CH302 Unit7 Day5 Activity- Chemical Kinetics Name: $\qquad$ LaBrake/Vanden Bout Spring 2013

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The purpose of this activity is to develop concepts of chemical kinetics: Specifically to deepen your understanding and familiarity with some integrated rate equations.

Complete the following table for the reactions in which the rate law depends on the concentration of A for the following:

|  | 0 order | $1^{\text {st }}$ order | $2^{\text {nd }}$ order |
| :---: | :--- | :--- | :--- |
| Rate law | Rate $=k$ | Rate $=k[\mathrm{~A}]$ | Rate $=\mathrm{k}[\mathrm{A}]^{2}$ |
| Integrated rate | $[\mathrm{A}]=[\mathrm{A}]_{0}-\mathrm{kt}$ | $[\mathrm{A}]_{\mathrm{l}}=[\mathrm{A}]_{\mathrm{o}} \mathrm{e}^{\mu t}$ <br> $\ln [\mathrm{~A}]_{\mathrm{c}}=-\mathrm{kt}+\ln [\mathrm{A}]_{0}$ | $1 /[\mathrm{A}]=1 /[\mathrm{A}]_{0}+\mathrm{kt}$ |
| Half life | $t_{1 / 2}=\frac{[A]_{0}}{2 k}$ | $t_{1 / 2}=\frac{\ln (2)}{k}$ | $t_{1 / 2}=\frac{1}{k[A]_{0}}$ |


|  | 0 order | $1^{\text {st }}$ order | $2^{\text {nd }}$ order |
| :--- | :--- | :--- | :--- |
| Plot to determine the <br> order of a reaction. <br> Determine what <br> should be plotted on <br> the y-axis for each <br> type of rate law. <br> Time will be on the <br> x- axis for each. <br> Sketch the plot that <br> gives the straight <br> line, and indicates <br> the order of the rate <br> law. |  | $\ln [\mathrm{A}]$ vs. t | $\frac{1}{[\mathrm{~A}]}$ vs. t |
| Slope of line plotted <br> will equal what? | -k |  |  |



1. The decomposition of $\mathrm{N}_{2} \mathrm{O}$ follows first-order kinetics. This means

$$
\mathrm{N}_{2} \mathrm{O}(g) \rightarrow \mathrm{N}_{2}(g)+\frac{1}{2} \mathrm{O}_{2}(g)
$$

(the rate of decomposition of $\mathrm{N}_{2} \mathrm{O}$ ) $=\mathrm{k}\left[\mathrm{N}_{2} \mathrm{O}\right.$ ]
If an initial sample has a concentration of 0.20 M , what is the concentration after 100 ms given the rate constant for this reaction is $\mathrm{k}=3.4 \mathrm{~s}^{-1}$ (at $780^{\circ} \mathrm{C}$ )?
$[\mathrm{A}](\mathrm{t})=[\mathrm{A}]_{0} \mathrm{e}^{-\mathrm{kt}}$
$[\mathrm{A}]=(0.2 \mathrm{M}) \mathrm{e}^{-(3.4)(0.1)}$
[A] $=0.14 \mathrm{M}$
Using the following data decide if the decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ is first order. How would you determine the value of the rate constant, k , from this data?

| $\mathrm{T}(\min )$ | $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{\mathrm{t}}(\mathrm{M})$ | $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{\mathrm{t}}$ |
| :--- | :--- | :--- |
| 0 | $15 \times 10^{-3}$ | -4.2 |
| 200 | $9.6 \times 10^{-3}$ | -4.6 |
| 400 | $6.2 \times 10^{-3}$ | -5.1 |
| 600 | $4.0 \times 10^{-3}$ | -5.5 |
| 800 | $2.5 \times 10^{-3}$ | -6.0 |
| 1000 | $1.6 \times 10^{-3}$ | -6.4 |



