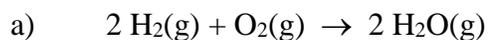Problems - Chapter 19 (with solutions)

1) Define the following terms:

a) catalyst - A substance that speeds up the rate of a reaction without itself being consumed or produced.
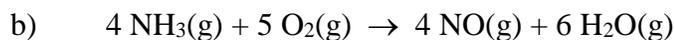
b) half-life - The time it takes for the initial concentration of a reactant to decrease to half (50 %) of its original value.

c) reaction intermediate - A substance that is produced in one step of a reaction mechanism and which is consumed in another step in the mechanism. Reactants, products, and catalysts are not reaction intermediates.

2) (19.10) Write the reaction rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of products.

a) $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$

rate $= -\frac{1}{2} (\Delta[H_2]/\Delta t) = - (\Delta[O_2]/\Delta t = \frac{1}{2} (\Delta[H_2O]/\Delta t)$

b) $4 NH_3(g) + 5 O_2(g) \rightarrow 4 NO(g) + 6 H_2O(g)$

rate $= -\frac{1}{4} (\Delta[NH_3]/\Delta t) = -\frac{1}{5} (\Delta[O_2]/\Delta t) = \frac{1}{4} (\Delta[NO]/\Delta t) = \frac{1}{6} (\Delta[H_2O]/\Delta t)$

3) Consider the reaction

$2 N_2O(g) \rightarrow 2 N_2(g) + O_2(g)$

a) Express the rate of reaction with respect to each of the reactants and products.

rate $= -\frac{1}{2} (\Delta[N_2O]/\Delta t) = \frac{1}{2} (\Delta[N_2]/\Delta t) = \Delta[O_2]/\Delta t$

b) In the first 15.0 s of the reaction, 0.015 mol of O_2 is produced in a reaction vessel with a volume of 0.500 L. What is the average rate of the reaction over this time interval (including correct units)?

The concentration of O_2 produced is

$\Delta[O_2] = \underline{0.015 \text{ mol}} = 0.030 \text{ mol/L}$
$\qquad\quad 0.500 \text{ L}$

average rate $= \underline{\Delta[O_2]} = \underline{0.030 \text{ mol/L}} = 0.0020 \text{ mol/L}\cdot\text{s}$
$\qquad\qquad\quad \Delta t \qquad 15.0 \text{ s}$

4) A reaction in which A, B, and C react to form products is zero order in A, second order in B, and first order in C.

a) Write a rate law for the reaction.

rate = k[B]^2[C]

b) What is the overall order of the reaction?

Overall order = 0 + 2 + 1 = 3rd order

c) By what factor does the reaction rate change if [A] is doubled, and the other reactants are held constant?

No change

d) By what factor does the reaction rate change if [B] is doubled, and the other reactants are held constant?

Rate increases by 2^2 = 4 times faster.

e) By what factor does the reaction rate change if [C] is doubled, and the other reactants are held constant?

Rate increases by 2^1 = 2 times faster.

f) By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

Rate increases by $2^0 2^2 2^1$ = 8 times faster.

5) (19.19) The rate law for the reaction

NH_4^+(aq) + NO_2^-(aq) → N_2(g) + 2 H_2O(ℓ)
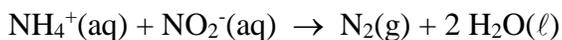
is

rate = k [NH_4^+] [NO_2^-]

At T = 25. °C, k = 3.0 x 10^{-4} L/mol•s. Find the rate of reaction when [NH_4^+] = 0.36 mol/L and [NO_2^-] = 0.075 mol/L.

rate = (3.0 x 10^{-4} L/mol•s) (0.36 mol/L) (0.075 mol/L) = 8.1 x 10^{-6} mol/L•s

6) (19.30) The thermal decomposition of phosphine (PH_3) into phosphorus and molecular hydrogen is a first order reaction

$$4 \ PH_3(g) \ \rightarrow \ P_4(g) + 2 \ H_2(g)$$

The half-life of the reaction is $t_{1/2} = 35.0$ s at $T = 680.$ °C. Find the following:

a) The first order rate constant for the reaction.

