Solutions to:
Kinetics Homework Problem Set

S.E. Van Bramer

1. The following experimenat data was collected for the reaction at 198 K.

$$2\,N_2O_5 \;\text{-->}\; 4\,NO_2 + O_2$$

a. What is the average rate of N2O5 loss and the average rate of the reaction between 1.0 and 1.1 seconds? Assume the reaction is zero order and calculate the rate constant (k) using this value. Assume the reaction is first order and calculate the rate constant (k) using this value. Assume the reaction is second order and calculate the rate constant (k) using this value.

$$rate_{N2O5} := \frac{9.340\times 10^{-4}\cdot mole\cdot liter^{-1} - 8.908\cdot 10^{-4}\cdot mole\cdot liter^{-1}}{1.1\cdot sec - 1.0\cdot sec}$$

$$rate_{N2O5} = 4.32\times 10^{-4}\,mole\cdot liter^{-1}\cdot sec^{-1}$$

$$rate_{rxn} := \frac{1}{2}\cdot rate_{N2O5}$$

$$rate_{rxn} = 2.16\times 10^{-4}\,mole\cdot liter^{-1}\cdot sec^{-1}$$

$$N2O5\_avg := \frac{9.340\cdot 10^{-4}\cdot mole\cdot liter^{-1} + 8.908\cdot 10^{-4}\cdot mole\cdot liter^{-1}}{2}$$

Assume zero order:

$$k := \frac{rate_{rxn}}{N2O5\_avg^{0}}$$

$$k = 2.16\times 10^{-4}\,mole\,sec^{-1}\,liter^{-1}$$

Assume first order:

$$k := \frac{rate_{rxn}}{N2O5\_avg^{1}}$$

$$k = 0.23674\,sec^{-1}$$

Assume second order:

$$k := \frac{rate_{rxn}}{N2O5\_avg^{2}}$$

$$k = 259.46764\,sec^{-1}\,mole^{-1}\,liter$$

a. What is the average rate of N2O5 loss and the average rate of the reaction between 5.0 and 5.1 seconds? Assume the reaction is zero order and calculate the rate constant (k) using this value. Assume the reaction is first order and calculate the rate constant (k) using this value. Assume the reaction is second order and calculate the rate constant (k) using this value.

$$rate_{N2O5} := \frac{1.404\times 10^{-4}\cdot mole\cdot liter^{-1} - 1.339\cdot 10^{-4}\cdot mole\cdot liter^{-1}}{5.1\cdot sec - 5.0\cdot sec}$$

$$rate_{N2O5} = 6.5\times 10^{-5}\, mole\cdot liter^{-1}\cdot sec^{-1}$$

$$rate_{rxn} := \frac{1}{2}\cdot rate_{N2O5}$$

$$rate_{rxn} = 3.25\times 10^{-5}\, mole\cdot liter^{-1}\cdot sec^{-1}$$

$$N2O5\_avg := \frac{1.404\cdot 10^{-4}\cdot mole\cdot liter^{-1} + 1.399\cdot 10^{-4}\cdot mole\cdot liter^{-1}}{2}$$

Assume zero order:

$$k := \frac{rate_{rxn}}{N2O5\_avg^{0}}$$

$$k = 3.25\times 10^{-5}\, mole\, sec^{-1}\, liter^{-1}$$

Assume first order:

$$k := \frac{rate_{rxn}}{N2O5\_avg^{1}}$$

$$k = 0.23189\, sec^{-1}$$

Assume second order:

$$k := \frac{rate_{rxn}}{N2O5\_avg^{2}}$$

$$k = 1.65462\times 10^{3}\, sec^{-1}\, mole^{-1}\, liter$$

Based upon the answers the reaction is first order. Because when we assumed that the reaction was first order the rate constant (k) was the same for both problems. When we assumed that the reaction was zero order or second order, the rate constant (k) was very different for the two problems.

e. Graphic analysis of rate consnstant. Graph the data to check if it is zero order, first order, and second order. Using these graphs determine the rate constant (k).

