Past-paper walk-through

Concentration Changes Over Time ▪ 5.3

eXercise

Questions in this set

- 2026 Q2
- 2024 Q6
- 2022 Q5
- 2019 Q6
- 2018 Q7
- 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

2026 ▪ Q2

Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

(a)(i) The bonds between chromium and oxygen in CrO_4^{2-} can be represented as covalent bonds. One possible Lewis diagram for the CrO_4^{2-} ion is shown in Figure 1.

[Figure 1: Lewis diagram of CrO_4^{2-} — a central Cr atom single-bonded to three O atoms (each with three lone pairs) and double-bonded to one O atom (with two lone pairs), the whole structure enclosed in brackets with a $2-$ charge.]

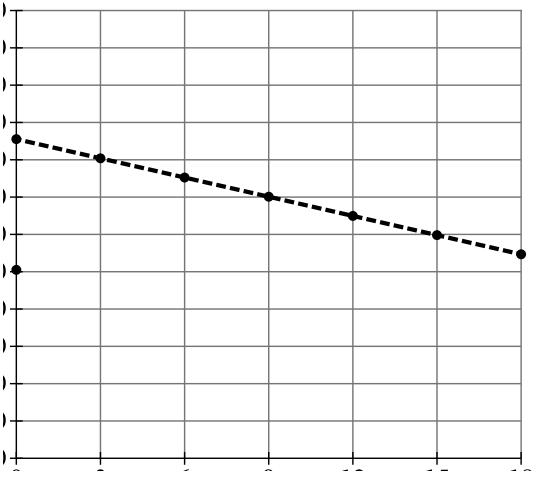
Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.

(a)(ii) On Figure 2, **draw** a complete Lewis diagram for a resonance structure of CrO_4^{2-} that results in a formal charge of zero on two of the O atoms and a formal charge of -1 on the other two O atoms. Your diagram should contain the same number of valence electrons as in Figure 1.

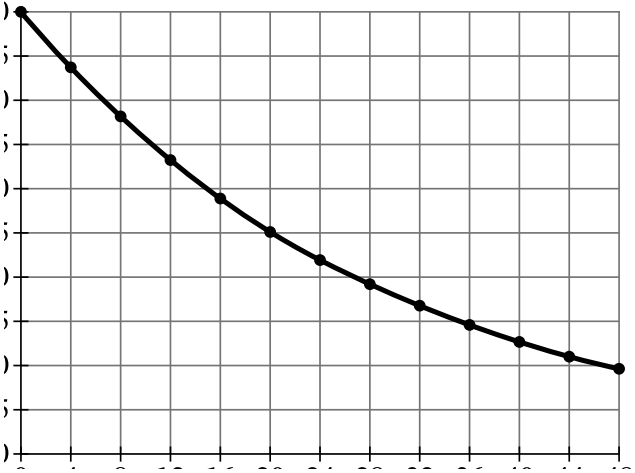
Question 2

[Figure 2: A blank template showing Cr in the center bonded to four O atoms arranged above, left, right, and below, enclosed in brackets with a $2-$ charge, for the student to complete.]

Question 2



Question 2



Question 2

2026 ▪ Q2

Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

(b)(i) When reacted with a strong acid like $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

Write a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ and a strong acid.

(b)(ii) Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

Question 2

2026 ▪ Q2

Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

(c) The following information applies to parts C and D.

In acidic solutions, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

Equation 1: $Cr_2O_7^{2-}(aq) + 2H_3O^+(aq) \rightarrow 2CrO_3(aq) + 3H_2O(l)$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

Equation 2: $CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O(l) \qquad E^\circ = -1.32\ V$

Question 2

Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG°. Show the work that leads to your answer.

Question 2

2026 ▪ Q2

Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

(d) **Calculate** the number of grams of $Cr(s)$ that could be plated onto the surface of a steel rod when 15.0 A of current is applied for 3250 seconds. Show the work that leads to your answer.

