mol)		Bond	Enthalpy (kJ/mol)
N–O	201		C=N	615		H–C	413
C=O	745		C≡N	891		H–N	391

Question 2

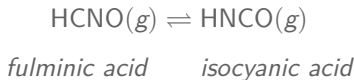
2017 ■ Q2

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Fulminic acid can convert to isocyanic acid according to the equation below.



| Fulminic Acid | Isocyanic Acid | $|\text{—}|\text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

Question 2

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of $\text{HCNO}(g)$ to form $\text{HNCO}(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
— — — — — —	N—O 201	C=N 615	H—C 413	C=O 745	C≡N 891
H—N 391					

Question 2

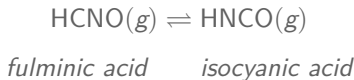
2017 ■ Q2

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Fulminic acid can convert to isocyanic acid according to the equation below.



| Fulminic Acid | Isocyanic Acid | $|\text{—}|\text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

Question 2

(c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.

Question 2

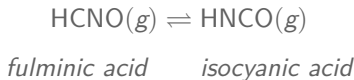
2017 ■ Q2

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Fulminic acid can convert to isocyanic acid according to the equation below.



| Fulminic Acid | Isocyanic Acid | $|\text{—}| \text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

Question 2

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

Question 2

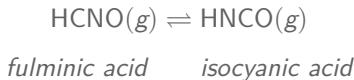
2017 ■ Q2

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Fulminic acid can convert to isocyanic acid according to the equation below.



| Fulminic Acid | Isocyanic Acid | $|\text{—}|\text{—}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

Question 2

(e)(i) The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\text{CO}(\text{NH}_2)_2$, represented below.



A student studying the decomposition reaction runs the reaction at 90°C . The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[\text{CO}(\text{NH}_2)_2]$	—	0	0.1000	5	0.0707	10	0.0500	15
0.0354	20	0.0250	25	0.0177	30	0.0125			

[Graph: y-axis $[\text{CO}(\text{NH}_2)_2]$ from 0.00 to 0.10 in increments of 0.02; x-axis "Time (hours)" from 0 to 30; a smooth exponential-decay curve starting at (0, 0.10) and decreasing to approximately (30, 0.0125), consistent with the data table above.]

Question 2

The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

Explain how the data support the student's proposed rate law.

(e)(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k . Include units with your answer.

Question 2

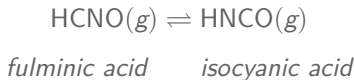
2017 ■ Q2

Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

[Two Lewis structures side by side: Left: $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (H bonded to C by a single bond, C triple-bonded to N, N bonded to O by a single bond, O has two lone pairs) Right: $\text{H}-\text{C}=\text{N}=\ddot{\text{O}}:$ (H bonded to C by a single bond, C double-bonded to N, N double-bonded to O, C has one lone pair, O has two lone pairs)]

Fulminic acid can convert to isocyanic acid according to the equation below.



| Fulminic Acid | Isocyanic Acid | $|\text{---}|$ | $\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$ (O has two lone pairs) | $\text{H}-\text{N}=\text{C}=\ddot{\text{O}}:$ (N has one lone pair, O has two lone pairs) |

Question 2

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $\text{OH}^{-}(\text{aq})$.

Solution 2

(a)

Mark scheme

- In the left diagram ($\text{H-C triple-bond N-O:}$ with O having 3 lone pairs... i.e. $\text{H-C}\equiv\text{N-O:}$), the C atom has a formal charge of 0 and the O atom has a formal charge of -1. In the right diagram ($\text{H-C(double bond)N(double bond)O:}$), the C atom has a formal charge of -1 and the O atom has a formal charge of 0. The diagram on the left is the better representation because it puts the negative formal charge on oxygen, which is more electronegative than carbon. 1 point earned for a correct assignment of formal charges in the two diagrams; 1 point earned for a correct explanation.

Solution 2

(b)

Mark scheme

- Sum bond enthalpies from each Lewis structure. HCNO (bonds broken): H-C (413) + C $\equiv$ N triple bond (891) + N-O (201) = 1505 kJ/mol. HNCO (bonds formed): H-N (391) + C=N (615) + C=O (745) = 1751 kJ/mol. ΔH (standard) = sum(enthalpies of bonds broken) - sum(enthalpies of bonds formed) = 1505 kJ/mol - 1751 kJ/mol = -246 kJ/mol_{rxn}. 1 point earned for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken; 1 point earned for the correct determination of ΔH (standard).