$i := 0, 1 .. 7$

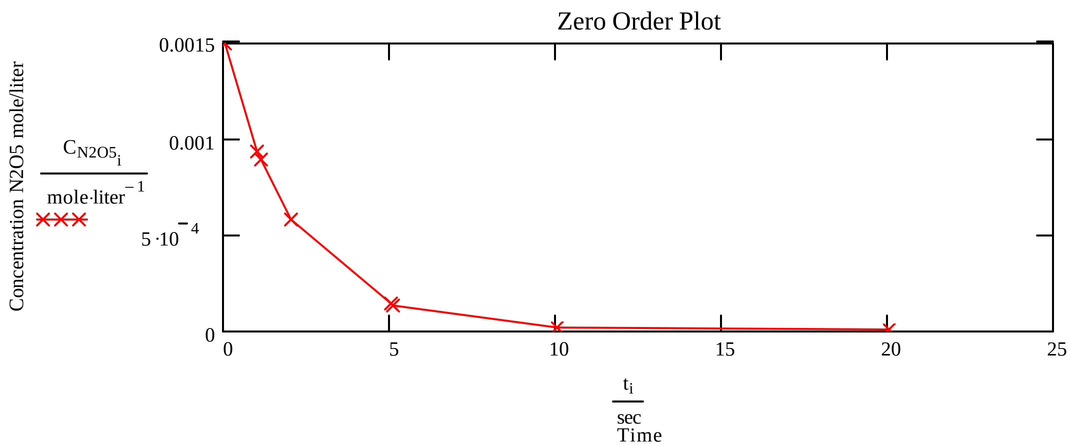
$t_i :=$

$0 \cdot sec$
$1 \cdot sec$
$1.1 \cdot sec$
$2 \cdot sec$
$5 \cdot sec$
$5.1 \cdot sec$
$10 \cdot sec$
$20 \cdot sec$

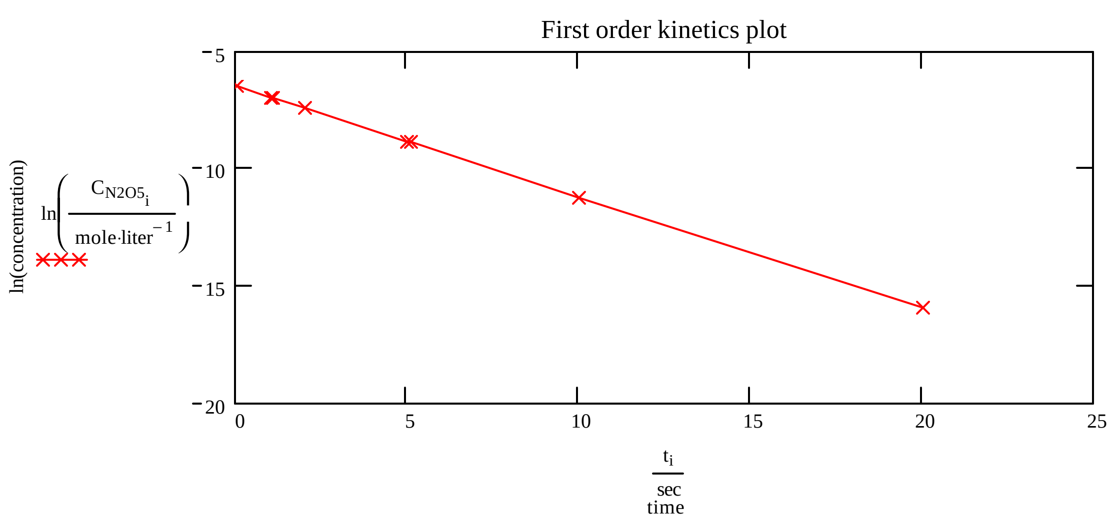
$C_{N2O5_i} :=$

$1.500 \cdot 10^{-3} \cdot mole \cdot liter^{-1}$
$9.340 \cdot 10^{-4} \cdot mole \cdot liter^{-1}$
$8.908 \cdot 10^{-4} \cdot mole \cdot liter^{-1}$
$5.816 \cdot 10^{-4} \cdot mole \cdot liter^{-1}$
$1.404 \cdot 10^{-4} \cdot mole \cdot liter^{-1}$
$1.339 \cdot 10^{-4} \cdot mole \cdot liter^{-1}$
$1.315 \cdot 10^{-5} \cdot mole \cdot liter^{-1}$
$1.152 \cdot 10^{-7} \cdot mole \cdot liter^{-1}$