Question 2

2026 ▪ Q2

Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

(e) In a separate experiment, an iron wire is placed directly in a solution of 0.50 *M* $Cr_2O_7^{2-}(aq)$ with pH $= 1.99$. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

[Figure 3: Graph of $[Cr_2O_7^{2-}]$ (M) vs. Time (minutes); y-axis 0.00 to 0.50 in increments of 0.05, x-axis 0 to 48 in increments of 4; curve is concave up, decreasing from approximately $(0, 0.50)$ through $(4, 0.44)$, $(8, 0.38)$, $(12, 0.33)$, $(16, 0.29)$, $(20, 0.26)$, $(24, 0.23)$, $(28, 0.21)$, $(32, 0.18)$, $(36, 0.16)$, $(40, 0.14)$, $(44, 0.12)$, to approximately $(48, 0.10)$.]

Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

Question 2

2026 ▪ Q2

Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

(f) The following information applies to parts F and G.

The student creates a plot of $\ln[Cr_2O_7^{2-}]$ versus time for a trial with an initial concentration of 0.50 *M* $Cr_2O_7^{2-}(aq)$, as shown in Figure 4.

[Figure 4: Graph of $\ln[Cr_2O_7^{2-}]$ vs. Time (minutes); y-axis -2.40 to 0.00 in increments of 0.20, x-axis 0 to 18 in increments of 3; dashed line of best fit through points starting near $(0, -0.65)$ decreasing roughly linearly to approximately $(18, -1.35)$.]

Calculate the value of the rate constant, *k*, for the reaction. Report your answer in units of min^{-1}. Show the work that leads to your answer.

Question 2

2026 ▪ Q2

Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

(g) The student then runs a second trial of the experiment under identical conditions but uses an initial concentration of 0.25 *M* $Cr_2O_7^{2-}(aq)$ instead of 0.50 *M* $Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln[Cr_2O_7^{2-}]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

Question 6

2024 ▪ Q6

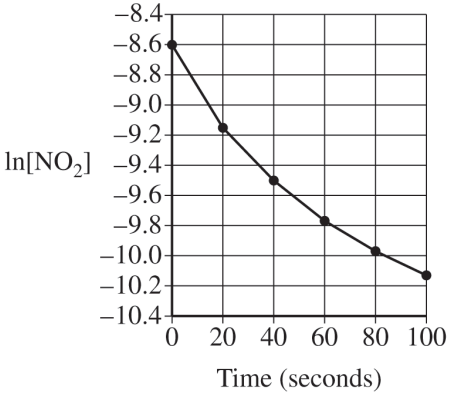
$$2\,NO_2 \rightarrow 2\,NO + O_2$$

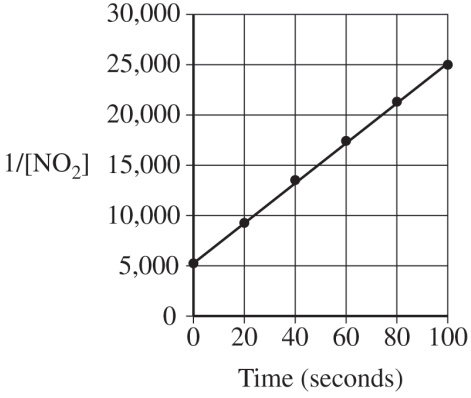
6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.
A scientist measures the change in $[NO_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate the following two graphs.
[Graph 1: $\ln[NO_2]$ vs. Time (seconds); y-axis from -10.4 to -8.4 in increments of 0.2, x-axis 0 to 100 s in increments of 20. Data points (approximately): (0, -8.6), (20, -9.15), (40, -9.55), (60, -9.85), (80, -10.05), (100, -10.15); points connected by a

Question 6

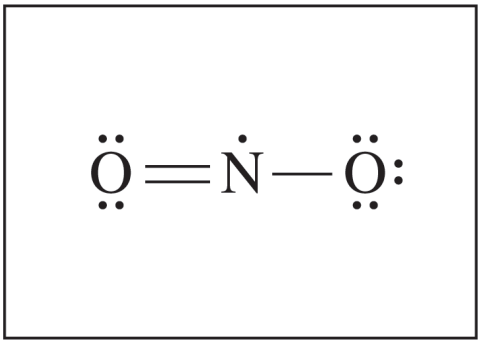
smooth decreasing curve, concave up (linearizing downward but curving), consistent with a non-linear $\ln[NO_2]$ vs. t relationship.]
[Graph 2: $1/[NO_2]$ vs. Time (seconds); y-axis from 0 to 30,000 in increments of 5,000, x-axis 0 to 100 s in increments of 20. Data points (approximately): (0, 5000), (20, 9800), (40, 13800), (60, 18000), (80, 21800), (100, 25200); points lie on a straight line of constant positive slope.]
Based on these data, the scientist makes the claim that the rate law for the reaction is $rate = k[NO_2]^2$.
(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2.

