

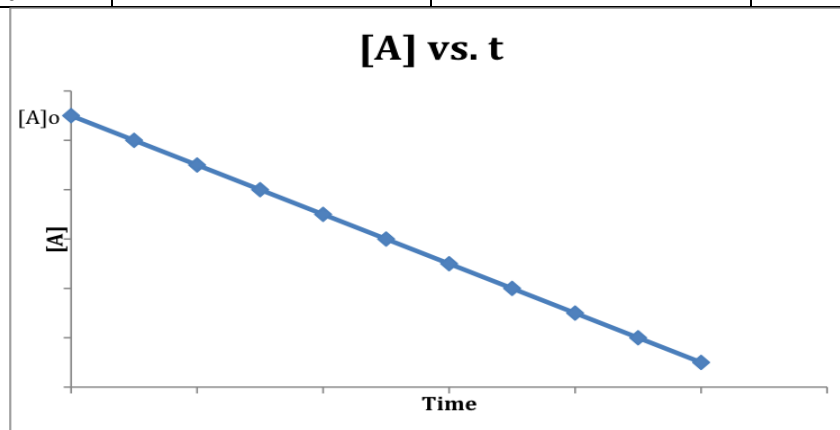
### Kinetics Unit Activity – Chemical Kinetics II KEY

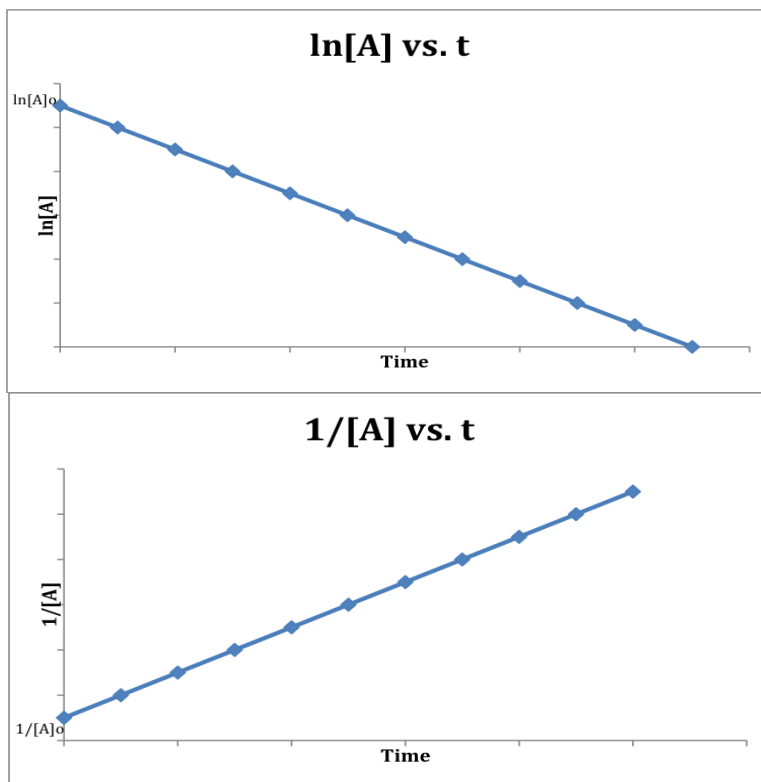
The purpose of this activity is to develop concepts of chemical kinetics: Specifically to deepen your understanding and familiarity with some integrated rate equations.

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

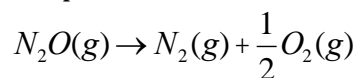
	<b>0 order</b>	<b>1<sup>st</sup> order</b>	<b>2<sup>nd</sup> order</b>
Rate law	Rate = k	Rate = k[A]	Rate = k[A] <sup>2</sup>
Integrated rate	[A] = [A] <sub>0</sub> - kt	[A] <sub>t</sub> = [A] <sub>0</sub> e <sup>-kt</sup> ln[A] <sub>t</sub> = -kt + ln[A] <sub>0</sub>	4.762 = (2.36 × 10 <sup>-2</sup> )t
Half life	t <sub>1/2</sub> = $\frac{[A]_0}{2k}$	t <sub>1/2</sub> = $\frac{\ln(2)}{k}$	t <sub>1/2</sub> = $\frac{1}{k[A]_0}$

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





1. The decomposition of  $N_2O$  follows first-order kinetics. This means



(the rate of decomposition of  $N_2O$ ) =  $k[N_2O]$

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  $k = 3.4 \text{ s}^{-1}$  (at  $780^\circ\text{C}$ )?

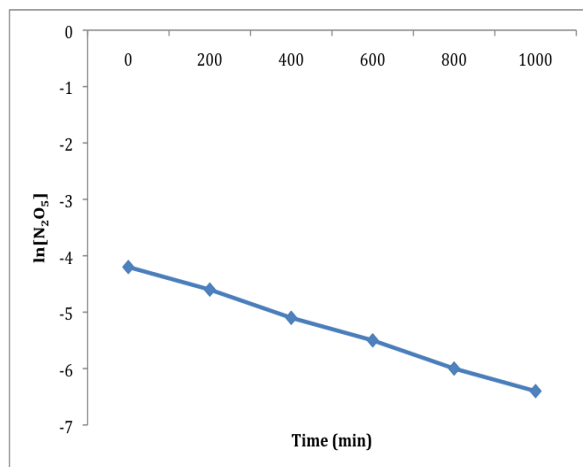
$$[A](t) = [A]_0 e^{-kt}$$

$$[A] = (0.2\text{M})e^{-(3.4)(0.1)}$$

$$[A] = 0.14 \text{ M}$$

2. Using the following data decide if the decomposition of  $N_2O_5$  is first order. How would you determine the value of the rate constant,  $k$ , from this data?

T(min)	$[N_2O_5]_t$ (M)	$\ln[N_2O_5]_t$
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 N<sub>2</sub>O<sub>5</sub> 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.

3. 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 A → products with k = 1.0 s<sup>-1</sup>?

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 [A] over [A]<sub>0</sub> such that you can use a ratio of the two concentrations

Then...

$$[A]_t = [A]_0 e^{-kt}$$

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$\frac{1}{100} = 0.01 = e^{-(1.0)t}$$

$$\ln(0.01) = -t$$

$$4.6 \text{ s} = t$$

4. 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.

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

$$24000 = \frac{\ln(2)}{k}$$



$$k = 2.888 \times 10^{-5}$$

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 [Pu] over [Pu]<sub>0</sub> such that you can use a ratio of the two concentrations

$$[A](t) = [A]_0 e^{-kt}$$

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$\frac{30}{100} = 0.3 = e^{-(2.888 \times 10^{-5})t}$$

$$\ln(0.3) = -2.888 \times 10^{-5}t$$

$$t = 41687 \text{ years}$$

5. 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  $k = 2.36 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . Given the initial concentration of A,  $[A]_0 = 0.84 \text{ M}$ , 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 100g or 100kg 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.

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

$$\frac{1}{0.168} = \frac{1}{0.84} + (2.36 \times 10^{-2})t$$

$$\frac{1}{0.168} - \frac{1}{0.84} = (2.36 \times 10^{-2})t$$

$$4.762 = (2.36 \times 10^{-2})t$$

$$201.8 \text{ seconds} = t$$