To calculate the rate constant, k, from the half-life of a first-order reaction, we use the relationship

$$t_{1/2} = \frac{\ln(2)}{k}$$

$$k = \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{35.0s} = 0.0198 \ s^{-1}$$

b) The time required for 95.0 % of the initial phosphine to disappear.

The relationship between the concentration of a reactant at different times in a first-order reaction is given in the text. We are asked to determine the time required for 95% of the phosphine to decompose. If we initially have 100% of the compound and 95% has reacted, then what is left must be $(100\% - 95\%)$, or 5%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is,

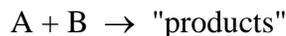$$[A]_t/[A]_0 = (5 \ \% \ / \ 100 \ \%), \text{ or } 0.05/1.00 = 0.050$$

The time required for 95% of the phosphine to decompose can be found using

$$\ln\{[A]_t/[A]_0\} = - \ kt$$

Solving for t gives

$$t = - \ (1/k) \ \ln([A]_t/[A]_0) = - \ \frac{\ln 0.050}{0.0198 \ s^{-1}} = 151. \ s$$

7) Consider the reaction

$$A + B \rightarrow \text{"products"}$$

Initial rate data, obtained at T = 360. K, are given below.

Trial	$[A]_0$ (mol/L)	$[B]_0$ (mol/L)	Initial Rate (mol/L·min)
1	0.0100	0.0100	3.6×10^{-5}
2	0.0200	0.0100	14.6×10^{-5}
3	0.0100	0.0200	7.0×10^{-5}

Find the following:

a) The order of the reaction with respect to A and with respect to B.

We assume a rate law of the form rate = $k[A]^p[B]^q$.

To find the reaction order for A we can compare trials 2 and 1

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{14.6 \times 10^{-5} \text{ mol/L·min}}{3.6 \times 10^{-5} \text{ mol/L·min}} = \frac{k[A_2]^p[B_2]^q}{k[A_1]^p[B_1]^q} = \frac{k(0.02000 \text{ M})^p(0.0100 \text{ M})^q}{k(0.0100 \text{ M})^p(0.0100 \text{ M})^q}$$

The term $k(0.0100 \text{ M})^q$ appears in both the numerator and denominator, and so cancels, leaving

$$(14.6 \times 10^{-5}/3.6 \times 10^{-5}) = (0.0200/0.0100)^p$$

$$4.06 = 2^p \qquad p = 2$$

To find the reaction order for B we can compare trials 3 and 1

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{7.0 \times 10^{-5} \text{ mol/L·min}}{3.6 \times 10^{-5} \text{ mol/L·min}} = \frac{k[A_3]^p[B_3]^q}{k[A_1]^p[B_1]^q} = \frac{k(0.01000 \text{ M})^p(0.0200 \text{ M})^q}{k(0.0100 \text{ M})^p(0.0100 \text{ M})^q}$$

The term $k(0.0100 \text{ M})^p$ appears in both the numerator and denominator, and so cancels, leaving

$$(7.0 \times 10^{-5}/3.6 \times 10^{-5}) = (0.0200/0.0100)^q$$

$$1.94 = 2^q \qquad q = 1$$

Notice that we have picked p and q as the integer values that give the best agreement with the experimental results.

Our rate law, therefore, is rate = $k[A]^2[B]$ (second order in A, first order in B, third order overall.

b) The rate constant for the reaction (including correct units).

