AP CHEMISTRY

TOPIC 8: KINETICS, MORE PRACTICE

Day 106:

Answer the following questions related to the kinetics of chemical reactions.

$$I^{-1}{}_{(aq)} + ClO^{-1}{}_{(aq)} \xrightarrow{OH^{-1}} IO^{-1}{}_{(aq)} + Cl^{-1}{}_{(aq)}$$

Iodide ion, I^{-1}, is oxidized to hypoiodite, IO^{-1}, by hypochlorte, ClO^{-1}, in basic solution according to the equation above. Three initial rate experiments were conducted; the results are shown in the following table:

Experiment	$[I^-]$ ($mol\ L^{-1}$)	$[ClO^-]$ ($mol\ L^{-1}$)	Initial Rate of Formation of IO^- ($mol\ L^{-1}\ s^{-1}$)
1	0.017	0.015	0.156
2	0.052	0.015	0.476
3	0.016	0.061	0.596

(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.

(i) $I^{-1}{}_{(aq)}$

$$\frac{Rate\ 2}{Rate\ 1} = \frac{0.476}{0.156} = 3.05 = \frac{k\ (0.052)^m\,\cancel{(0.015)^n}}{k\ (0.017)^m\,\cancel{(0.015)^n}}$$

$$3.05 = \frac{(0.052)^m}{(0.017)^m} \quad \textbf{;} \quad 3.05 = 3.05^m \quad \textbf{;} \quad \boldsymbol{m = 1}$$

(i) $ClO^{-1}{}_{(aq)}$

$$\frac{Rate\ 3}{Rate\ 1} = \frac{0.596}{0.156} = 3.82 = \frac{k\ (0.016)^1\,(0.061)^n}{k\ (0.017)^1\,(0.015)^n}$$

$$3.82 = (0.94)\frac{(0.061)^n}{(0.015)^n} \quad \textbf{;} \quad \frac{3.82}{0.94} = \frac{(0.061)^n}{(0.015)^n} \quad \textbf{;} \quad 4.06 = 4.06^n \quad \textbf{;} \quad \boldsymbol{n = 1}$$

(b) For the reaction,

(i) write the rate law that is consistent with the calculations in part (a):

$$\text{Rate} = k\ [\,I^{-1}\,]\ [\,ClO^{-1}\,] \quad \textbf{OR} \quad \text{Rate} = k\ [\,I^{-1}\,]^1\ [\,ClO^{-1}\,]^1$$

(ii) calculate the value of the specific rate constant, *k*, and specify units.

$$k = \frac{0.596\ M}{(0.016\ M)\ (\text{sec})(0.061\ M)} = 611\ M^{-1}\ \text{sec}^{-1} \quad \text{or} \quad 610\ M^{-1}\ \text{sec}^{-1}$$

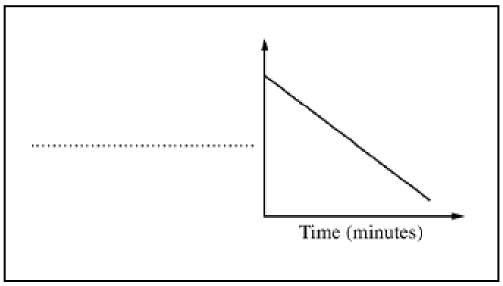
The catalyzed decomposition of hydrogen peroxide, $H_2O_{2\,(aq)}$, is represented by the following equations.

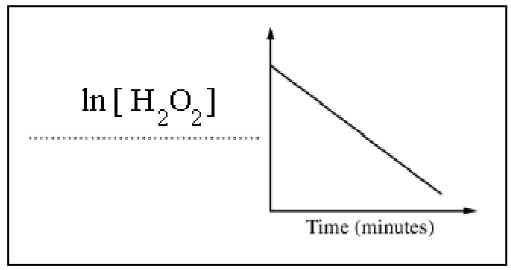
$$2\ H_2O_{2\,(aq)} \xrightarrow{catalyst} H_2O_{(l)} + O_{2\,(g)}$$

The kinetics of the decomposition reaction were studied and the analysis of the results show that it is a first-order reaction. Some of the experimental data are shown in the table below:

$[H_2O_2]$ (mol L^{-1})	Time (minutes)
1.00	0.0
0.78	5.0
0.61	10.0

(c) During the analysis of the data, the graph below was produced.