Solution 2

(c)

Mark scheme

- The change from fulminic acid to isocyanic acid is a rearrangement of atoms (isomerization) with no change in phase and no change in the number of molecules, so there is essentially no change in the number of accessible microstates and ΔS (standard) is close to zero. 1 point earned for a correct explanation.

Solution 2

(d) Mark scheme

- Isocyanic acid (HNCO) is present in higher concentration at equilibrium. Delta G (standard) is essentially equal to delta H (standard) because delta S (standard) is essentially zero, so delta G (standard) is approximately $-246 \text{ kJ/mol}_{\text{rxn}}$, indicating the forward reaction ($\text{HCNO} \rightarrow \text{HNCO}$) is thermodynamically favorable. Since delta G (standard) is negative, $K > 1$ ($\Delta G_{\text{standard}} = -RT \ln K$), resulting in a higher equilibrium concentration of product (HNCO) than reactant (HCNO). 1 point earned for the correct choice WITH a valid justification (calculation of delta G standard is sufficient justification); 1 point earned for correctly connecting thermodynamic favorability to the equilibrium constant K.

Solution 2

(e)(i)

Mark scheme

- From inspecting the data table or the graph, the decomposition reaction has a constant half-life (the urea concentration approximately halves every 10 hours: 0.1000 to 0.0500 over the first 10 h, 0.0500 to 0.0250 over the next 10 h, etc.), which indicates the reaction is first order. 1 point earned for a correct explanation.

Solution 2

(e)(ii)

Mark scheme

- Since the reaction is first order: $k = 0.693 / t(1/2) = 0.693 / 10. \text{ h} = 0.069 \text{ h}^{-1}$ (equivalently $k = (\ln[A]_0 - \ln[A]_t)/t = (\ln 0.1000 - \ln 0.0500) / 10. \text{ h} = 0.069 \text{ h}^{-1}$). 1 point earned for the correct value of k with correct units.

Solution 2

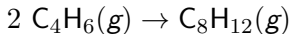
(f)

Mark scheme

- Perform the experiment again starting at a different initial concentration of $\text{OH}^-(\text{aq})$ (changing only $[\text{OH}^-]$, holding other variables such as temperature and initial urea concentration constant), and measure how the concentration of $\text{CO}(\text{NH}_2)_2$ changes over time; compare the resulting rate/rate constant to that obtained at pH 13. 1 point earned for the description of a valid experiment (correct changed initial condition and data to be gathered).

Question 5

2016 ■ Q5



At high temperatures the compound C_4H_6 (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.

[Graph 1: " $[\text{C}_4\text{H}_6]$ vs. Time" — x-axis Time (s) from 0 to 20; y-axis $[\text{C}_4\text{H}_6]$ (mol/L) from 0 to 0.020. Trial 1 (open circles) starts at approximately (0, 0.0183) and decays smoothly to approximately (20, 0.0065). Trial 2 (filled squares) starts at approximately (0, 0.0096) and decays smoothly to approximately (20, 0.0049). Both curves show a decreasing, concave-up (leveling-off) shape.]

Question 5

[Graph 2: " $\ln[\text{C}_4\text{H}_6]$ vs. Time" — x-axis Time (s) from 0 to 20; y-axis $\ln[\text{C}_4\text{H}_6]$ from -5.5 to -3.5. Trial 1 (open circles) starts at approximately (0, -4.0) and decreases roughly linearly-curved to approximately (20, -5.0). Trial 2 (filled squares) starts at approximately (0, -4.65) and decreases to approximately (20, -5.3). Both curves are slightly concave, not perfectly straight lines.]

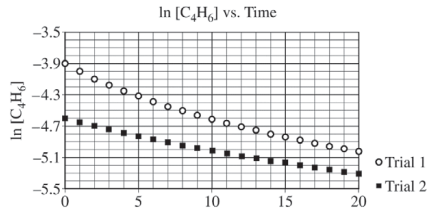
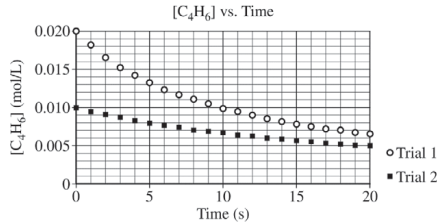
[Graph 3: " $1/[\text{C}_4\text{H}_6]$ vs. Time" — x-axis Time (s) from 0 to 20; y-axis $1/[\text{C}_4\text{H}_6]$ (L/mol) from 0 to 250. Trial 1 (open circles) starts at approximately (0, 55) and increases in a straight line to approximately (20, 155). Trial 2 (filled squares) starts at approximately (0, 104) and increases in a straight line to approximately (20, 205). Both trials appear linear in this plot.]