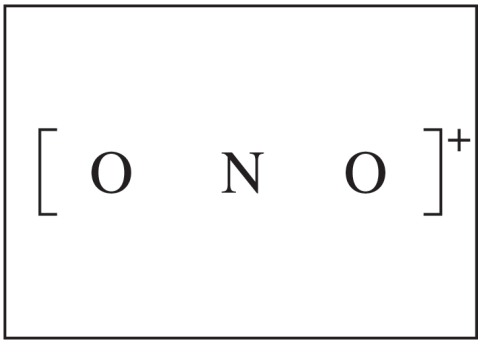
Question 6


−8.4
−8.6
−8.8
−9.0
−9.2
−9.4
−9.6
−9.8
−10.0
−10.2
−10.4
ln[NO2]
0
20
40
60
80
100
Time (seconds)


30,000
25,000
20,000
15,000
10,000
5,000
0
1/[NO2]
0
20
40
60
80
100
Time (seconds)

Question 6





Question 6

2024 ▪ Q6

$$2\,NO_2 \rightarrow 2\,NO + O_2$$

6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.
A scientist measures the change in $[NO_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate the following two graphs.
[Graph 1: $\ln[NO_2]$ vs. Time (seconds); y-axis from -10.4 to -8.4 in increments of 0.2, x-axis 0 to 100 s in increments of 20. Data points (approximately): (0, -8.6), (20, -9.15), (40, -9.55), (60, -9.85), (80, -10.05), (100, -10.15); points connected by a smooth decreasing curve, concave up (linearizing downward but curving), consistent with a non-linear $\ln[NO_2]$ vs. t relationship.]

Question 6

[Graph 2: $1/[NO_2]$ vs. Time (seconds); y-axis from 0 to 30,000 in increments of 5,000, x-axis 0 to 100 s in increments of 20. Data points (approximately): (0, 5000), (20, 9800), (40, 13800), (60, 18000), (80, 21800), (100, 25200); points lie on a straight line of constant positive slope.]

Based on these data, the scientist makes the claim that the rate law for the reaction is $rate = k[NO_2]^2$.

(b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be 6.52×10^{-7} M/s.

Determine the rate of appearance, in M/s, of O_2 at this same point in the reaction.

Question 6

2024 ▪ Q6

$$2\,NO_2 \rightarrow 2\,NO + O_2$$

6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.
A scientist measures the change in $[NO_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate the following two graphs.
[Graph 1: $\ln[NO_2]$ vs. Time (seconds); y-axis from -10.4 to -8.4 in increments of 0.2, x-axis 0 to 100 s in increments of 20. Data points (approximately): (0, -8.6), (20, -9.15), (40, -9.55), (60, -9.85), (80, -10.05), (100, -10.15); points connected by a smooth decreasing curve, concave up (linearizing downward but curving), consistent with a non-linear $\ln[NO_2]$ vs. t relationship.]

Question 6

[Graph 2: $1/[NO_2]$ vs. Time (seconds); y-axis from 0 to 30,000 in increments of 5,000, x-axis 0 to 100 s in increments of 20. Data points (approximately): (0, 5000), (20, 9800), (40, 13800), (60, 18000), (80, 21800), (100, 25200); points lie on a straight line of constant positive slope.]
Based on these data, the scientist makes the claim that the rate law for the reaction is $rate = k[NO_2]^2$.

(c) NO_2 is a molecule that contains an odd number of electrons and can be oxidized to form the NO_2^+ ion. In NO_2, the unpaired electron is presumed to be localized on the nitrogen atom, as shown in the Lewis diagram in the box on the left.

[Two boxes side by side. Left box: Lewis structure of NO_2 — O (with two lone pairs) double-bonded on the left to a central N (bearing an unpaired dot, single electron, above it), N single-bonded on the right to another O (bearing three lone pairs, i.e., a negative-type oxygen with full octet): $\ddot{O} = \dot{N} - \ddot{O}$: with all lone pairs shown as dots. Right box: empty bracket template $[\ O \quad N \quad O\ ]^+$ for the student to complete with

Question 6

the Lewis structure of NO_2^+, showing atoms O, N, O in a row inside square brackets with a superscript plus charge, currently drawn with no bonds or lone pairs (blank template for the student to fill in).]

