

# Kinetics Problem Set

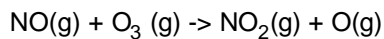
S.E. Van Bramer 1/14/96

## 1. Reaction Rates and Rate laws

For the following reaction:

$i := 0..4$

$ms := 10^{-3} \cdot sec$



$t_{NO_i} :=$

$C_{NO_i} :=$

$t_{O_3_i} :=$

$C_{O_3_i} :=$

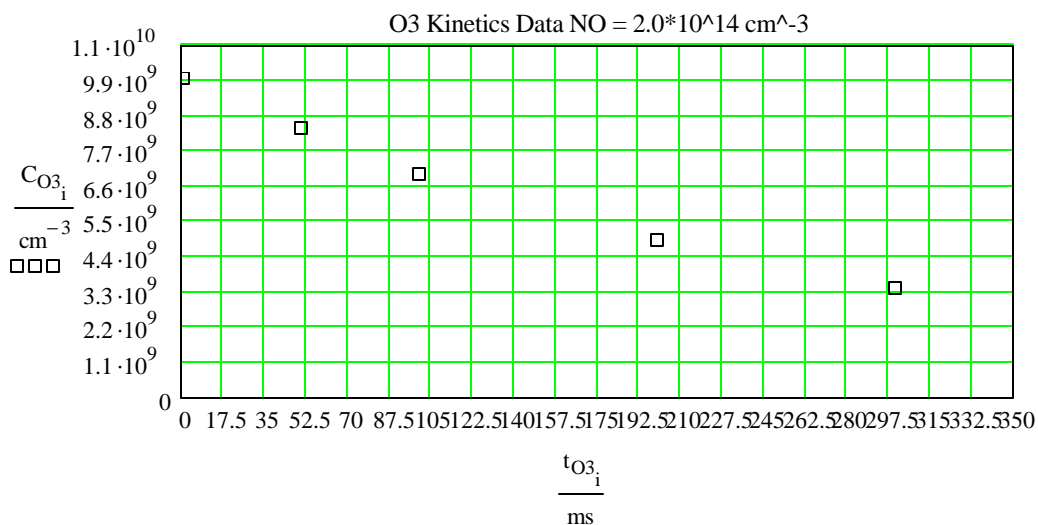
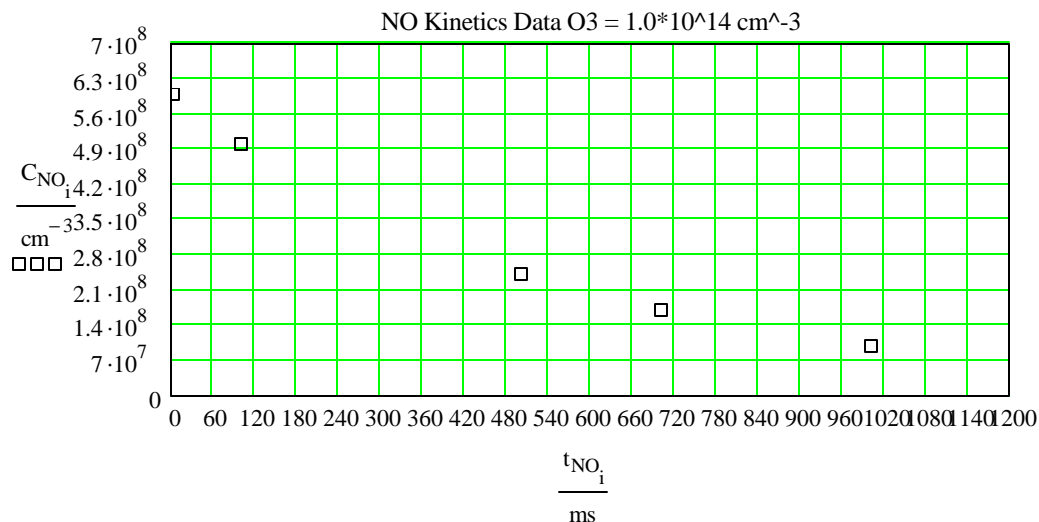
0·ms
100·ms
500·ms
700·ms
1000·ms

