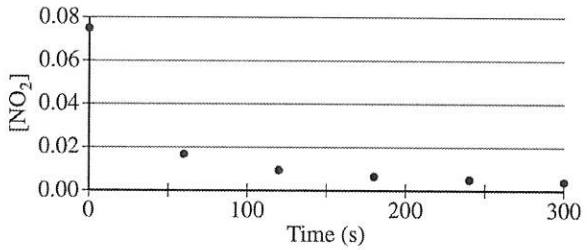
AP® CHEMISTRY
2019 SCORING GUIDELINES

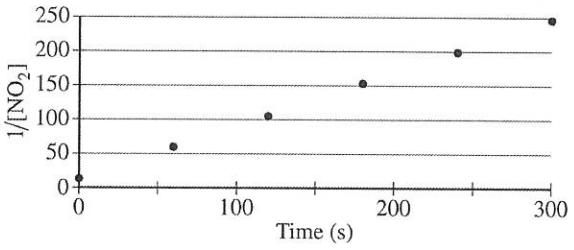
Question 6

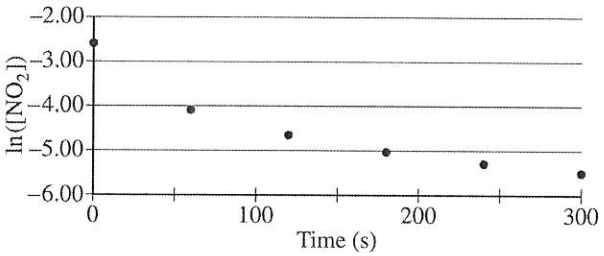
Nitrogen dioxide, $NO_2(g)$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

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

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.

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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.