(c)(i) In the box on the right, complete the Lewis diagram for NO_2^+. Be sure to show all bonding and nonbonding electrons.

(c)(ii) A student makes the claim that the bond angles in NO_2 and NO_2^+ are different from each other. Do you agree or disagree with the student's claim? Justify your answer.

Solution 6

(a)

Mark scheme

- The plot of $1/[\mathrm{NO_2}]$ versus time is the most linear of the tested plots, which indicates that the reaction is second order with respect to $\mathrm{NO_2}$ (a linear $1/[A]$ vs. t plot is the diagnostic signature of second-order kinetics).

Solution 6

(b)

Mark scheme

- Rate of appearance of O_2
  $= 6.52 \times 10^{-7}\ M/\text{s} \times \dfrac{1\ \text{mol}\ O_2}{2\ \text{mol}\ NO_2} = 3.26 \times 10^{-7}\ M/\text{s}.$

Solution 6

(c)

Mark scheme

- Context only — shows the given Lewis structure of NO_2 (O with two lone pairs double-bonded to a central N bearing one unpaired/nonbonding electron, N singly bonded to a second O with three lone pairs); sets up parts (c)(i) and (c)(ii). No separate scorable response for this leaf.

Solution 6

(c)(i)

Mark scheme

- Lewis diagram for NO_2^+ (isoelectronic with CO_2): linear $O = N = O$ structure, $[\ddot{O} = N = \ddot{O}]^+$, each O atom has two lone pairs, N has no lone pair and no unpaired electron (all 4 electron domains are used in the two double bonds), overall ion charge $+1$.

Solution 6

(c)(ii)

Mark scheme

- Agree. Accept either justification: (1) NO_2^+ no longer has a nonbonding/unpaired electron on the central N (unlike NO_2), so the two O atoms spread farther apart into a linear 180° geometry, different from NO_2's bent shape. (2) N in NO_2 is sp^2 hybridized (bond angle $\approx 120°$), while N in NO_2^+ is *sp* hybridized (bond angle $= 180°$), so the bond angles differ.

Question 5

2022 ▪ Q5

The following equation represents the decomposition of N_2O_5, for which the rate law is rate $= k[N_2O_5]$.

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

A sample of pure $N_2O_5(g)$ is placed in an evacuated container and allowed to decompose at a constant temperature of 300 K. The concentration of $N_2O_5(g)$ in the container is measured over a period of time, and the measurements are recorded in the following table.

Time (hr)	$[N_2O_5]$ (M)
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 $N_2O_5(g)$.

Step 1: $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$

Step 2: $NO_2(g) + NO_3(g) \rightarrow NO_2(g) + NO(g) + O_2(g)$

Step 3: $N_2O_5(g) + NO(g) \rightarrow 3\,NO_2(g)$

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: $k = 0.693/t_{½} = 0.693/1.67\ hr = 0.415\ hr^{-1}$ (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 hr $= 0.415\ hr^{-1}$; $\ln(0.160) - \ln(0.0400)$ over 3.33 hr $= 0.416\ hr^{-1}$; or $\ln(0.160) - \ln(0.0200)$ over 5.00 hr $= 0.416\ hr^{-1}$). 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[N2O5], 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, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

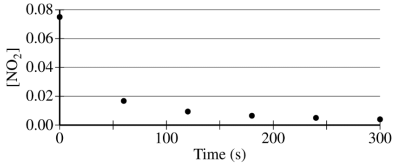
The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.

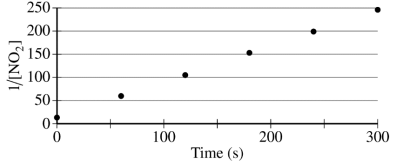
[Graph 1: $[NO_2]$ (mol/L, y-axis 0.00 to 0.08) vs. Time (s, x-axis 0 to 300); data points approximately: (0, 0.075), (60, 0.018), (120, 0.010), (180, 0.008), (240, 0.007), (300, 0.005) — a decaying curve]

Question 6

[Graph 2: $1/[NO_2]$ (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: $\ln([NO_2])$ (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.