$6.0 \cdot 10^8 \cdot cm^{-3}$
$5.0 \cdot 10^8 \cdot cm^{-3}$
$2.4 \cdot 10^8 \cdot cm^{-3}$
$1.7 \cdot 10^8 \cdot cm^{-3}$
$9.9 \cdot 10^7 \cdot cm^{-3}$

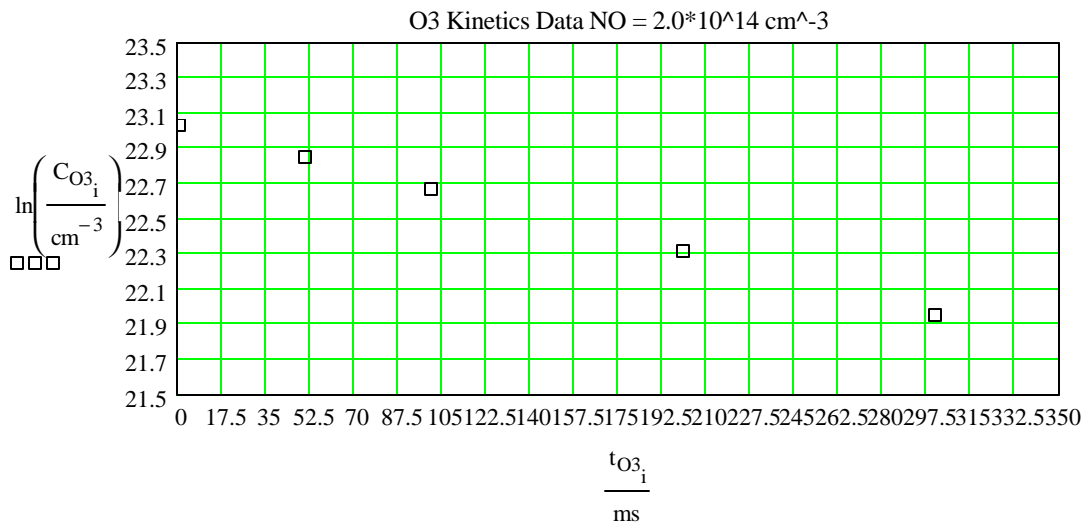
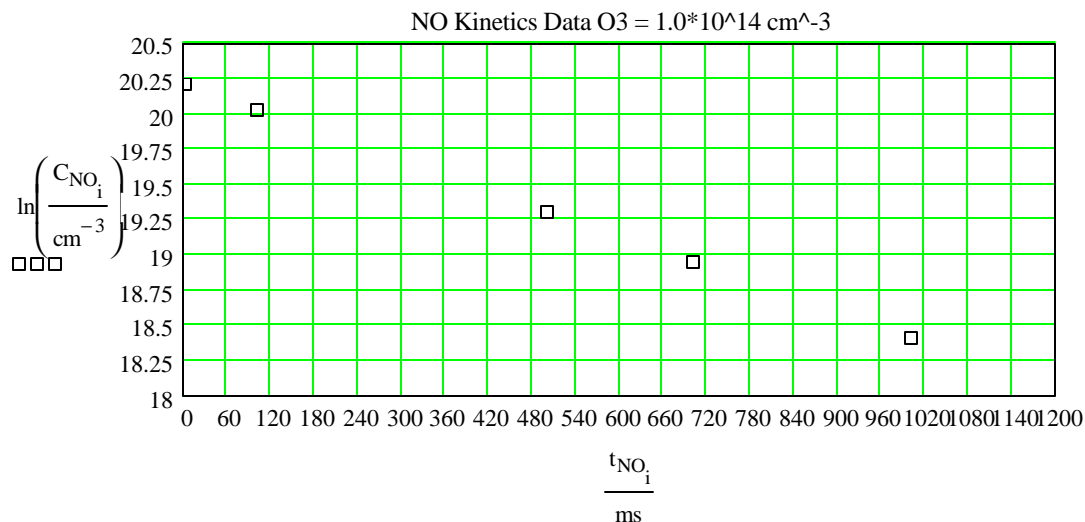
0·ms
50·ms
100·ms
200·ms
300·ms

