

Past-paper walk-through

Reaction Mechanism and Rate Law ■ 5.8

eXercise

Questions in this set

- 2022 Q5
- 2019 Q6

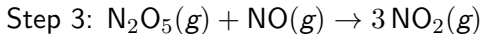
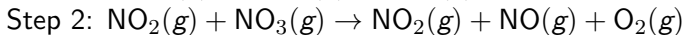
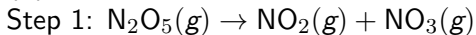
Reading the mark scheme

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

Solution 5

(c)

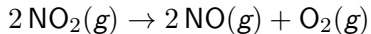
Mark scheme

- 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]

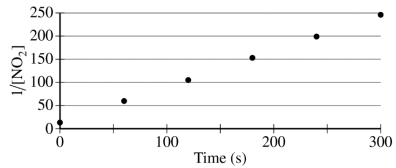
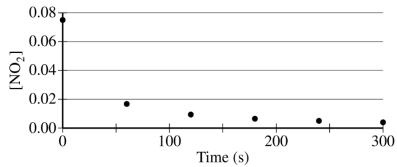
Question 6

[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]

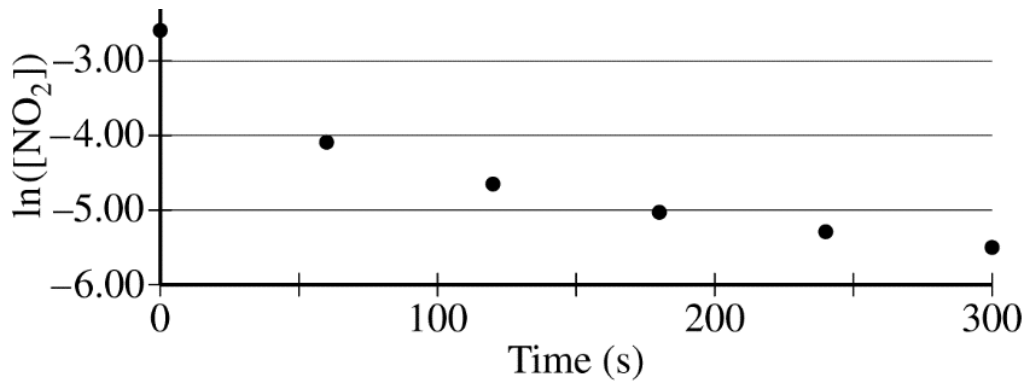
[Graph 3: $\ln([\text{NO}_2])$ (y-axis -6.00 to -2.00) vs. Time (s, x-axis 0 to 300); data points approximately: (0, -2.6), (60, -4.1), (120, -4.6), (180, -5.05), (240, -5.2), (300, -5.4) — a curved, decreasing, concave-up trend]

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

Question 6



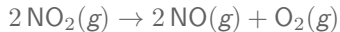
Question 6



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2019 ■ Q6

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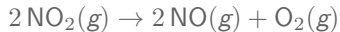
(b) Write the rate law for the decomposition of $\text{NO}_2(g)$.

Consider two possible mechanisms for the decomposition reaction.

Question 6

2019 ■ Q6

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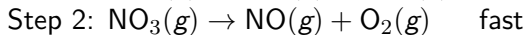
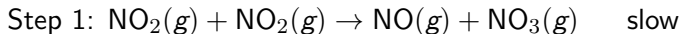
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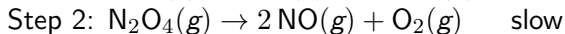
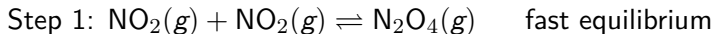
(c)(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

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.