2019

AP® CollegeBoard

AP® Chemistry

Sample Student Responses and Scoring Commentary

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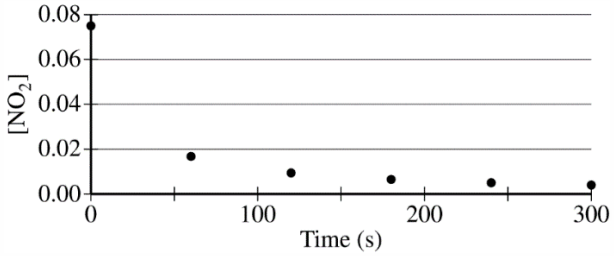
AP® CHEMISTRY
2019 SCORING GUIDELINES

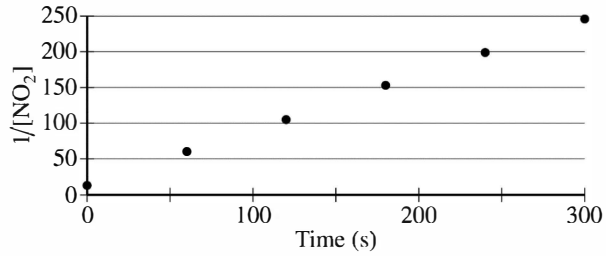
Question 6

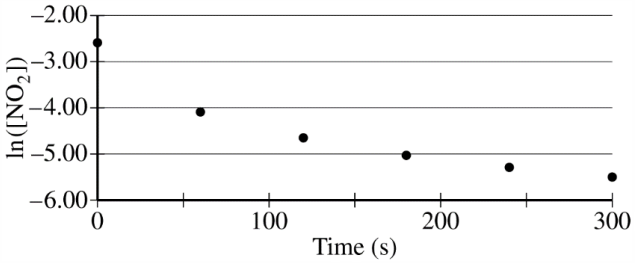
Nitrogen dioxide, $NO_2(g)$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

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

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.







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

The linear graph of $\frac{1}{[NO_2]}$ vs. time indicates a second-order reaction.	1 point is earned for the correct answer.

Question 6 (continued)

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

rate = $k[NO_2]^2$	1 point is earned for the correct answer.

(c) Consider two possible mechanisms for the decomposition reaction.

(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*

Yes. Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[NO_2][NO_2] = k[NO_2]^2$, which is consistent with the second-order rate law in part (b).	1 point is earned for the correct answer with justification.

(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: $NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$ *fast equilibrium*

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

Yes. Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[N_2O_4]$. Because N_2O_4 is an intermediate, it cannot appear in the rate law of the overall reaction. Because $K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$ in step 1, $[N_2O_4] = K_{eq}[NO_2]^2$. Then, substituting $K_{eq}[NO_2]^2$ for $[N_2O_4]$ in the rate law of step 2 gives rate = $(k\,K_{eq})[NO_2]^2$, which is consistent with the rate law in part (b).	1 point is earned for the correct answer with justification.