(a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6 .

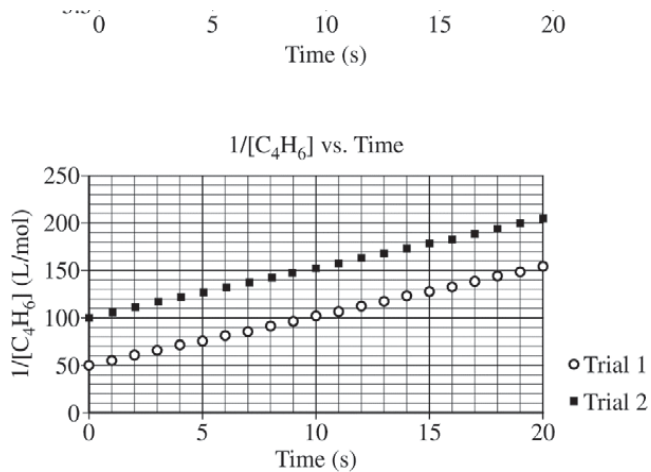
Question 5

- (b)** Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6 .
- (c)** The initial rate of the reaction in trial 1 is $0.0010 \text{ mol}/(\text{L} \cdot \text{s})$. Calculate the rate constant, k , for the reaction at 625 K.

Question 5



Question 5



Solution 5

(a)

Mark scheme

- For trial 1, $n/V = 0.020 \text{ mol/L}$ (assuming the vessel volume is 1.0 L, $n(\text{C}_4\text{H}_6) = 0.020 \text{ mol}$). Using $PV = nRT$: $P = nRT/V = (0.020 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(625 \text{ K}) / (1.0 \text{ L}) = 1.0 \text{ atm}$. 1 point for a correct setup, 1 point for the correct answer ($\approx 1.0 \text{ atm}$).

Solution 5

(b)

Mark scheme

- Second order with respect to C_4H_6 , because the plot of $1/[\text{C}_4\text{H}_6]$ versus time is a straight line (linear), which is the signature of a second-order integrated rate law. 1 point for correctly identifying second order.

Solution 5

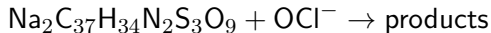
(c)

Mark scheme

- Using the second-order differential rate law, $\text{rate} = k[\text{C}_4\text{H}_6]^2$: $k = \text{rate} / [\text{C}_4\text{H}_6]^2 = 0.0010 \text{ mol}/(\text{L} \cdot \text{s}) / (0.020 \text{ mol}/\text{L})^2 = 2.5 \text{ L}/(\text{mol} \cdot \text{s})$.
(Equivalently, from the integrated form $1/[\text{C}_4\text{H}_6]_t = 2kt + 1/[\text{C}_4\text{H}_6]_0$, the slope of the $1/[\text{C}_4\text{H}_6]$ vs. time plot equals $2k = 5.0 \text{ L}/(\text{mol} \cdot \text{s})$, giving $k = 2.5 \text{ L}/(\text{mol} \cdot \text{s})$; a student who uses this method but omits the factor of 2, reporting $k = 5.0 \text{ L}/(\text{mol} \cdot \text{s})$, still earns the point.) 1 point for the correct value of k ($2.5 \text{ L}/(\text{mol} \cdot \text{s})$ via the differential method, or $5.0 \text{ L}/(\text{mol} \cdot \text{s})$ if the slope method is used without doubling).

Question 5

2015 ■ Q5

*blue**colorless*

Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.

[Graph I: x-axis "Time (s)" from 0 to 100; y-axis "Absorbance" from 0.0 to 0.9. Points plotted approximately: (0, 0.80), (20, 0.40), (30, 0.28), (40, 0.20), (50, 0.14), (60,

Question 5

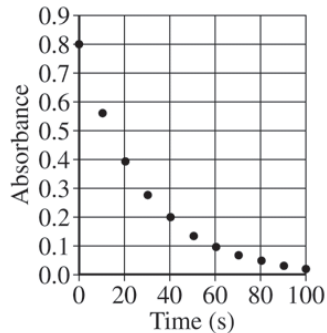
0.10), (70, 0.07), (80, 0.05), (90, 0.04), (100, 0.03) — a curve that decays steeply and levels off, concave up.]