If we solve our rate law for k, we get

$$k = \frac{rate}{[A]^2[B]}$$

Using the data from the first trial, we get

$$k = \frac{(3.6 \text{ x } 10^{-5} \text{ mol/L} \cdot \text{min})}{(0.0100 \text{ M})^2(0.0100 \text{ M})} = 36.0 \text{ L}^2/\text{mol}^2 \cdot \text{min}$$

Note that if we calculated k from one of the other trials we would get a slightly different value (36.5 $L^2/\text{mol}^2 \cdot$min for trial 2, 35.0 $L^2/\text{mol}^2 \cdot$min for trial 3). If this was a real experiment we would take the average of the three experimental values. On an exam, however, you can just pick one data set to calculate k.

c) The initial rate of the reaction when $[A]_0 = 0.01500$ M, $[B]_0 = 0.0300$ M.

rate = $k[A]^2[B]$ = (36.0 $L^2/\text{mol}^2 \cdot$min)(0.0150 M)^2(0.0300 M)
$$= 20.2 \text{ x } 10^{-5} \text{ mol/L} \cdot \text{min}$$

8) The data below show the concentration of N_2O_5 verses time for the reaction

$$N_2O_5(g) \rightarrow NO_3(g) + NO_2(g)$$

time (s)	$[N_2O_5]$ (M)	time (s)	$[N_2O_5]$ (M)
0.0	1.000	125.0	0.377
25.0	0.822	150.0	0.310
50.0	0.677	175.0	0.255
75.0	0.557	200.0	0.210
100.0	0.458		

a) Determine the order of the reaction, the value for the rate constant (including correct units), and the half-life for the reaction.

The general procedure used in these types of problems is as follows:

1) plot ln (concentration) vs time. A straight line means a 1st order reaction.
2) plot 1/(concentration) vs time. A straight line means a 2nd order reaction.
3) plot concentration vs time. A straight line means a 0th order reaction.

If none of these gives a straight line, then the reaction order is different than 1st, 2nd, or 0th order. (Note that there are more general methods that can be used to determine the experimental order, but they have not been discussed in the book and so will not be discussed here).

The values needed to do the necessary plots are given in the table below.

time	[N$_2$O$_5$]	ln [N$_2$O$_5$]	1/[N$_2$O$_5$]
0.	1.000	0.000	1.000
25.	0.822	- 0.196	1.217
50.	0.677	- 0.390	1.477
75.	0.557	- 0.585	1.795
100.	0.458	- 0.781	2.183
125.	0.377	- 0.976	2.653
150.	0.310	- 1.171	3.226
175.	0.255	- 1.366	3.922
200.	0.210	- 1.561	4.762

I will give all of the plots discussed above, though usually we would plot them in order, as suggested above, and stop if a linear plot was found.
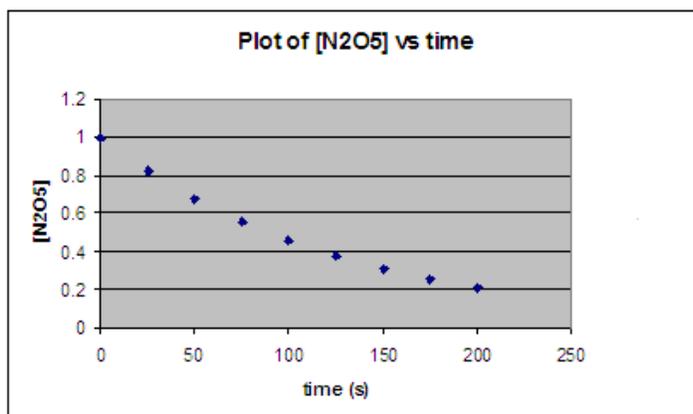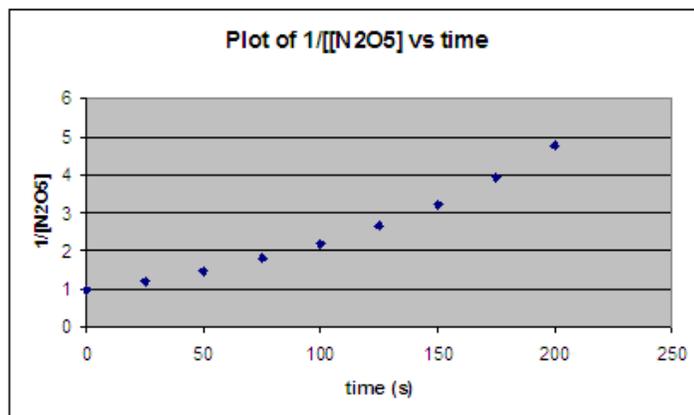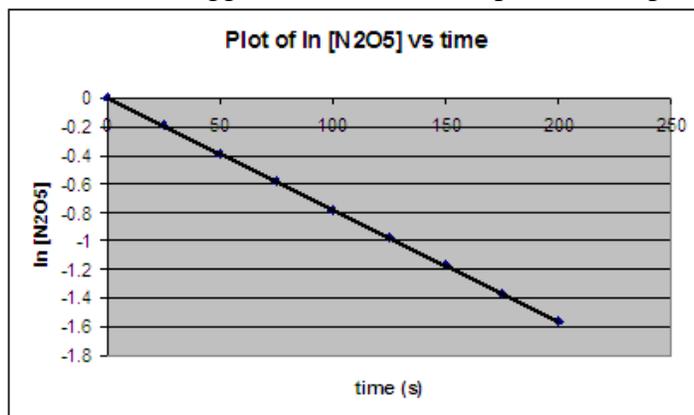
Note that of the three plots the only one that gives a linear relationship is the plot of ln $[N_2O_5]$ vs time. Therefore the reaction is <u>first order</u>. So k = - (slope)