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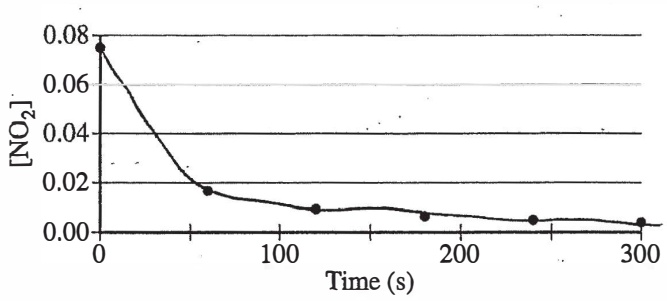
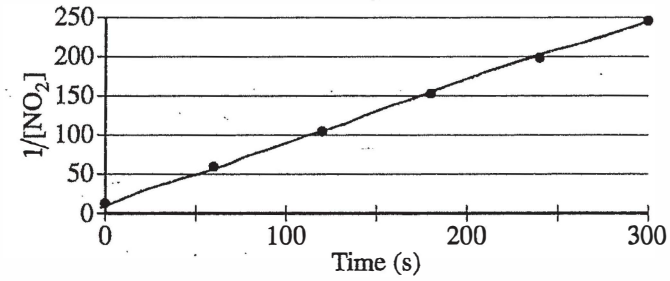
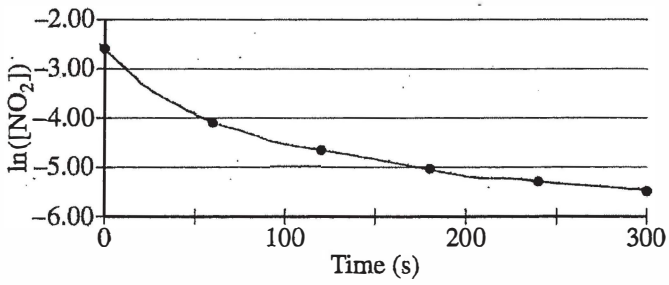
6. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

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

The concentration of a sample of NO2(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.







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

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

(c) Consider two possible mechanisms for the decomposition reaction.

(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*

(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:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\,NO(g) + O_2(g)$	*slow*

6. a) The graph with $1/[NO_2]$ plotted on its y-axis is the most linear, which indicates a second order reaction.

b) Rate = $K[NO_2]^2$

c)i) Yes, the rate law described by mechanism I is consistent with the rate law written in (b) because the rate limiting step is the slow step. The slow step in mechanism I yields a rate of $K[NO_2][NO_2]$ which is equal to $K[NO_2]^2$.

ii) Yes it is because the slow step yields a rate of $K_1[N_2O_4]$. However, N_2O_4 is an intermediate. From the equilibrium equation, we find that rate = $K_2[NO_2][NO_2] = K_3[N_2O_4]$. Using substitution, we find that the rate of the slow step = $\frac{K_1 K_2}{K_3}[NO_2]^2$. Because K, K_1, K_2, and K_3 are all constants, we can define $K = \frac{K_1 K_2}{K_3}$, so we get the rate = $K[NO_2]^2$.

GO ON TO THE NEXT PAGE.

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(c) Consider two possible mechanisms for the decomposition reaction.

(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*

(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:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\,NO(g) + O_2(g)$	*slow*

a) the graph of $1/[NO_2]$ vs. time(s) is a straight line, indicating the reaction is second order

b) rate = $k[NO_2]^2$

c) Yes. The rate law relies on the slow step. In this mechanism the rate law would be rate = $k[NO_2][NO_2]$ which is the same as rate = $k[NO_2]^2$

c) NO. The rate law relies on the slow step. In this mechanism the rate law would be rate = $k[N_2O_4]$, which is not the same as rate = $k[NO_2]^2$

GO ON TO THE NEXT PAGE.

(c) Consider two possible mechanisms for the decomposition reaction.

(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*

(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:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\,NO(g) + O_2(g)$	*slow*

a) The graph that shows $\frac{1}{[NO_2]}$ vs time is in a straight line with a positive slope. This indicates that the reaction is second order. The other two graphs don't show straight lines so it cannot be 0 or 1st order

b) = rate = $k[NO_2]^2$

c) i) Yes, the slow step or rate-determining step is consistant with the rate with respect to NO_2 which is second order

ii) Yes the slow step indicates $[N_2O_4]$ is first order. ~~$[N_2O_4]$ is equal to two NO_2~~ N_2O_4 is not in the rate law however so we need to translate it to terms of NO_2. In step one 1 mol N_2O_4 is equal to 2 mols NO_2 indicating a second order reaction ~~for~~ with respect to NO_2 which is consistent with the rate law.

AP® CHEMISTRY
2019 SCORING COMMENTARY

Question 6

Note: Student samples are written verbatim and may contain spelling and grammatical errors.