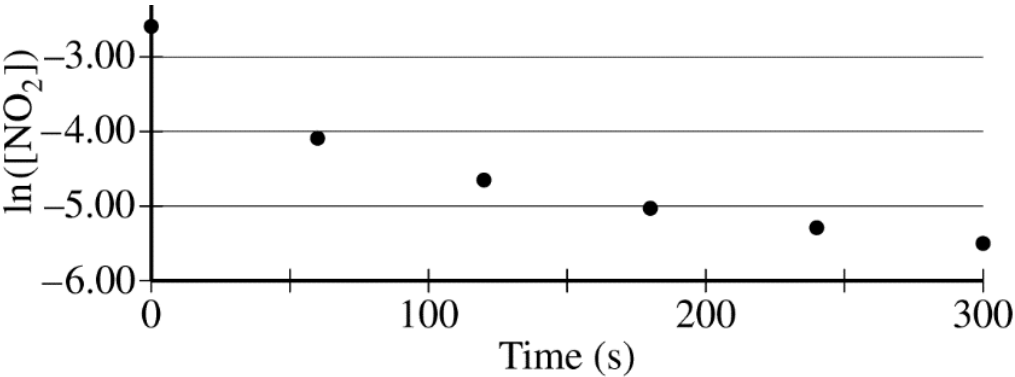
Question 6


0.08
0.06
0.04
0.02
0.00
[NO2]
0
100
200
300
Time (s)


250
200
150
100
50
0
1/[NO2]
0
100
200
300
Time (s)


−2.00

Question 6



Question 6

2019 ▪ Q6

Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ 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: $[NO_2]$ (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]
[Graph 2: $1/[NO_2]$ (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]

Question 6

[Graph 3: $\ln([NO_2])$ (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]

(b) Write the rate law for the decomposition of $NO_2(g)$.

Consider two possible mechanisms for the decomposition reaction.

Question 6

2019 ▪ Q6

Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ 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.
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[Graph 2: $1/[NO_2]$ (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]

Question 6

[Graph 3: $\ln([NO_2])$ (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]

(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

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ slow

Step 2: $NO_3(g) \rightarrow NO(g) + O_2(g)$ fast

(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

Step 1: $NO_2(g) + NO_2(g) \rightleftharpoons N_2O_4(g)$ fast equilibrium

Step 2: $N_2O_4(g) \rightarrow 2\,NO(g) + O_2(g)$ slow

Solution 6

(a)

Mark scheme

- The graph of 1/[NO2] 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

- rate = k[NO2]^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 ($NO2 + NO2 \rightarrow NO + NO3$) is the slow step, so it is rate-determining. The rate law for this elementary step is $\text{rate} = k[NO2][NO2] = k[NO2]^2$, 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 ($N_2O_4 \rightarrow 2NO + O_2$) is slow and rate-determining, giving rate = $k[N_2O_4]$. Since N_2O_4 is a reaction intermediate, it must be eliminated using the fast pre-equilibrium of step 1: $K_{eq} = [N_2O_4]/[NO_2]^2$, so $[N_2O_4] = K_{eq}[NO_2]^2$. Substituting into the rate law gives rate = $(k \cdot K_{eq})[NO_2]^2$, which is second order in $[NO_2]$ and consistent with part (b). 1 point for the correct answer (yes) with this justification.

Question 7

2018 ▪ Q7

[Graph: Photoelectron spectrum. Y-axis "Relative Number of Electrons" (unlabeled scale, showing peak heights). X-axis "Binding Energy (MJ/mol)" from 45 down to 0, in increments of 5, decreasing left to right. Peaks: one medium-height peak at approximately 40 MJ/mol; two peaks close together near 2 MJ/mol — a medium-height peak just above 2, and a tall peak (tallest in the spectrum) just below 2, close to 0.]

The complete photoelectron spectrum of an element is represented above.

(a) Identify the element.