Based on fitting the data in the plot of ln $[N_2O_5]$ vs time, I get

slope = - 0.0078 s^{-1}

So k = - (slope) = 0.0078 s^{-1}

b) Predict the concentration of N_2O_5 at 250.0 s.

At t = 250. s,

$[N_2O_5]_t$ = $[N_2O_5]_0$ exp [(- 0.0078 s^{-1}) (250. s)] = (1.000 mol/L) e$^{-1.95}$

$[N_2O_5]$ = (1.000 mol/L) (0.142) = 0.142 mol/L

9) (19.32) The reaction

2 NO$_2$(g) → 2 NO(g) + O$_2$(g)
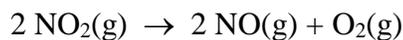
is second order in NO$_2$ and second order overall. The rate constant for the reaction at T = 300. °C is k = 0.54 L/mol·s. How long (in seconds) will it take for the concentration of NO$_2$ to decrease from 0.65 mol/L to 0.18 mol/L?

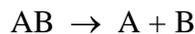The reaction is second order in NO$_2$, and so

$$\frac{1}{[NO_2]_t} = \frac{1}{[NO_2]_0} + kt$$

{ (1/$[NO_2]_t$) - (1/$[NO_2]_0$) } = kt

or   t = (1/k) { (1/$[NO_2]_t$) - (1/$[NO_2]_0$) }

$$= \frac{1}{0.54 \text{ L/mol·s}} \{ (1/0.18 \text{ mol/L}) - (1/0.65 \text{ mol/L}) \} = 7.4 \text{ s}$$

10) The following reaction was monitored as a function of time

$$AB \rightarrow A + B$$

A plot of 1/[AB] vs time yields a straight line with slope m = 0.055 L/mol·s.

a) What is the value of the rate constant, k, (including correct units) for this reaction at this temperature?

The plot of 1/[AB] vs time gives a straight line. Therefore, the reaction is second order, and so k = 0.055 L/mol·s.

b) Write the rate law for the reaction.

$$\text{rate} = k \,[AB]^2 \text{ also } [AB]_t = \frac{[AB]_0}{1 + kt \,[AB]_0}$$

c) What is the half-life when the initial concentration is 0.55 mol/L?

For a second order reaction $t_{1/2} = 1/k[AB]_0$.