Overview

This question focuses on interpreting kinetic data from the conversion of NO_2 into NO and O_2 and evaluating whether a proposed mechanism is consistent with the rate law. Part (a) shows three plots ($[NO_2]$ vs. time, $1/[NO_2]$ vs. time, and $\ln[NO_2]$ vs. time) and asks students to explain how they show that the reaction is second order. Only the plot of $1/[NO_2]$ vs. time is linear, which is a unique characteristic of second-order reactions (LO 4.2; SP 5.1, 6.4).

In part (b) students must use their knowledge of second-order reactions to write a rate law expression for the reaction (LO 4.2; SP 5.1, 6.4). The remainder of Question 6 addresses LO 4.7; SP 6.5. Part (c)(i) provides a possible two-step reaction mechanism with slow and fast steps labeled. The student is asked to indicate whether the mechanism is consistent with the rate law expression that they wrote in part (b) and to justify their answer. Similarly, part (c)(ii) proposes a different two-step mechanism in which the first step is a fast equilibrium and the second step is slow; students must again indicate whether the mechanism is consistent with the rate law expression that they wrote in part (b) and justify their answer.

Sample: 6A
Score: 4

In part (a) the student states that the inverse concentration vs. time graph is linear and identifies this is as a characteristic of a second-order reaction; thus, the point was earned. In part (b) the student's rate law for the decomposition of NO_2 is correct and, therefore, earned the point. In part (c)(i) the student writes that the slow step in a mechanism is the rate-limiting step. The student correctly writes the rate law for step 1 of the mechanism as rate = $k[NO_2][NO_2]$ and states that it is consistent with the experimental rate law written in part (b); thus, the point was earned. In part (c)(ii) the student correctly identifies N_2O_4 as an intermediate in the mechanism and writes a rate law for the slow step as rate = $k[N_2O_4]$. The student correctly notes that for an equilibrium system the rate of the forward reaction equals the rate of the reverse reaction. The student correctly labels all the rate constants and substitutes for $[N_2O_4]$ in the rate expression. The student correctly combines *k*s into a single rate constant, *k*, and notes that the rate law is consistent with the experimental rate law in part (b); thus, the point was earned.

Sample: 6B
Score: 3

In part (a) the student states the inverse concentration vs. time graph is linear and identifies this as a characteristic of a second order reaction. This statement answers the question; thus, 1 point was earned. In part (b) the student's rate law for the decomposition of NO_2 is correct; therefore the response earned 1 point. In part (c)(i) the student writes that the rate law relies on the slow step in a mechanism. The student specifies that in this mechanism, the rate law is rate = $k[NO_2][NO_2]$, which is the same as the rate in part (b); thus, 1 point was earned. In part (c)(ii) the student states incorrectly that the rate law for mechanism II is not consistent with the rate law from part (b). The student does not identify N_2O_4 as an intermediate in the mechanism. The student writes the rate law expression for mechanism II as rate = $k[N_2O_4]$; thus, no point was earned.

Sample: 6C
Score: 2

In part (a) the student states the inverse concentration vs. time graph is a straight line and identifies this as a characteristic of a second-order reaction. The student also points out that the other graphs are not straight lines. These two statements answer the question; thus, 1 point was earned. In part (b) the student's rate law

Question 6 (continued)

for the decomposition of NO_2 is correct; therefore, the response earned 1 point. In part (c)(i) the student writes that the slow step or rate-determining step is consistent with NO_2 being second order. The student does not write the rate law for this mechanism; thus, the point was not earned. In part (c)(ii) the student states that the rate law for mechanism II is first order with respect to $[N_2O_4]$. The student correctly comments that N_2O_4 is not part of the rate law. The student states that 1 mole of N_2O_4 is equal to 2 moles of NO_2. This cannot be used as justification for declaring it a second-order reaction; thus, no point was earned.