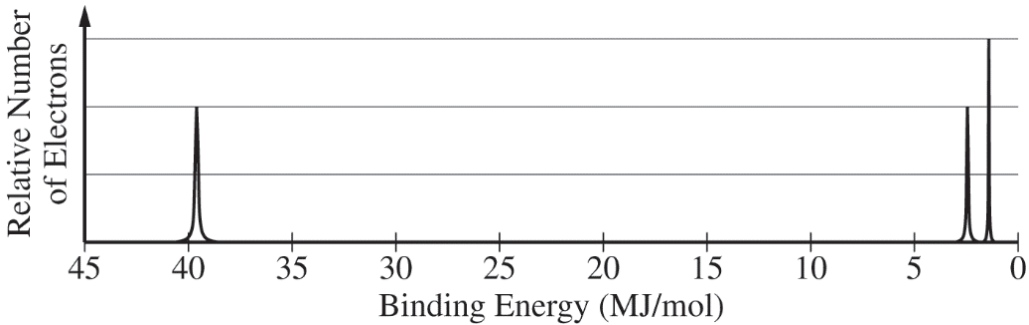
A radioactive isotope of the element decays with a half-life of 10. minutes.

(b) Calculate the value of the rate constant, k, for the radioactive decay. Include units with your answer.

Question 7

(c) If 64 atoms of the radioactive isotope are originally present in a sample, what is the expected amount of time that will pass until only one atom of the isotope remains? Show how you arrived at your answer.

Question 7


Relative Number of Electrons
45
40
35
30
25
20
15
10
5
0
Binding Energy (MJ/mol)

Solution 7

(a)

Mark scheme

- The element is nitrogen, N. (The photoelectron spectrum shows a peak near 40 MJ/mol for the core 1s electrons and two peaks near 0-5 MJ/mol for the valence 2s and 2p electrons; the pattern and relative peak heights across the 7 total electrons identify $Z = 7$, nitrogen.) 1 point is earned for correctly identifying the element.

Solution 7

(b)

Mark scheme

- For first-order radioactive decay, $k = 0.693/t(1/2) = 0.693/10.$ min $= 0.069$ min^{-1}. 1 point is earned for the correct numerical answer; 1 point is earned for the correct unit (min^{-1}).

Solution 7

(c)

Mark scheme

- 64 -> 32 -> 16 -> 8 -> 4 -> 2 -> 1 requires 6 half-lives: 6 x 10. min = 60. min. (Equivalently, using ln[A]t - ln[A]0 = -kt: t = [ln(1) - ln(64)] / (-0.069 min^-1) = 60. min.) 1 point is earned for the correct answer (60. min) AND a valid method.

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: H–C N–Ö: (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: H–C̈=N=Ö: (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.

$$\mathrm{HCNO}(g) \rightleftharpoons \mathrm{HNCO}(g)$$

fulminic acid *isocyanic acid*

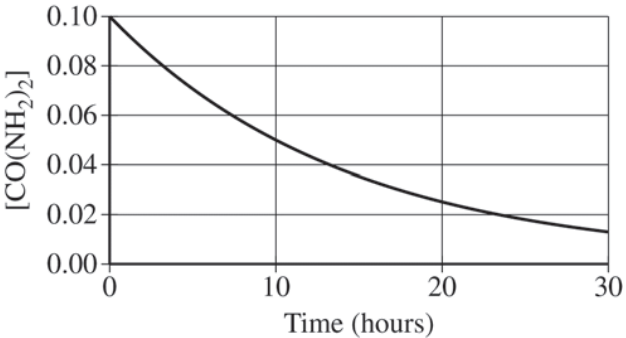
Question 2

| Fulminic Acid | Isocyanic Acid | |—|—| | H–C N–Ö: (O has two lone pairs) | H–N̈=C=Ö: (N has one lone pair, O has two lone pairs) |

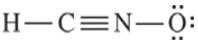
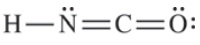
(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Question 2

Time (hours)	$[CO(NH_2)_2]$
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
	

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

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: H–C N–Ö: (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: H–C̈=N=Ö: (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.

$$\mathrm{HCNO}(g) \rightleftharpoons \mathrm{HNCO}(g)$$

fulminic acid *isocyanic acid*

| Fulminic Acid | Isocyanic Acid | |—|—| | H–C N–Ö: (O has two lone pairs) | H–N̈=C=Ö: (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 HCNO(g) to form 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

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

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$$\mathrm{HCNO}(g) \rightleftharpoons \mathrm{HNCO}(g)$$

fulminic acid *isocyanic acid*

| Fulminic Acid | Isocyanic Acid | |—|—| | H–C N–Ö: (O has two lone pairs) | H–N̈=C=Ö: (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

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: H–C N–Ö: (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: H–C̈=N=Ö: (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)]

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$$\mathrm{HCNO}(g) \rightleftharpoons \mathrm{HNCO}(g)$$

fulminic acid *isocyanic acid*

| Fulminic Acid | Isocyanic Acid | |—|—| | H–C N–Ö: (O has two lone pairs) | H–N̈=C=Ö: (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

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: H–C N–Ö: (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: H–C̈=N=Ö: (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.