[Graph II "ln (absorbance)": x-axis "Time (s)" from 0 to 100; y-axis "ln (absorbance)" from -4.0 to 0.0. Points plotted approximately: (0, -0.2), (20, -0.9), (30, -1.6), (40, -2.0), (50, -2.4), (60, -2.7), (70, -3.1), (80, -3.3), (90, -3.5) — points fall roughly on a straight line with negative slope.]

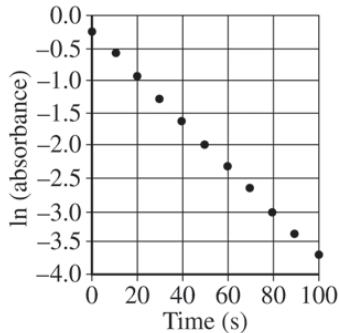
[Graph III "1/(absorbance)": x-axis "Time (s)" from 0 to 100; y-axis "1/(absorbance)" from 0 to 45. Points plotted approximately: (0, 1), (20, 2.5), (30, 3.5), (40, 5), (50, 7), (60, 10), (70, 14), (80, 20), (90, 28), (100, 40) — points curve upward, increasingly steeply, not a straight line.]

(a) Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?

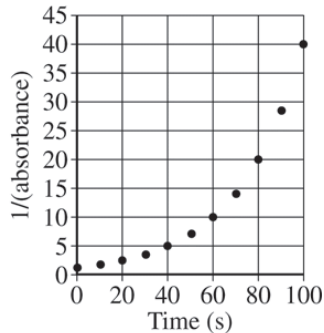
Question 5



Graph I



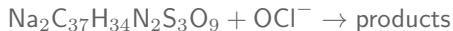
Graph II



Graph III

Question 5

2015 ■ Q5



blue

colorless

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[Graph 1: x-axis "Time (s)" from 0 to 100; y-axis "Absorbance" from 0.0 to 0.9. Points plotted approximately: (0, 0.80), (20, 0.40), (30, 0.28), (40, 0.20), (50, 0.14), (60, 0.10), (70, 0.07), (80, 0.05), (90, 0.04), (100, 0.03) — a curve that decays steeply and levels off, concave up.]

Question 5

[Graph II " $\ln(\text{absorbance})$ ": x-axis "Time (s)" from 0 to 100; y-axis " $\ln(\text{absorbance})$ " from -4.0 to 0.0 . Points plotted approximately: $(0, -0.2)$, $(20, -0.9)$, $(30, -1.6)$, $(40, -2.0)$, $(50, -2.4)$, $(60, -2.7)$, $(70, -3.1)$, $(80, -3.3)$, $(90, -3.5)$ — points fall roughly on a straight line with negative slope.]

[Graph III " $1/(\text{absorbance})$ ": x-axis "Time (s)" from 0 to 100; y-axis " $1/(\text{absorbance})$ " from 0 to 45. Points plotted approximately: $(0, 1)$, $(20, 2.5)$, $(30, 3.5)$, $(40, 5)$, $(50, 7)$, $(60, 10)$, $(70, 14)$, $(80, 20)$, $(90, 28)$, $(100, 40)$ — points curve upward, increasingly steeply, not a straight line.]

(b) The reaction is known to be first order with respect to bleach. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance

Question 5

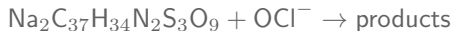
near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem, and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

Question 5

2015 ■ Q5



blue

colorless

Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.

[Graph 1: x-axis "Time (s)" from 0 to 100; y-axis "Absorbance" from 0.0 to 0.9. Points plotted approximately: (0, 0.80), (20, 0.40), (30, 0.28), (40, 0.20), (50, 0.14), (60, 0.10), (70, 0.07), (80, 0.05), (90, 0.04), (100, 0.03) — a curve that decays steeply and levels off, concave up.]

Question 5

[Graph II " $\ln(\text{absorbance})$ ": x-axis "Time (s)" from 0 to 100; y-axis " $\ln(\text{absorbance})$ " from -4.0 to 0.0 . Points plotted approximately: $(0, -0.2)$, $(20, -0.9)$, $(30, -1.6)$, $(40, -2.0)$, $(50, -2.4)$, $(60, -2.7)$, $(70, -3.1)$, $(80, -3.3)$, $(90, -3.5)$ — points fall roughly on a straight line with negative slope.]

