# Past-paper walk-through

## Reaction Rates ▪ 5.1

eXercise

# Questions in this set

- 2024 Q6
- 2023 Q3

# 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 6

2024 ▪ Q6

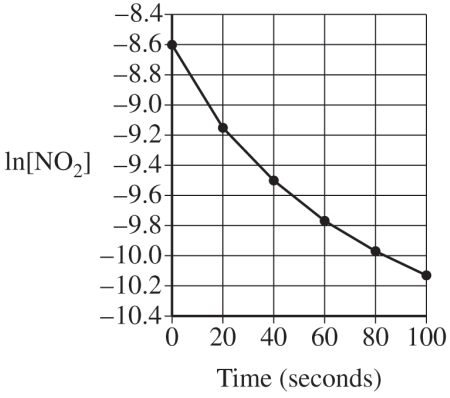
$$2\,NO_2 \rightarrow 2\,NO + O_2$$

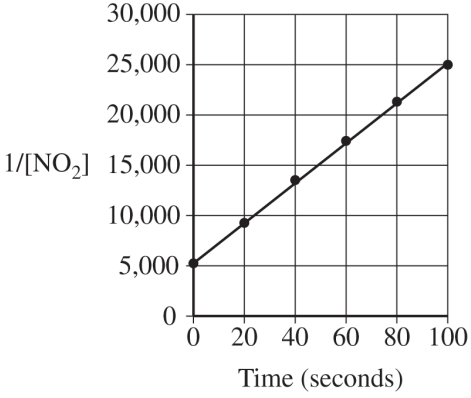
6. At elevated temperatures, $NO_2$ undergoes decomposition in the gas phase, forming NO and $O_2$ as represented by the following equation.
A scientist measures the change in $[NO_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate 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

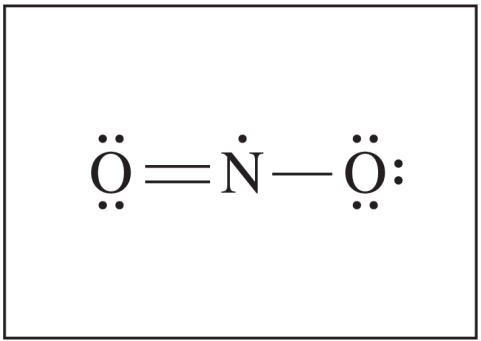
smooth decreasing curve, concave up (linearizing downward but curving), consistent with a non-linear $\ln[NO_2]$ vs. $t$ relationship.]
[Graph 2: $1/[NO_2]$ vs. Time (seconds); y-axis from 0 to 30,000 in increments of 5,000, x-axis 0 to 100 s in increments of 20. Data points (approximately): (0, 5000), (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 $NO_2$.

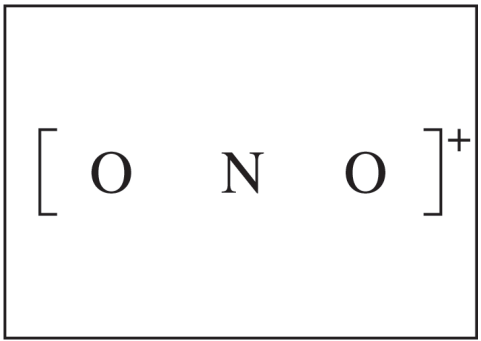
# Question 6


−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

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# 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 $6.52 \times 10^{-7}$ $M$/s.

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

# Question 6

2024 ▪ Q6

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

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# Question 6

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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 3

2023 ▪ Q3

Answer the following questions about an experiment in which $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

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

# Question 3

2023 ▪ Q3

Answer the following questions about an experiment in which $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

**(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 $HCl(aq)$ at $21.2°C$ with 1.00 g of $CaCO_3(s)$ and measures the time required for the reaction to go to completion. The data are given in the following table.

| Trial | Concentration of $HCl(aq)$ (M) | Particle Size of $CaCO_3(s)$ | 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

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$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

**(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 $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

**(d)** The student claims that the reaction is zero order with respect to $HCl(aq)$. 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 $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

**(e)** The $HCl(aq)$ was present in excess in all trials of the experiment. Determine the molarity of the $HCl(aq)$ 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 $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

**(f)**

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In order to measure the enthalpy of the reaction shown, the student repeats trial 1 by mixing 50.0 mL of $HCl(aq)$ with 1.00 g of $CaCO_3(s)$ 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 (°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 $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

**(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 $4.0\ J/(g \cdot {}^\circ C)$.
Calculate the magnitude of heat transfer, $q$, in joules.
**(g)(ii)** Calculate the enthalpy of reaction in units of $kJ/mol_{rxn}$. Include the algebraic sign on your answer.

# Solution 3

**(a)**

**Mark scheme**

- Balanced net ionic equation:
  $CaCO_3(s) + 2\,H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$ (equivalently with hydronium: $CaCO_3(s) + 2\,H_3O^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + 3\,H_2O(l)$).
  State symbols not required.

# Solution 3

**(b)**

**Mark scheme**

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

# Solution 3

## (e) Mark scheme

- Moles of HCl reacted: $1.00$ g $CaCO_3 \times \dfrac{1 \text{ mol}}{100.09 \text{ g}} = 0.00999$ mol $CaCO_3$; $0.00999$ mol $CaCO_3 \times \dfrac{2 \text{ mol HCl}}{1 \text{ mol } CaCO_3} = 0.0200$ mol HCl reacted (1 point). Remaining [HCl]: initial HCl $= 0.0500$ L $\times\ 1.00$ mol/L $= 0.0500$ mol; $0.0500 - 0.0200 = 0.0300$ mol remaining; $\dfrac{0.0300 \text{ mol}}{0.0500 \text{ L}} = 0.600$ *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**

- $q_{sys} = -q_{surr} = -140$ J $= -0.14$ kJ; moles reacted
  $= 1.00$ g $CaCO_3 \times \dfrac{1 \text{ mol } CaCO_3}{100.09 \text{ g } CaCO_3} \times \dfrac{1 \text{ mol}_{rxn}}{1 \text{ mol } CaCO_3} = 0.00999 \text{ mol}_{rxn}$;
  $\Delta H^{\circ}_{rxn} = \dfrac{-0.14 \text{ kJ}}{0.00999 \text{ mol}_{rxn}} = -14 \text{ kJ/mol}_{rxn}$ (include the algebraic sign).