$1.0 \cdot 10^{10} \cdot cm^{-3}$
$8.4 \cdot 10^9 \cdot cm^{-3}$
$7.0 \cdot 10^9 \cdot cm^{-3}$
$4.9 \cdot 10^9 \cdot cm^{-3}$
$3.4 \cdot 10^9 \cdot cm^{-3}$

a. Graph each data set.



b. Graph ln[] vs time.



c. Determine the average rate for the reaction, between each data point.

j := 0, 1.. 3

$$\text{rateNO}_j := \frac{C_{\text{NO}_j} - C_{\text{NO}_{j+1}}}{t_{\text{NO}_{j+1}} - t_{\text{NO}_j}} \quad \text{rateNO} = \begin{pmatrix} 1 \times 10^9 \\ 6.5 \times 10^8 \\ 3.5 \times 10^8 \\ 2.367 \times 10^8 \end{pmatrix} \text{cm}^{-3} \cdot \text{sec}^{-1}$$

$$\text{rateO3}_j := \frac{C_{\text{O3}_j} - C_{\text{O3}_{j+1}}}{t_{\text{O3}_{j+1}} - t_{\text{O3}_j}} \quad \text{rateO3} = \begin{pmatrix} 3.2 \times 10^{10} \\ 2.8 \times 10^{10} \\ 2.1 \times 10^{10} \\ 1.5 \times 10^{10} \end{pmatrix} \text{cm}^{-3} \cdot \text{sec}^{-1}$$

d. Use your graph to determine the instantaneous reaction rate at 250 ms.

Find the slope from the concentration vs time graph. Your value should be approximately:

$$\text{NO} = 7 \times 10^8 \text{ cm}^{-3} \text{ sec}^{-1}$$

$$\text{O}_3 = 1.5 \times 10^{10} \text{ cm}^{-3} \text{ sec}^{-1}$$

e. Given that the reaction is first order in NO and in O<sub>3</sub>, determine the rate constant using your calculated rate for each set of data points

If the reaction is first order for NO and O<sub>3</sub> the rate equation is:

$$\text{rate} = k \cdot C_{\text{NO}} \cdot C_{\text{O}_3}$$

For the NO experiment:

$$C_{\text{O}_3\_a} := 1.0 \cdot 10^{14} \cdot \text{cm}^{-3}$$

$$k_{\text{NO}_j} := \frac{\text{rate}_{\text{NO}_j}}{\left( \frac{C_{\text{NO}_j} + C_{\text{NO}_{j+1}}}{2} \right) \cdot C_{\text{O}_3\_a}}$$

$$k_{\text{NO}} = \begin{pmatrix} 1.818 \times 10^{-14} \\ 1.757 \times 10^{-14} \\ 1.707 \times 10^{-14} \\ 1.76 \times 10^{-14} \end{pmatrix} \text{cm}^3 \cdot \text{sec}^{-1}$$

For the O<sub>3</sub> experiment:

$$C_{\text{NO}_a} := 2.0 \cdot 10^{14} \cdot \text{cm}^{-3}$$

$$k_{\text{O}_3_j} := \frac{\text{rate}_{\text{O}_3_j}}{\left( \left( \frac{C_{\text{O}_3_j} + C_{\text{O}_3_{j+1}}}{2} \right) \right) \cdot C_{\text{NO}_a}}$$

$$k_{\text{O}_3} = \begin{pmatrix} 1.739 \times 10^{-14} \\ 1.818 \times 10^{-14} \\ 1.765 \times 10^{-14} \\ 1.807 \times 10^{-14} \end{pmatrix} \text{cm}^3 \cdot \text{sec}^{-1}$$

f. Use the  $\ln[\ ]$  vs time graph to determine the rate constant.

Since the  $\ln$  concentration vs time graph is linear the reaction is first order for each of these. Note that in each experiment the "other" reagent is in large excess. So that for the first experiment where  $[O_3] = 1.0 \times 10^{14}$  and the  $[NO]$  is measured with time. Because  $O_3$  is in large excess its concentration is unchanged (for all practical purposes). So the reaction is "pseudo" first order in  $NO$  under these conditions. Likewise for  $O_3$  in the second experiment.