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fulminic acid *isocyanic acid*

| Fulminic Acid | Isocyanic Acid | |—|—| | H–C N–Ö: (O has two lone pairs) | H–N̈=C=Ö: (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, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftharpoons NH_4^+(aq) + OCN^-(aq)$$

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)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125

[Graph: y-axis $[CO(NH_2)_2]$ 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: H–C N–Ö: (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: H–C̈=N=Ö: (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.

$$\mathrm{HCNO}(g) \rightleftharpoons \mathrm{HNCO}(g)$$

fulminic acid *isocyanic acid*

| Fulminic Acid | Isocyanic Acid | |—|—| | H–C N–Ö: (O has two lone pairs) | H–N̈=C=Ö: (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 $OH^-(aq)$.

Solution 2

(a)

Mark scheme

- In the left diagram (H-C triple-bond N-O: with O having 3 lone pairs... i.e. H-C#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 (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#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. delta H (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 delta H (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 delta S (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 kJ/mol_rxn, indicating the forward reaction (HCNO -> HNCO) is thermodynamically favorable. Since delta G (standard) is negative, K $>$ 1 (delta G 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. h = 0.069 h^-1 (equivalently k = (ln[A]0 - ln[A]t)/t = (ln 0.1000 - ln 0.0500) / 10. h = 0.069 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 OH-(aq) (changing only [OH-], holding other variables such as temperature and initial urea concentration constant), and measure how the concentration of CO(NH2)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

$$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$$

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: "$[C_4H_6]$ vs. Time" — x-axis Time (s) from 0 to 20; y-axis $[C_4H_6]$ (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

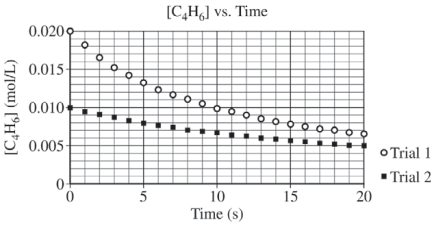
[Graph 2: "$\ln[C_4H_6]$ vs. Time" — x-axis Time (s) from 0 to 20; y-axis $\ln[C_4H_6]$ from -5.5 to -3.5. Trial 1 (open circles) starts at approximately (0, -4.0) and decreases roughly linearly-curved to approximately (20, -5.0). Trial 2 (filled squares) starts at approximately (0, -4.65) and decreases to approximately (20, -5.3). Both curves are slightly concave, not perfectly straight lines.]
[Graph 3: "$1/[C_4H_6]$ vs. Time" — x-axis Time (s) from 0 to 20; y-axis $1/[C_4H_6]$ (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.

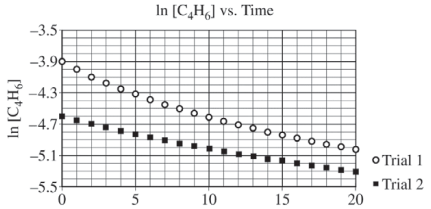
Question 5

(b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

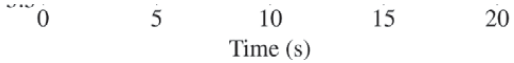
(c) The initial rate of the reaction in trial 1 is 0.0010 mol/(L · s). Calculate the rate constant, k, for the reaction at 625 K.