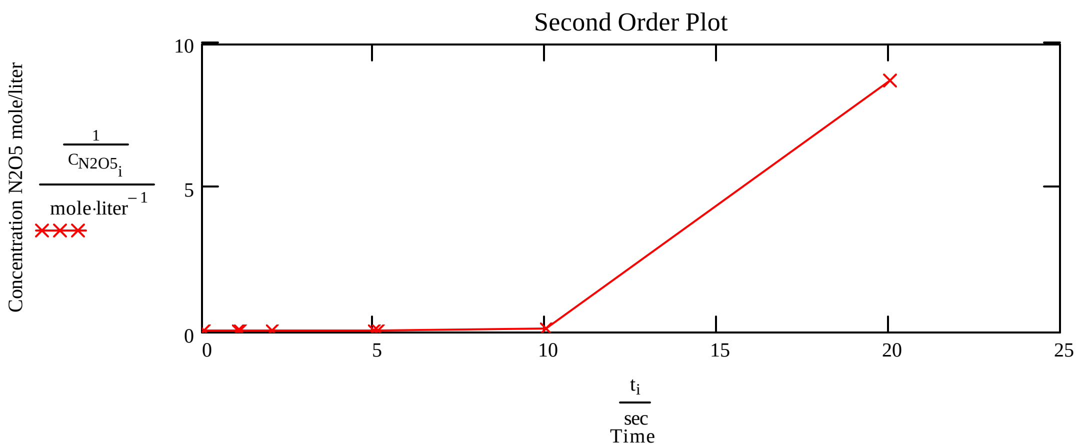
Zero Order Plot



First Order Plot



Second Order Plot



Since the first order (ln vs t) plot is linear, the rate constant for N2O5 is the slope of the plot. The rate constant for the reaction is the 1/2 slope of the above plot. The 1/2 comes from the stoiciometry of the balanced equation:

$$y_i := \ln\left(\frac{C_{N2O5_i}}{\text{mole}\cdot\text{liter}^{-1}}\right) \qquad x_i := t_i$$

$$k := -\left(\frac{1}{2}\cdot\text{slope}(x,y)\right)$$

$$k = 0.23685\,\text{sec}^{-1}$$

Note this is the same value as obtained above.

f. Assume that the reaction is second order. Graph the data to show if this assumption is correct and if so use the graph to determine the rate constant.

2. The above experiment is repeated at several temperatures to obtain the following experimental data:

a. Based upon this experimental data, determine the activation energy for this reaction and the preexponential factor.

The activation energy and preexponential may be determined using any two of these data points. If you have access to a spreadsheet, a linear regression may be used to include all of the data points (this is ideal, but not practical for an exam)

Recall the Arrhaneous equation:

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

This experiment is preformed at two temperatures (T) to find two rate constants (k):

$$T_1 := (273 + 0) \cdot K \qquad k_1 := 9.16 \cdot 10^{-3} \cdot sec^{-1}$$

$$T_2 := (273 + 70) \cdot K \qquad k_2 := 25.017 \cdot sec^{-1}$$

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

From the Arrhaneous equation

$$k_1 = A \cdot e^{-\frac{E_a}{R \cdot T_1}} \qquad k_2 = A \cdot e^{-\frac{E_a}{R \cdot T_2}}$$

These may be combined into one equation by dividing both sides so that :

$$\frac{k_1}{k_2} = \frac{A \cdot e^{-\frac{E_a}{R \cdot T_1}}}{A \cdot e^{-\frac{E_a}{R \cdot T_2}}}$$

Which simplifies to:

$$\frac{k_1}{k_2} = \exp\left[-E_a \cdot \frac{\left(T_2 - T_1\right)}{\left[R \cdot \left(T_1 \cdot T_2\right)\right]}\right]$$

Substitute in known values and solve for Ea:

$$E_a := \frac{-\ln\left(\frac{k_1}{k_2}\right)}{\left[\frac{1}{(R\cdot T_1)} - \frac{1}{(R\cdot T_2)}\right]}$$

$$E_a = 8.79996\times 10^4\ \text{joule}\cdot\text{mole}^{-1}$$

Now substitute this back in to either equation and solve for A

$$k_1 = A\cdot e^{-\frac{E_a}{R\cdot T_1}}$$

$$A := \frac{k_1}{\exp\left[\frac{-E_a}{(R\cdot T_1)}\right]}$$

$$A = 6.309\times 10^{14}\ \text{sec}^{-1}$$

Alternatively using graphical methods the solution is found by graphing ln(k) vs 1/T. The slope of this is the activation energy and the intercept is the prexponential factor. This relationship is derived from the Arrhaneus equation as follows:

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

$$\ln(k) = \ln\left(A\cdot e^{-\frac{E_a}{R\cdot T}}\right)$$

$$\ln(k) = \ln(A) + \ln\left(e^{-\frac{E_a}{R\cdot T}}\right)$$

$$\ln(k) = \ln(A) - \left(\frac{1}{R\cdot T}\right)\cdot E_a$$

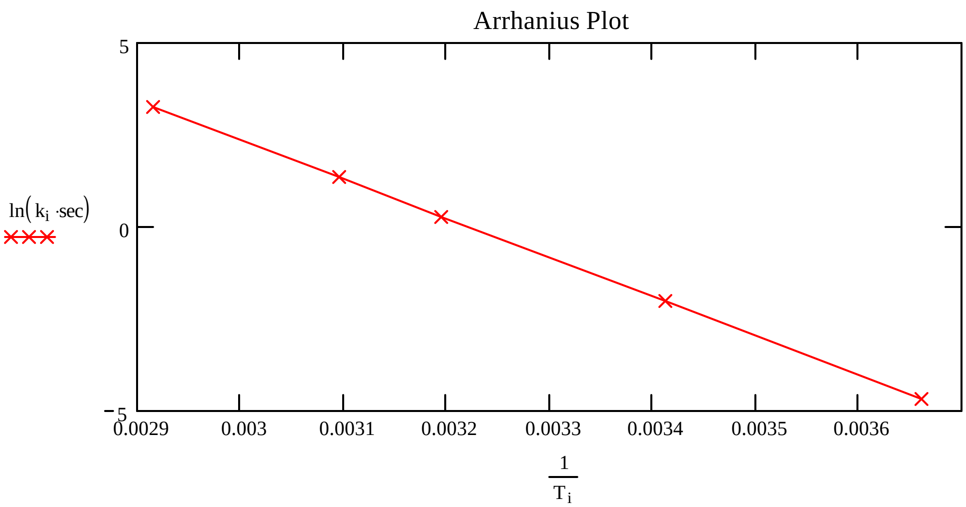
$$\ln(k) = \ln(A) - \left(\frac{E_a}{R}\right)\cdot\left(\frac{1}{T}\right)$$

This has the form y=mx + b where
- x axis is 1/T
- y axis is ln(k)
- y intercept is ln(A)
- slope is -Ea/R

$i := 0, 1 .. 4$ $T_i :=$ $k_i :=$ $x := 0$

$y := 0$

T_i	k_i
$273.15 \cdot K$	$9.16 \cdot 10^{-3} \cdot sec^{-1}$
$293.15 \cdot K$	$0.12919 \cdot sec^{-1}$
$313.15 \cdot K$	$1.2993 \cdot sec^{-1}$
$323.15 \cdot K$	$3.7017 \cdot sec^{-1}$
$343.15 \cdot K$	$25.017 \cdot sec^{-1}$



$x_i := \frac{1}{T_i}$ $R := 8.134 \cdot joule \cdot K^{-1} \cdot mole$

$y_i := \ln(k_i \cdot sec)$

$E_a := -slope(x, y) \cdot R$ $E_a = 8.61796 \times 10^4 \, mole^2 \, joule \cdot mole^{-1}$

$A := e^{intercept(x, y)} \cdot sec^{-1}$ $A = 6.41821 \times 10^{14} \, sec^{-1}$

3. Using the constants determined above if the initial concentration of N_2O_5 is 3.0 x 10^{-4} M

$$C_{initial} := 3.0\cdot 10^{-4}\cdot mole\cdot liter^{-1}$$

i. What is the concentration of NO2 and N2O5 after 5 seconds at 10 C?

$$T := (273 + 10)\cdot K$$

$$t := 5\cdot sec$$

$$k := A\cdot e^{-\frac{E_a}{R\cdot T}}$$

$$k\_N2O5 := 2\cdot k \qquad k\_N2O5 = 0.07068\,sec^{-1}$$

From the integrated rate equation find the concentration of N2O5

$$\ln\left(\frac{C_{initial}}{C_t}\right) = k\_N2O5\cdot t$$

$$C_t := \frac{C_{initial}}{\exp(k\_N2O5\cdot t)}$$

$$C_t = 2.10692\times 10^{-4}\,mole\cdot liter^{-1}$$

The concentration of NO2:

$$C_{NO2} := 2\cdot\left(C_{initial} - C_t\right)$$

$$C_{NO2} = 1.78616\times 10^{-4}\,mole\cdot liter^{-1}$$

i. What is the concentration of NO2 and N2O5 after 5 seconds at 20 C?

$$T := (273 + 20) \cdot K$$

$$t := 5 \cdot sec$$

$$k := A \cdot e^{-\frac{E_a}{R \cdot T}}$$

$$k\_N2O5 := 2 \cdot k \qquad k\_N2O5 = 0.25363\,sec^{-1}$$

From the integrated rate equation find the concentration of N2O5

$$C_t := \frac{C_{initial}}{\exp(k\_N2O5 \cdot t)}$$

$$C_t = 8.44061 \times 10^{-5}\,mole \cdot liter^{-1}$$

The concentration of NO2:

$$C_{NO2} := 2 \cdot \left(C_{initial} - C_t\right)$$

$$C_{NO2} = 4.31188 \times 10^{-4}\,mole \cdot liter^{-1}$$