[Graph III " $1/(\text{absorbance})$ ": x-axis "Time (s)" from 0 to 100; y-axis " $1/(\text{absorbance})$ " from 0 to 45. Points plotted approximately: $(0, 1)$, $(20, 2.5)$, $(30, 3.5)$, $(40, 5)$, $(50, 7)$, $(60, 10)$, $(70, 14)$, $(80, 20)$, $(90, 28)$, $(100, 40)$ — points curve upward, increasingly steeply, not a straight line.]

(c) In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?

Solution 5

(a)

Mark scheme

- The reaction is first order with respect to the blue food coloring. This is shown because Graph II, a plot of $\ln(\text{absorbance})$ vs. time, is linear – the diagnostic straight-line test for a first-order process (a plot of $1/\text{absorbance}$ vs. time, Graph III, being linear would instead indicate second order). 1 point for the correct order (first order).

Solution 5

(b) Mark scheme

- 'Increasing the concentration of the food coloring' is the modification that should be circled (1 point for the correct choice). If the initial concentration of blue food coloring is increased, then more time is required, regardless of the reaction order found in part (a), for the (roughly constant, large-excess) bleach to oxidize the larger amount of food coloring present, so the absorbance takes longer to fall near zero (1 point for this correct explanation). (Increasing temperature or increasing bleach concentration would each speed the reaction up further, making the problem worse, not better.)

Solution 5

(c)

Mark scheme

- The student should set the spectrophotometer to a different wavelength – one at which red food coloring (rather than blue) strongly absorbs light – and otherwise repeat the same kinetics procedure (measuring absorbance vs. time with bleach in large excess) to determine the order with respect to red food coloring. 1 point for this correct answer.

Question 7

2014 ■ Q7

[Structural diagrams: cis-2-butene (H_3C and CH_3 on the same side of the $\text{C}=\text{C}$ double bond, H atoms on the same side opposite) in equilibrium (double harpoon arrows) with trans-2-butene (H_3C and CH_3 on opposite sides of the $\text{C}=\text{C}$ double bond).]

The half-life ($t_{1/2}$) of the catalyzed isomerization of cis-2-butene gas to produce trans-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis-2-butene}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

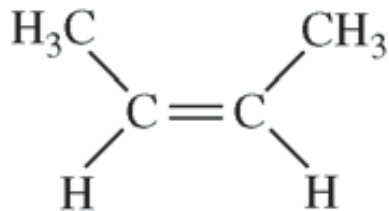
Question 7

- (b)** Calculate the rate constant, k , for the reaction at 350. K. Include appropriate units with your answer.
- (c)** Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.
- (d)** The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

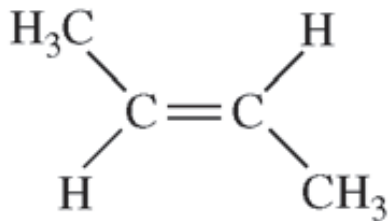
Question 7

Trial Number	Initial $P_{cis-2-butene}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

Question 7



cis-2-butene



trans-2-butene

Solution 7

(a)

Mark scheme

- For a first-order reaction, the half-life is independent of the initial reactant concentration (or pressure) at constant temperature. This is consistent with trials 1, 2, and 3: even though the initial pressure of cis-2-butene doubles (300. $\rightarrow$ 600. torr, trial 1 vs. 2) and the volume changes (trial 1 vs. 3), the half-life remains 100. s in all three trials at 350. K.

Solution 7

(b)

Mark scheme

$$\blacksquare k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100. \text{ s}} = 0.00693 \text{ s}^{-1}.$$

Solution 7

(c)

Mark scheme

- The initial rate in trial 1 is less than the initial rate in trial 2, because rate = $k[\text{cis-2-butene}]$ (or rate = $kP_{\text{cis-2-butene}}$); since k is constant (same temperature, 350. K) and the initial pressure of cis-2-butene in trial 1 (300. torr) is less than in trial 2 (600. torr), the initial rate in trial 1 must be lower.

Solution 7

(d)

Mark scheme

- The temperature in trial 4 (365 K) is higher than in trial 1 (350. K), so the average kinetic energy (KE_{avg}) of the molecules is greater in trial 4. Consequently, a greater fraction of molecular collisions have sufficient energy to overcome the activation energy barrier, so the rate constant and rate are greater in trial 4, giving it the shorter half-life.