The pseudo first order rate constant is determined from the slope of the  $\ln[\ ]$  vs time graph.  
For the  $NO$  kinetics experiment:

$$x := t_{NO}$$

$$y_i := \ln \left( \frac{C_{NO_i}}{cm^{-3}} \right)$$

$$\text{slope} = k \cdot C_{O_3\_a}$$

$$k_{NO} := \frac{-\text{slope}(x,y)}{C_{O_3\_a}}$$

$$k_{NO} = 1.802 \times 10^{-14} \text{ cm}^3 \cdot \text{sec}^{-1}$$

For the  $O_3$  kinetics experiment:

$$x := t_{O_3}$$

$$y_i := \ln \left( \frac{C_{O_3_i}}{cm^{-3}} \right)$$

$$\text{slope} = k \cdot C_{NO\_a}$$

$$k_{O_3} := \frac{-\text{slope}(x,y)}{C_{NO\_a}}$$

$$k_{O_3} = 1.799 \times 10^{-14} \text{ cm}^3 \cdot \text{sec}^{-1}$$

$$k := \frac{1}{2} \cdot k_{NO} + \frac{1}{2} \cdot k_{O_3}$$

g. What is the overall rate law?

Notice that both experiments give essentially the same rate constant: So that the rate equation is:

$$\text{rate} = 1.80 \cdot 10^{-14} \cdot \frac{\text{cm}^3}{\text{sec}} \cdot C_{NO} \cdot C_{O_3}$$

h. Convert the units of the rate constant to moles, liters, and seconds.

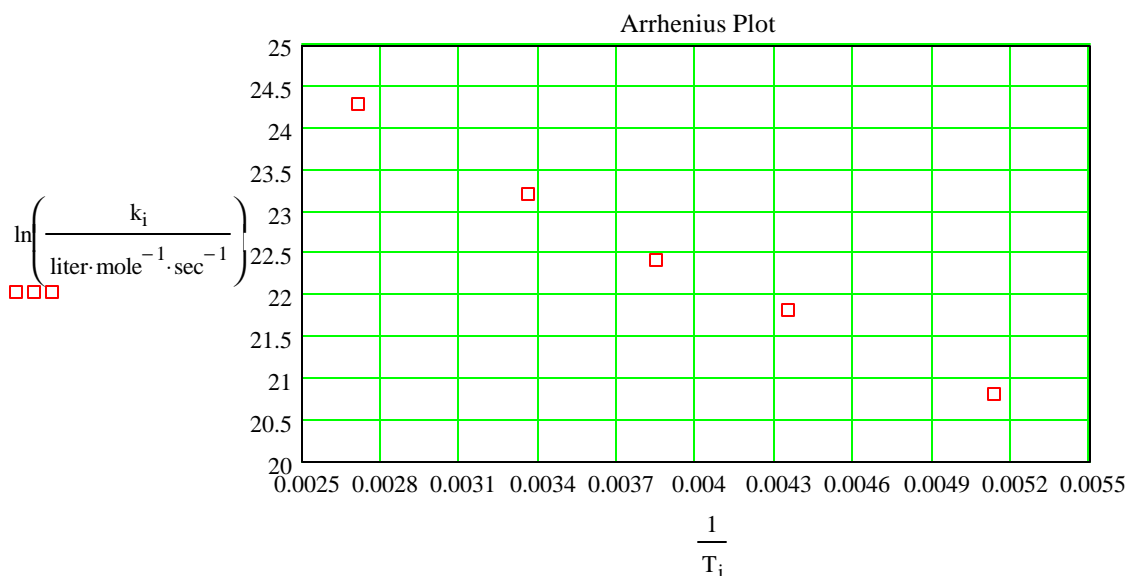
$$k = 1.8 \times 10^{-14} \text{ cm}^3 \cdot \text{sec}^{-1}$$

$$1.8 \cdot 10^{-14} \cdot \text{cm}^3 \cdot \text{sec}^{-1} \cdot (6.02 \cdot 10^{23} \cdot \text{mole}^{-1}) \cdot \left( \frac{1 \cdot \text{liter}}{10^3 \cdot \text{cm}^3} \right) = 1.084 \times 10^7 \text{ liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$

