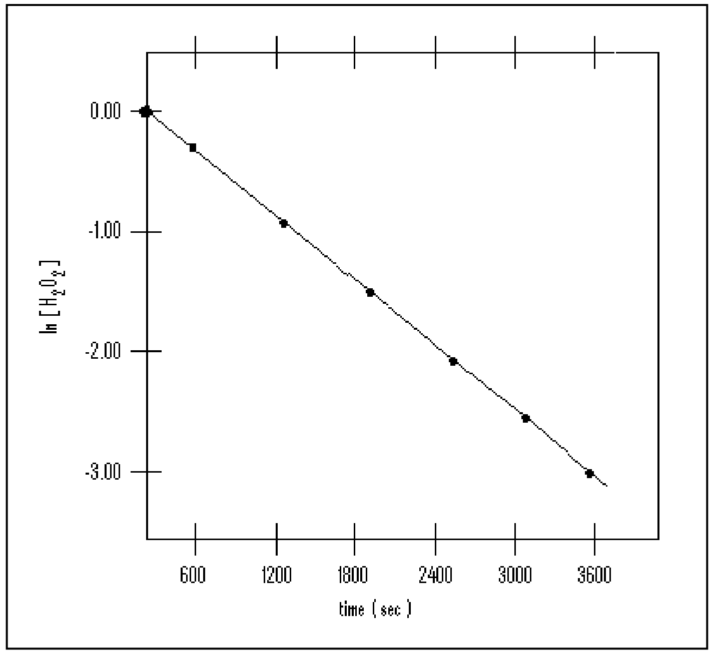
AP CHEMISTRY

TOPIC 8: KINETICS, PART C, Day 102:

- First-Order Reactions
- Half-Life
- Second-Order Reactions

1. The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (sec)	[H_2O_2]	ln [H_2O_2]
0	1.00	0.000
120	0.91	- 0.0943
300	0.78	- 0.248
600	0.59	- 0.528
1200	0.37	- 0.994
1800	0.22	- 1.514
2400	0.13	- 2.040
3000	0.082	- 2.501
3600	0.050	- 2.996
4000		



Determine: a) the rate law, b) the reaction order, c) the Value of the rate constant, and finally, d) calculate the [H_2O_2] at 4000 seconds after the start of the reaction.

Rate Law: **Rate = *k* [H_2O_2]** , First-order reaction since the graph forms a "straight line" from the natural log values of the concentrations.

Reaction Order: Since the reactant is first-order and there is only one reactant, the **reaction order is first-order**.

Rate constant: $\ln\left(\frac{0.91}{1.00}\right) = -k(120 \text{ sec})$; $\frac{\ln\left(\frac{0.91}{1.00}\right)}{-120 \text{ sec}} = k = 7.86 \text{ x } 10^{-4} \text{ sec}^{-1}$

Concentration at 4000 sec: $\ln\left(\frac{[H_2O_2]}{1.00}\right) = -\left(7.86\times10^{-4} \text{ sec}^{-1}\right)(4000 \text{ sec})$; $\ln[H_2O_2] = -3.14$

$$e^{\left(\ln\frac{[H_2O_2]}{1.0 \ M}\right)} = e^{-3.14} \ ; \ \frac{[H_2O_2]}{1.0 \ M} = 0.0431 \ ; \ [H_2O_2] = 0.0431 \ M$$

2. A certain first-order reaction is 45.0% complete in 65 seconds. Calculate the rate constant and the half-life for this process?

[A] = 55% of [A]₀ or [A] = 0.55 [A]₀ ; $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$, $\ln\left(\frac{0.55}{1.00}\right) = -k\ (\ 65\ \ \text{sec}\ )$

$$k = \frac{-0.598}{-65\ \ \text{sec}} = 9.20\times10^{-3}\ \ \text{sec}^{-1} \quad ; \quad \textit{Half-life:}\quad t_{1/2} = \frac{\ln(0.5)}{-k} = \frac{-0.693(\text{sec})}{-9.20\times10^{-3}} = 75.3\ \ \text{sec}$$

3. A certain reaction has the following general form:

$$\text{a A} \rightarrow \text{b B}$$

At a particular temperature, concentration versus time data were collected for this reaction and a plot of **ln [A]** versus time resulted in a straight line with a slope value of $-6.90 \times 10^{-2}\ \text{sec}^{-1}$.

a) Determine the rate law for this reaction,
b) the reaction order,
c) and the value of the rate constant for this reaction.
d) Calculate the half-life for this reaction.
e) Calculate time is required for this reaction to be 87.5% complete?

ANSWERS: Note: The balanced equation given…

a) **Rate = *k* [A]^1** , straight line with ln [A] versus time graph. Since only one reactant, and reactant is first-order, then the reaction order is also first-order. The negative Rate Constant (- *k*) is equal to the negative slope,

therefore,

$$-k = -6.90 \times 10^{-2}\ \ \text{sec}^{-1} \quad \textbf{\textit{OR}} \quad k = 6.90 \times 10^{-2}\ \ \text{sec}^{-1}$$

b) *Half – life*

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt, \quad \ln\left(\frac{0.50}{1.00}\right) = -\left(\ 6.90\times10^{-2}\ \ \text{sec}^{-1}\ \right)\ t$$

$$t_{1/2} = \frac{\ln(0.50)(\text{sec})}{-6.90\times10^{-2}} = 10.0\ \ \text{sec}$$

c) 87.5% consumed, 12.5% remains, how much time is required for this reaction:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt, \quad \ln\left(\frac{0.125}{1.00}\right) = -\left(\ 6.90\times10^{-2}\ \ \text{sec}^{-1}\ \right)\ t$$

$$t = \frac{\ln(0.125)(\text{sec})}{-6.90\times10^{-2}} = 30.1\ \ \text{sec}$$

4. A first-order reaction is 38.5% complete in 480 seconds.

a) Calculate the rate constant.
b) What is the value at the half-life.
c) How long will it take for the reaction to go to 25%, 75%, and 95% completion.

ANSWERS:

a) $$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt\,, \quad \ln\left(\frac{0.615}{1.00}\right) = -k\,(\ 480\ \text{sec}\ ) \quad ; \quad k = \frac{\ln(0.615)}{-480\ \text{sec}} = 1.01\times10^{-3}\ \text{sec}^{-1}$$

b) $$\textit{Half-life} \qquad t_{1/2} = \frac{\ln(0.5)}{-k} = \frac{-0.693(\text{sec})}{-1.01\times10^{-3}} = 684\ \text{sec}$$

c) 25% consumed, 75% remains, how much time is required for this reaction:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt\,, \quad \ln\left(\frac{0.75}{1.00}\right) = -\left(\ 1.01\times10^{-3}\ \text{sec}^{-1}\ \right) t \quad ; \quad t = \frac{\ln(0.75)(\text{sec})}{-1.01\times10^{-3}} = 285\ \text{sec}$$

75% consumed, 25% remains, how much time is required for this reaction:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt\,, \quad \ln\left(\frac{0.25}{1.00}\right) = -\left(\ 1.01\times10^{-3}\ \text{sec}^{-1}\ \right) t \quad ; \quad t = \frac{\ln(0.25)(\text{sec})}{-1.01\times10^{-3}} = 1373\ \text{sec}$$

95% consumed, 5% remains, how much time is required for this reaction:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt\,, \quad \ln\left(\frac{0.05}{1.00}\right) = -\left(\ 1.01\times10^{-3}\ \text{sec}^{-1}\ \right) t \quad ; \quad t = \frac{\ln(0.05)(\text{sec})}{-1.01\times10^{-3}} = 2966\ \text{sec}$$