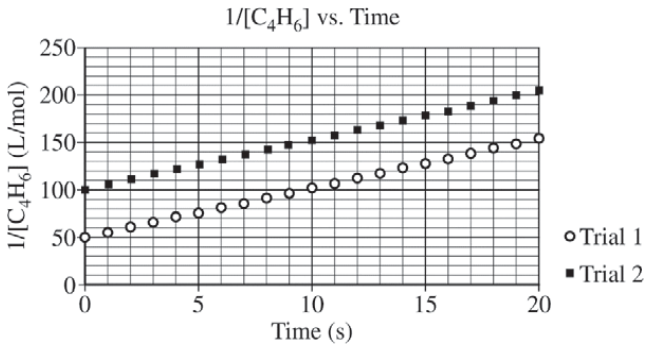
Question 5


[C4H6] vs. Time
0.020
0.015
0.010
0.005
0
[C4H6] (mol/L)
0
5
10
15
20
Time (s)
Trial 1
Trial 2


ln [C4H6] vs. Time
−3.5
−3.9
−4.3
−4.7
−5.1
−5.5
ln [C4H6]
0
5
10
15
20
Trial 1
Trial 2

Question 5


0
5
10
15
20
Time (s)


1/[C4H6] vs. Time
250
200
150
100
50
0
1/[C4H6] (L/mol)
0
5
10
15
20
Time (s)
Trial 1
Trial 2

Solution 5

(a)

Mark scheme

- For trial 1, n/V = 0.020 mol/L (assuming the vessel volume is 1.0 L, n(C4H6) = 0.020 mol). Using PV = nRT: P = nRT/V = (0.020 mol)(0.08206 L $\cdot$ atm $\cdot$ mol ^{1} $\cdot$ K ^{1})(625 K) / (1.0 L) = 1.0 atm. 1 point for a correct setup, 1 point for the correct answer (1.0 atm).

Solution 5

(b)

Mark scheme

- Second order with respect to C4H6, because the plot of $1/[C_4H_6]$ 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, rate = k[C4H6]^2: k = rate / [C4H6]^2 = 0.0010 mol/(L · s) / (0.020 mol/L)^2 = 2.5 L/(mol · s). (Equivalently, from the integrated form 1/[C4H6]t = 2kt + 1/[C4H6]0, the slope of the 1/[C4H6] vs. time plot equals 2k = 5.0 L/(mol · s), giving k = 2.5 L/(mol · s); a student who uses this method but omits the factor of 2, reporting k = 5.0 L/(mol · s), still earns the point.) 1 point for the correct value of k (2.5 L/(mol · s) via the differential method, or 5.0 L/(mol · s) if the slope method is used without doubling).

Question 5

2015 ▪ Q5

$$Na_2C_{37}H_{34}N_2S_3O_9 + OCl^- \rightarrow \text{products}$$

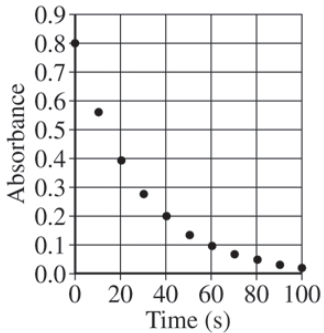
blue *colorless*

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,

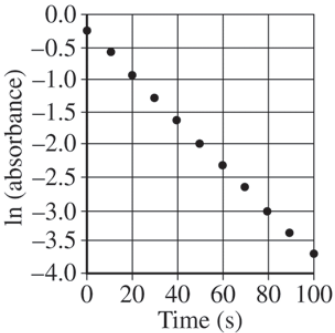
Question 5

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?

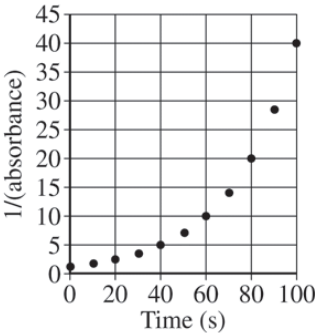
Question 5



Graph I



Graph II



Graph III

Question 5

2015 ▪ Q5

$$Na_2C_{37}H_{34}N_2S_3O_9 + OCl^- \rightarrow \text{products}$$

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, 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 (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.]

(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

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Question 5

[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.]

(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(absorbance) vs. time, is linear – the diagnostic straight-line test for a first-order process (a plot of 1/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

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[Structural diagrams: cis-2-butene (H_3C and CH_3 on the same side of the $C = C$ 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 $C = C$ 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 $P_{cis\text{-}2\text{-}butene}$ (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 $P_{cis\text{-2-butene}}$ (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

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

Solution 7

(c)

Mark scheme

- The initial rate in trial 1 is less than the initial rate in trial 2, because rate = k[cis-2-butene] (or rate = $kP_{cis\text{-}2\text{-butene}}$); 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.