## ChemQuest 44



## Information: First Order Reactions with One Reactant

As we consider what affects the rate of reactions it is desirable to examine how the concentration of a reactant changes with time. Let us consider reactions that have only one reactant and we will further restrict our considerations to first order reactants. As an example, consider the following reaction:

$$
\mathrm{SO}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{SO}_{2}+\mathrm{Cl}_{2}
$$

Table 1: Experimental data for the decomposition of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$

| Time (s) | $\left[\mathbf{S O}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}\right]$ |
| :---: | :---: |
| 0 | 0.0250 |
| 60 | 0.0228 |
| 120 | 0.0208 |
| 180 | 0.0190 |

It can be shown that the natural log of the concentration of a first order reactant varies directly with the time. So in this case $\ln \left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right]$ varies in direct proportion to the time.

1. Using the above data, prove on the graph below that $\ln \left[\mathbf{S O}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}\right]=-\mathbf{k t}+\boldsymbol{\operatorname { l n }}\left[\mathbf{S O}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}\right]_{0}$ is a straight line when graphed. Note the expression $\left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right]_{0}$ is the concentration of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ at a time of zero seconds. Label the axes.


Calculate $\ln \left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right]$ values and plot:

| Time | $\ln \left[\mathbf{S O}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}\right]$ |
| :---: | :---: |
| 0 | -3.689 |
| 60 | -3.781 |
| 120 | -3.873 |
| 180 | -3.963 |

2. Given this relationship between concentration and time $\left(\ln \left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right]=-\mathrm{kt}+\ln \left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right]_{0}\right)$, find the rate constant k .
Choose values to plug into equation; I'll use at time 120:

$$
\ln (0.0208)=-\mathrm{k}(120)+\ln (0.0250) \rightarrow \mathrm{k}=0.001531 / \mathrm{s}
$$

3. Find the half-life for this reaction. What this means is that you need to find the time it takes for half of the reactant to get used up.

Find the time $(\mathrm{t})$ when $\left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right]=1 / 2(0.0250)=0.0125$

$$
\ln (0.0125)=-(0.00153)(\mathrm{t})+\ln (0.0250) \rightarrow \mathrm{t}=453 \text { seconds }
$$

## Information: Second Order Reactions with One Reactant

Consider the following reaction: $2 \mathrm{NO}_{2} \rightarrow 2 \mathrm{NO}+\mathrm{O}_{2}$. The following experimental data was gathered for this reaction:

Table 2: Experimental data for the decomposition of $\mathrm{NO}_{2}$

| Time (s) | $\left[\mathbf{N O}_{2}\right]$ |
| :---: | :---: |
| 0 | 0.0370 |
| 45 | 0.0338 |
| 90 | 0.0311 |
| 135 | 0.0288 |

If you attempted a plot of $\ln$ vs. $t$ as you did in question 2 above you would not get a straight line. Instead, for second order reactants, the inverse of the concentration varies directly with time.

## Critical Thinking Questions

4. Using the following graph and the above data, prove that the following equation yields a straight line.

5. What is the value of the rate constant, k , for this reaction?

$$
1 / 0.0311=\mathrm{k}(90)+1 / 0.0370 \rightarrow \mathrm{k}=0.05701 / \mathrm{Ms}
$$

6. Find the half-life for this reaction.

Need to find the time, t , when $\left[\mathrm{NO}_{2}\right]=1 / 2(0.0370)=0.0185 \mathrm{M}$
$1 / 0.0185=(0.0570)(\mathrm{t})+1 / 0.0370 \rightarrow \mathrm{t}=474 \mathrm{~s}$

## Skill Practice Question

7. Given the following reaction and table of experimental data, answer the following questions.

| $2 \mathrm{~N}_{2} \mathrm{O}_{5} \rightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}$ |  |
| :---: | :---: |
| Time $(\mathbf{s})$ | $\left[\mathbf{N}_{\mathbf{2}} \mathbf{O}_{\mathbf{5}}\right]$ |
| 0 | 0.0200 |
| 100 | 0.0169 |
| 200 | 0.0142 |
| 300 | 0.0120 |
| 400 | 0.0101 |
| 500 | 0.0086 |
| 600 | 0.0072 |
| 700 | 0.0061 |

a) Is the reaction $1^{\text {st }}$ order or second order with respect to $\mathrm{N}_{2} \mathrm{O}_{5}$ ? How do you know?

It is $1^{\text {st }}$ order because the data fits the equation $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]=-\mathrm{kt}+\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{0}$ much more closely than it fits the $2^{\text {nd }}$ order equation.
b) What is the value for the rate constant?

Using $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]=-\mathrm{kt}+\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{0}$ and plugging in data $\ldots$ $\ln (0.0086)=-\mathrm{k}(500)+\ln (0.0200) \rightarrow \mathrm{k}=0.00171 / \mathrm{s}$
c) What is the half life for this reaction?

$$
\ln (0.0100)=-(0.0017)\left(\mathrm{t}_{1 / 2}\right)+\ln (0.0200) \rightarrow \mathrm{t}=408 \mathrm{~s}
$$

d) How many seconds are required for the concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ to reach a level of 0.0025 M ?

$$
\ln (0.0025)=-(0.0017)(\mathrm{t})+\ln (0.0200) \rightarrow 1223 \mathrm{~s}
$$