If we plot the natural $\log$ of $\mathrm{N}_{2} \mathrm{O}_{5}$ against time, a fairly linear relationship is observed. Therefore, we can conclude that this is a first order reaction. We could determine k by finding the slope of this linear relationship and multiplying it by negative one.
2. How long will it take for the concentration of " A " to decrease to $1.0 \%$ of its initial value in a first order reaction of the form $\mathrm{A} \rightarrow$ products with $\mathrm{k}=1.0 \mathrm{~s}^{-1}$ ?
Let's say that I have 100 kg of A. After a certain amount of time I will be left with $1 \%$ of 100 kg or 1 kg .
OR rearrange to put $[\mathrm{A}]$ over $[\mathrm{A}]_{0}$ such that you can use a ratio of the two concentrations Then...

$$
[\mathrm{A}]_{\mathrm{t}}=[\mathrm{A}]_{0} \mathrm{e}^{-\mathrm{kt}}
$$

$$
\begin{aligned}
& \frac{[A]}{[A]_{0}} \frac{30}{100} \mathrm{o} \frac{[\mathrm{~A}]}{[\mathrm{A}]_{0}}=\mathrm{e}^{-\mathrm{kt}} \\
& \frac{1}{100}=0.01=\mathrm{e}^{-(1.0) \mathrm{t}} \\
& \ln (0.01)=-\mathrm{t} \\
& 4.6 \mathrm{~s}=\mathrm{t}
\end{aligned}
$$

3. Pu-239 has a half-life of 24,000 years. It is a by-product of nuclear power plants. How many years must pass before the radioactivity drops to $30 \%$ of its initial value.
Half-lives are first order kinetics, so we can use first-order concepts to help us.
Before we can jump into the integrated rate law, we need to find the value of k .
$\mathrm{t}_{1 / 2}=\frac{\ln (2)}{\mathrm{k}}$
$24000=\frac{\ln (2)}{\mathrm{k}}$
$\mathrm{k}=2.888 \times 10^{-5}$
Now we can use the first-order rate law to find time, t. Let's say that I have 100 g of Pu-239. After a certain amount of time I will be left with $30 \%$ of 100 g or 30 g .
OR rearrange to put $[\mathrm{Pu}]$ over $[\mathrm{Pu}]_{0}$ such that you can use a ratio of the two concentrations $[\mathrm{A}](\mathrm{t})=[\mathrm{A}]_{0} \mathrm{e}^{-\mathrm{kt}}$
$\frac{[\mathrm{A}]}{[\mathrm{A}]_{0}} \mathrm{o}=\mathrm{e}^{-\mathrm{kt}}$
$\frac{30}{100}=0.3=\mathrm{e}^{-(2.888 \times 10-5) \mathrm{t}}$
$\ln (0.3)=-2.888 \times 10^{-5} \mathrm{t}$
$\mathrm{t}=41687$ years
4. A particular reaction is second order with respect to a reactant A (and zeroth order with respect to all other reactants). The rate constant for this reaction is $\mathrm{k}=$ $2.36 \times 10^{-2} \mathrm{M}^{-1} \mathrm{~s}^{-1}$. Given the initial concentration of $\mathrm{A},[\mathrm{A}]_{0}=0.84 \mathrm{M}$, calculate the time needed for the concentration of A to decrease to $20 \%$ of its original value.
Now we have a defined starting amount, so we no longer have to imagine that we have 100 g or 100 kg of the substance. We can find $20 \%$ of 0.84 M by multiplying 0.84 M by 0.2 . After a certain amount of time the concentration of A would reach $20 \%$ of 0.84 M or 0.168 M .

$$
\begin{aligned}
& \frac{1}{[\mathrm{~A}]}=\frac{1}{[\mathrm{~A}]_{0}}+\mathrm{kt} \\
& \frac{1}{0.168}=\frac{1}{0.84}+\left(2.36 \times 10^{-2}\right) \mathrm{t} \\
& \frac{1}{0.168}-\frac{1}{0.84}=\left(2.36 \times 10^{-2}\right) \mathrm{t} \\
& 4.762=\left(2.36 \times 10^{-2}\right) \mathrm{t} \\
& 201.8 \text { seconds }=\mathrm{t}
\end{aligned}
$$