So $t_{1/2} = \dfrac{1}{(0.055 \text{ L/mol·s}) \,(0.55 \text{ mol/L})} = 33.1 \text{ s}$

d) If the initial concentration of AB is 0.250 mol/L, and the reaction initially contains no products, what are the concentrations of A and B after 75.0 s?

$$[AB] = \frac{(0.250 \text{ mol/L})}{1 + (0.055 \text{ L/mol·s}) \,(75 \text{ s}) \,(0.250 \text{ mol/L})} = 0.123 \text{ mol/L}$$

Since no A or B were initially present in the system, the concentration of these species at t = 75. s is the same as the concentration of AB that has disappeared. Therefore

$$[A] = [B] = [\,0.250 \text{ M} - 0.123 \text{ M}\,] = 0.127 \text{ M}$$

11) The diagram below shows the energy of the reaction as the reaction progresses. Label each of the following in the diagram (reactants, products, activation energy, enthalpy of reaction). Also, is the reaction exothermic or endothermic? How do you know?

The figure, with labels, is given below. Since energy decreases as we go from reactants to products, the reaction is exothermic ($\Delta H_{rxn} < 0$)
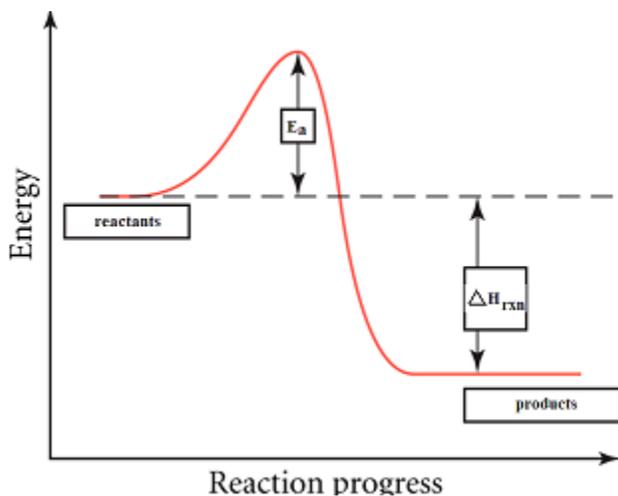
12) (19.49) Rate constants are given for the first order reaction

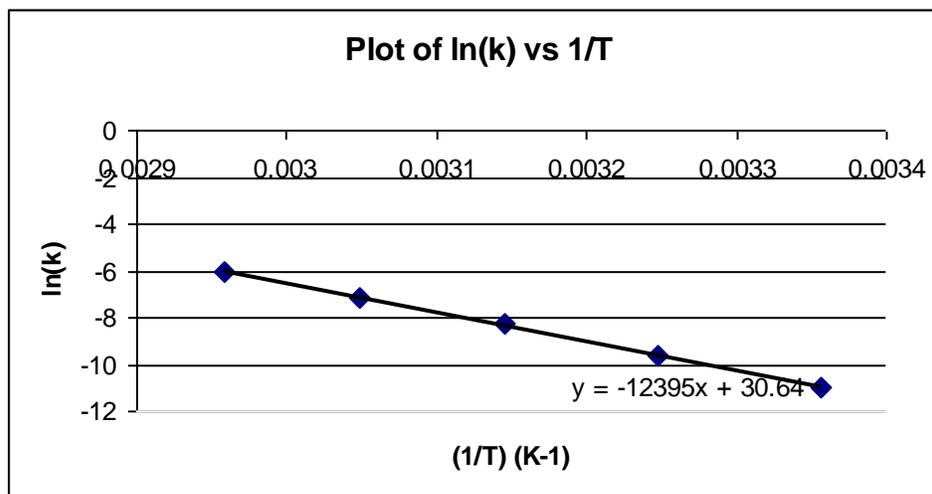$$2\ N_2O_5(g) \rightarrow 2\ N_2O_4(g) + O_2(g)$$

in the following table. Determine graphically the activation energy and pre-exponential factor for the reaction (including correct units).

