Past-paper walk-through

Pre-Equilibrium Approximation ▪ 5.9

eXercise

Questions in this set

- 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 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.

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

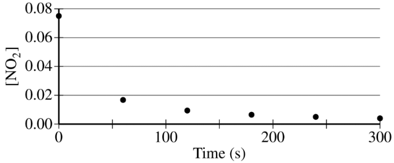
The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.

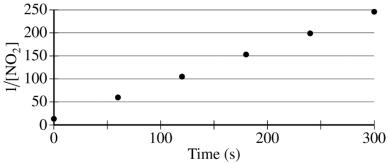
[Graph 1: $[NO_2]$ (mol/L, y-axis 0.00 to 0.08) vs. Time (s, x-axis 0 to 300); data points approximately: (0, 0.075), (60, 0.018), (120, 0.010), (180, 0.008), (240, 0.007), (300, 0.005) — a decaying curve]

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.

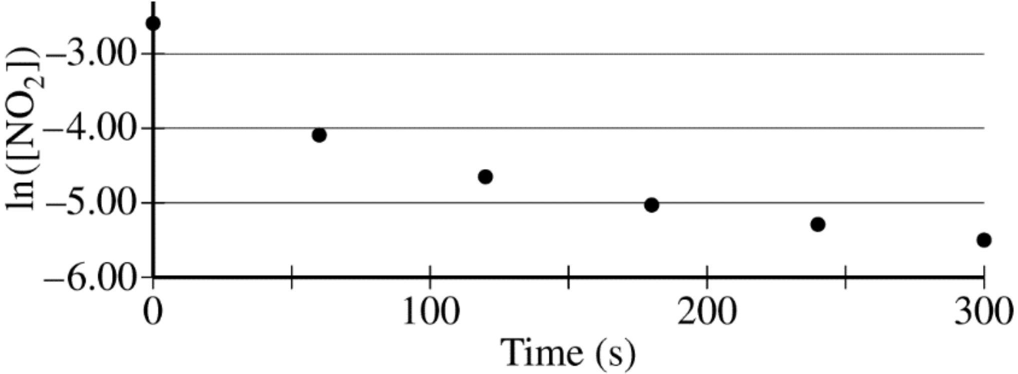
Question 6


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

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Question 6

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

Consider two possible mechanisms for the decomposition reaction.

Question 6

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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

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 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 ($N2O4 \rightarrow 2NO + O2$) is slow and rate-determining, giving rate $=$ k[N2O4]. Since N2O4 is a reaction intermediate, it must be eliminated using the fast pre-equilibrium of step 1: Keq $= [N2O4]/[NO2]^2$, so $[N2O4] = Keq[NO2]^2$. Substituting into the rate law gives rate $= (k \cdot Keq)[NO2]^2$, which is second order in [NO2] and consistent with part (b). 1 point for the correct answer (yes) with this justification.