ANSWER: (above)

(i) Label the vertical axis of the graph

(ii) What are the units of the rate constant, k , for the decomposition of $H_2O_{2\,(aq)}$?

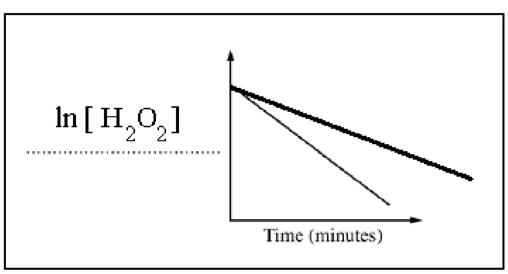
FIRST-ORDER REACTION (Given in question): Rate (units for ALL reactions) = M min^{-1}

Rate Law (for this reaction) is ; Rate = k [H_2O_2]

$$k = \frac{\left(\frac{M}{\text{min}}\right)}{M} = \text{min}^{-1}$$

(ii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 M $H_2O_{2\,(aq)}$.

ANSWER:



Explanation of the graph above: The concentrations of the first order reaction will be HIGHER as time advances during the reaction (compared with a catalyzed reaction) – this is because the reaction is NOT able to react AS FAST. Also, recall that the natural log of a first order reaction will generate a negative (straight line) slope when plotted versus time. The darker line represents the un-catalyzed reaction.

2. A certain first-order reaction is 82.7 % complete in 231 seconds. What are the rate constant and the half-life for this process?

[A]$_t$ = 17.3 % of [A]$_0$ or [A]$_t$ = 0.173 [A]$_0$; $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$, $\ln\left(\frac{0.173}{1.00}\right) = -k\ (\ 231\ \text{sec}\ )$

$$k \ = \ \frac{-1.7545}{-231\ \text{sec}} \ = \ 0.007595\ \text{sec}^{-1}$$

$$\textit{Half-life:} \quad \ln\left(\frac{0.50}{1.00}\right) = -\left(0.007595\ \text{sec}^{-1}\right)\ t \quad ; \quad \frac{\ln(0.50)(\text{sec})}{-0.007595} = \ t \ = \ 91.2\ \text{sec}$$

OR

$$t_{1/2} \ = \ \frac{0.693(\text{sec})}{0.007595} \ = \ 91.2\ \text{sec}$$

3. A second-order reaction is 63.8% complete in 79.3 seconds.

a) Calculate the rate constant.
b) What is the value (time) at the half-life.
c) How long did it take for the reaction to go to 33.6 % completion.

a)

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt\ , \quad \frac{1}{(0.362\ M)} - \frac{1}{(1.0\ M)} = k(79.3\ \text{sec}) \quad ; \quad \frac{1.7624}{M} = k(79.3\ \text{sec}) \quad ;$$

$$\frac{1.7624}{M(79.3\ \text{sec})} \ = \ k \ = \ \frac{0.022225}{M\cdot\text{sec}}$$

b)

$$\textbf{Half-life} \quad ; \quad \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt\ , \quad \frac{1}{(0.50\ M)} - \frac{1}{(1.0\ M)} = \left(\frac{0.022225}{M\cdot\text{sec}}\right)t$$

$$\frac{2}{M} - \frac{1}{M} = \left(\frac{0.022225}{M\cdot\text{sec}}\right)t \quad ; \quad \frac{(1)(M\cdot\text{sec})}{(M)(0.022225)} = t = 45.0\ \text{sec}$$

OR

$$t_{1/2} = \frac{1}{k[A]_0} \quad ; \quad t_{1/2} = \frac{1(M\cdot\text{sec})}{0.022225(1.0\ M)} \ = \ 45.0\ \text{sec}$$

c) 33.6% consumed, 66.4 % remains, how much time is required for this reaction:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt\ , \quad \frac{1}{(0.664\ M)} - \frac{1}{(1.0\ M)} = \left(\frac{0.022225}{M\cdot\text{sec}}\right)t \quad ; \quad \frac{0.5060}{M} = \left(\frac{0.022225}{M\cdot\text{sec}}\right)t$$

$$\frac{0.5060}{M}\left(\frac{M\cdot\text{sec}}{0.022225}\right) = \ t \ = 22.77\ \text{sec}$$