T (K)	k (s^{-1})	T (K)	k (s^{-1})
298.	1.74 x 10^{-5}	328.	7.59 x 10^{-4}
308.	6.61 x 10^{-5}	338.	2.40 x 10^{-3}
318.	2.51 x 10^{-4}		

If we assume the Arrhenius equation applies, then we need to plot ln(k) vs 1/T. The data are given below

T (K)	1/T (K^{-1})	k(s^{-1})	ln(k)
298.	0.003356	1.74 x 10^{-5}	- 10.959
308.	0.003247	6.61 x 10^{-5}	- 9.624
318.	0.003145	2.51 x 10^{-4}	- 8.290
328	0.003049	7.59 x 10^{-4}	- 7.184
338.	0.002959	2.40 x 10^{-3}	- 6.032

The data are plotted below.

Plot of ln(k) vs 1/T

$y = -12395x + 30.64$

Axis labels: ln(k) (vertical), (1/T) (K-1) (horizontal)

Based on the best fitting line to the data, I get

slope = - E_a/R = - 12395. K E_a = - R(slope) = - (8.314 J/mol•K)(- 12395 K)

$$= 1.03 \times 10^5 \text{ J/mol} = 103. \text{ kJ/mol}$$

intercept = ln(A) = 30.64 $A = e^{30.64} = 2.0 \times 10^{13}$ s^{-1}.

Notice that A has the same units as the rate constant. This will always be true.

13) For a particular reaction k = 2.6 x 10^{-4} L/mol•s at T = 300. K, and k = 5.3 x 10^{-2} L/mol•s at T = 350. K. What are E_a and A, the activation energy and pre-exponential factor for the reaction?

To do this problem we can use the relationship

$$\ln(k_2/k_1) = - (E_a/R) [(1/T_2) - (1/T_1)]$$

Solving for E_a gives

$$E_a = - \frac{R \ln(k_2/k_1)}{[(1/T_2) - (1/T_1)]} = - \frac{(8.314 \text{ J/mol•K}) \ln(5.3 \times 10^{-2}/2.6 \times 10^{-4})}{[(1/350. \text{ K}) - (1/300 \text{ K})]}$$

$$= 9.28 \times 10^4 \text{ J/mol} = 92.8 \text{ kJ/mol}$$

Since from the Arrhenius equation k = A exp(-E_a/RT), then A = k exp(E_a/RT)

(Notice the sign change in the exponential term when we move it to the other side)

If we use the rate constant at T = 300. K, we get

$$A = (2.6 \times 10^{-4} \text{ L/mol} \cdot \text{s}) \exp[(9.28 \times 10^4 \text{ J/mol})/(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})]$$

$$= 3.8 \times 10^{12} \text{ L/mol} \cdot \text{s}$$

14) (19.44) The rate constant for a particular first order reaction is $k = 4.60 \times 10^{-4}$ s^{-1} at T = 350. °C. If the activation energy for the reaction is $E_a = 104.0$ kJ/mol, find the temperature where the rate constant is $k = 8.80 \times 10^{-4}$ s^{-1}.

To do this problem we can use the relationship

$$\ln(k_2/k_1) = - (E_a/R) [(1/T_2) - (1/T_1)]$$

We will let $T_1 = 350.$ °C = 623. K, $k_1 = 4.6 \times 10^{-4}$ s^{-1}, and $k_2 = 8.8 \times 10^{-4}$ s^{-1}
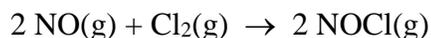
$$[(1/T_2) - (1/T_1)] = - (R/E_a) \ln(k_2/k_1)$$

$$(1/T_2) = (1/T_1) - (R/E_a) \ln(k_2/k_1)$$

$$= (1/623. \text{ K}) - [(8.314 \text{ J/mol} \cdot \text{K})/(104000. \text{ J/mol}] \ln[(8.8 \times 10^{-4})/(4.6 \times 10^{-4})]$$

$$= 1.605 \times 10^{-3} \text{ K}^{-1} - 5.18 \times 10^{-5} \text{ K}^{-1} = 1.553 \times 10^{-3} \text{ K}^{-1}$$

And so $T_2 = (1/1.553 \times 10^{-3} \text{ K}^{-1}) = 644.$ K = 371. °C

15) The rate law for the reaction

$$2 \text{ NO(g)} + \text{Cl}_2\text{(g)} \rightarrow 2 \text{ NOCl(g)}$$
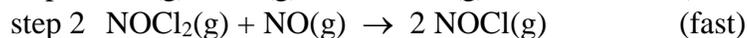
is given by the expression rate = k [NO][Cl$_2$].

a) What is the overall order of the reaction?