2. Given the following kinetics data for the above reaction:

$T_i :=$	$k_i :=$
195 K	$1.08 \cdot 10^9 \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$
230 K	$2.95 \cdot 10^9 \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$
260 K	$5.42 \cdot 10^9 \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$
298 K	$12.0 \cdot 10^9 \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$
369 K	$35.5 \cdot 10^9 \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$

a. Graph this data as  $\ln(k)$  vs  $1/T$ .



b. Determine the activation energy and the preexponential factor from the graph.  $x := 0 \quad y := 0$

$$x_i := \frac{1}{T_i}$$

$$y_i := \ln\left(\frac{k_i}{\text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}}\right)$$

$$R := 8.314 \cdot \text{joule} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$E_a := -\text{slope}(x, y) \cdot R \qquad E_a = 1.194 \times 10^4 \text{ mole}^{-1} \text{ joule}$$

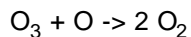
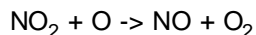
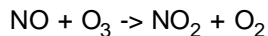
$$A := e^{\text{intercept}(x, y)} \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \qquad A = 1.553 \times 10^{12} \text{ liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$

c. What is the rate constant at 150 K?

$$T := 150 \text{ K}$$

$$k_{150} := A \cdot e^{-\frac{E_a}{R \cdot T}} \qquad k_{150} = 1.082 \times 10^8 \text{ liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$

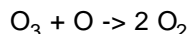
For the above reaction mechanism with several additional steps as shown below:



a. Which species is a catalyst? NO is the catalyst (not consumed by the reaction)

b. Which species is an intermediate? NO<sub>2</sub> is the intermediate

c. How does this catalyst effect the rate of the reaction shown below. E<sub>a</sub> = 11.9 kJ for the catalyzed reaction and E<sub>a</sub> = 14.0 kJ for the uncatalyzed reaction. Calculate the change in the reaction rate at 200, 250, and 300 K



Catalyzed by NO  $E_{a_1} := 11.9 \cdot 10^3 \cdot \text{joule} \cdot \text{mole}^{-1}$

If NOT Catalyzed by NO  $E_{a_2} := 14.0 \cdot 10^3 \cdot \text{joule} \cdot \text{mole}^{-1}$

From the Arrhenius equation

$$\text{Rate} = A \cdot e^{-\frac{E_a}{R \cdot T}}$$

To find a ratio of the rates:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{A \cdot e^{-\frac{E_a}{R \cdot T}}}{A \cdot e^{-\frac{E_a}{R \cdot T}}}$$

Simplifies to:

$$\text{ratio} = e^{\frac{E_{a_2} - E_{a_1}}{R \cdot T}}$$

Solves as:

$$T := 200 \cdot \text{K} \quad \text{ratio} := e^{\frac{E_{a_2} - E_{a_1}}{R \cdot T}} \quad \text{ratio} = 3.536$$

$$T := 250 \cdot \text{K} \quad \text{ratio} := e^{\frac{E_{a_2} - E_{a_1}}{R \cdot T}} \quad \text{ratio} = 2.747$$

$$T := 300 \cdot \text{K} \quad \text{ratio} := e^{\frac{E_{a_2} - E_{a_1}}{R \cdot T}} \quad \text{ratio} = 2.321$$

d. Draw an energy level diagram for this reaction, with and without catalysis. See figure 15.17 on page 735 in Kotz for a similar diagram.

e. For the catalytic destruction of O<sub>3</sub> by Cl E<sub>a</sub> = 2.1 kJ, Compare the reaction rate for the uncatalyzed reaction and the Cl catalyzed reaction at 250 K.

For the same reaction Catalyzed by Cl  $E_{a_1} := 2.1 \cdot 10^3 \cdot \text{joule} \cdot \text{mole}^{-1}$

$$T := 250 \cdot \text{K} \quad \text{ratio} := e^{\frac{E_{a_2} - E_{a_1}}{R \cdot T}} \quad \text{ratio} = 306.52$$