Overall reaction order is $1 + 1 = 2^{nd}$ order overall.

b) One proposed mechanism for the above reaction is the following:

|	
step 1 NO(g) + Cl$_2$(g) $\rightarrow$ NOCl$_2$(g)	(slow)
step 2 NOCl$_2$(g) + NO(g) $\rightarrow$ 2 NOCl(g)	(fast)

Is the above mechanism consistent with the proposed rate law? Explain

For the proposed mechanism the overall rate of reaction will be the rate of the slow step, and so

rate $= k_1$ [NO][Cl$_2$]

which is first order in NO and first order in Cl$_2$. This is the same as the experimental reaction orders, and so the mechanism is consistent with the experimental data. Note that this does not prove the mechanism is correct, as there could be other mechanisms that lead to a rate law with the same reaction orders.
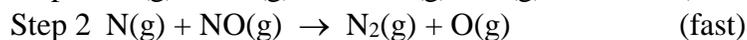
16) (19.63) The rate law for the reaction

2 H$_2$(g) + 2 NO(g) → N$_2$(g) + 2 H$_2$O(g)
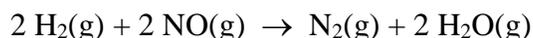
is rate $= k$ [H$_2$][NO]^2.

Which of the following is a possible mechanism for the reaction (Hint: Find the rate law corresponding to each mechanism, and see whether or not it agrees with the experimental rate law.)
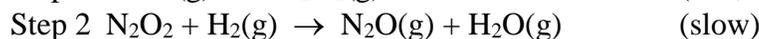
Mechanism I

Step 1 H$_2$(g) + NO(g) → H$_2$O(g) + N(g)   (slow)
Step 2 N(g) + NO(g) → N$_2$(g) + O(g)   (fast)
Step 3 O(g) + H$_2$(g) → H$_2$O(g)   (fast)

Mechanism II

Step 1 H$_2$(g) + 2 NO(g) → N$_2$O(g) + H$_2$O(g)   (slow)
Step 2 N$_2$O(g) + H$_2$(g) → N$_2$(g) + H$_2$O(g)   (fast)

Mechanism III

Step 1 2 NO(g) ↔ N$_2$O$_2$(g)   (fast, reversible)
Step 2 N$_2$O$_2$ + H$_2$(g) → N$_2$O(g) + H$_2$O(g)   (slow)
Step 3 N$_2$O(g) + H$_2$(g) → N$_2$(g) + H$_2$O(g)   (fast)

Mechanism I.   In Mechanism I the slow step is bimolecular and the rate law would be:
            rate $= k_1$ [H$_2$][NO]

Mechanism I can be discarded.

<u>Mechanism II</u>. The rate-determining step in Mechanism II involves the simultaneous collision of two NO molecules with one H_2 molecule. The rate law would be:

$$\text{rate} = k_1 [H_2][NO]^2$$

Mechanism II is a possibility.

<u>Mechanism III</u>. In Mechanism III the slow step is bimolecular and involves collision of a hydrogen molecule with a molecule of N_2O_2. The rate would be:

$$\text{rate} = k_2 [H_2][N_2O_2]$$

But $[N_2O_2]$ is a reaction intermediate. We may use the first step in the mechanism to find an expression for $[N_2O_2]$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = (k_1/k_{-1})[NO]^2$$

Substituting for $[N_2O_2]$ in the expression obtained from the slow step gives

$$\text{rate} = k_2[H_2](k_1/k_{-1})[NO]^2 = k[H_2][NO]^2 \;\; ; k = (k_1k_2)/k_{-1}$$

Mechanism III is also a possibility. We would need to do further experiments to decide if either of these mechanisms was actually the correct one for the reaction.