

Chem 1062

Note Title

7/16/2008

- * Tutoring
- * Any D2L issues?
- * D2L discussion boards
- * D2L Quizzes due Tues \Rightarrow Ch 12, 14, 15

14.49

Trial	$[\text{CO}_2]$ mol/L	$[\text{OH}^-]$ mol/L	Rate mol/(L·s)
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

use these trials to find y

$$\frac{0.00828}{0.00276} = 3$$

$$\text{Rate} = k [\text{CO}_2]^x [\text{OH}^-]^y$$

use trials 1 & 2 to find x

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k [\text{CO}_2]_1^x [\text{OH}^-]_1^y}{k [\text{CO}_2]_2^x [\text{OH}^-]_2^y}$$

$$[\text{OH}^-]_1 = [\text{OH}^-]_2$$

$$\log x^y = y \log x$$

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \left(\frac{[\text{CO}_2]_1}{[\text{CO}_2]_2} \right)^x \Rightarrow \frac{0.0248}{0.00276} = \left(\frac{0.060}{0.020} \right)^x$$

$$8.99 = 3^x$$

$$\log(8.99) = \log(3^x)$$

$$= \frac{\log(8.99)}{\log(3)} = x \frac{\log(3)}{\log(3)}$$

$$x = 2$$

$$\text{Rate} = k [\text{ClO}_2]^2 [\text{OH}^-]$$

Since tripling $[\text{OH}^-]$ triples rate (while holding $[\text{ClO}_2]$ constant), then 1st order with respect to $[\text{OH}^-]$

$$\frac{\text{Rate}}{[\text{ClO}_2]^2 [\text{OH}^-]} = \frac{k [\text{ClO}_2]^2 [\text{OH}^-]}{[\text{ClO}_2]^2 [\text{OH}^-]} \quad \frac{\frac{\text{mol}}{\text{L} \cdot \text{s}} \frac{\text{L}^2}{\text{mol}^2}}{\left(\frac{\text{mol}}{\text{L}}\right)^2 \left(\frac{\text{mol}}{\text{L}}\right)}$$

$$k = 2.3 \times 10^2 \frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}}$$

$$\text{L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$$

In a 1st order process, how is concentration related to time?

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

Integrated Rate Law for a 1st order process

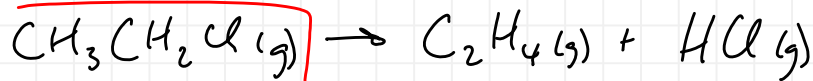
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

for a 2nd order process

$$[A]_t = -kt + [A]_0$$

for a 0th order process

14.55



A

1st order process

$$[A]_0 = 0.00100 \text{ M}$$

$$\text{@ } t = 155 \text{ s, } [A]_t = 0.00067 \text{ M}$$

$$\text{@ } t = 256 \text{ s, } [A]_t = ? \quad 0.00052 \text{ M}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$10^{\log x} = x$$

$$\ln \left(\frac{0.00067 \text{ M}}{0.00100 \text{ M}} \right) = -k(155 \text{ s})$$

$$e^{\ln x} = x$$

$$\frac{-0.400}{155 \text{ s}} = \frac{-k(155 \text{ s})}{155 \text{ s}} = 0.00258 \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

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

$$\begin{aligned} [A]_t &= [A]_0 e^{-kt} = (0.00100 \text{ M}) e^{-(0.00258 \text{ s}^{-1})(256 \text{ s})} \\ &= 5.2 \times 10^{-4} \text{ M} \\ &= 0.00052 \text{ M} \end{aligned}$$

For a 1st order process, determine an equation that shows the relation between the half-life and k .

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$[A]_t = \frac{1}{2} [A]_0$$

$$\ln \frac{\frac{1}{2} [A]_0}{[A]_0} = -kt$$

$$\frac{\ln(0.5)}{-k} = \frac{-kt}{-k} = \frac{+0.693}{+k} =$$

$$t_{1/2} = \frac{0.693}{k} \quad \Leftarrow \text{1st order process}$$

$$t_{1/2} = \frac{1}{k[A]_0} \quad \Leftarrow \text{2nd order}$$

$$t_{1/2} = \frac{[A]_0}{2k} \quad \Leftarrow \text{0th order}$$

14.59

$$k = 2.0 \times 10^{-6} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{2.0 \times 10^{-6} \text{ s}^{-1}} = 346,500 \text{ s}$$

$$346,500 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ h}}{60 \text{ min}} = 96 \text{ h}$$

# of half-lives	% remaining	time (h)
0	100	0
1	50	96
2	25	192
3	12.5	288
4	6.25	384

14.63

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (\text{1st order process})$$

85.0% reaction \Rightarrow 15.0% remains

$$[A]_t = 0.15 [A]_0$$

$$\ln \frac{0.15 [A]_0}{[A]_0} = -kt$$

$$\frac{\ln 0.15}{-2.0 \times 10^{-6}} = \frac{-\cancel{(2.0 \times 10^{-6} \text{ s}^{-1})} t}{\cancel{-2.0 \times 10^{-6}}}$$

$$948,560 \text{ s} \times \frac{1 \text{ h}}{3600 \text{ s}} = 260 \text{ h}$$

$$= \boxed{2.6 \times 10^2 \text{ h}}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{x}{y} = \ln x - \ln y$$

$$\ln [A]_t - \ln [A]_0 = -kt$$

$$\underbrace{\ln [A]_t}_{y} = -kt + \underbrace{\ln [A]_0}_{b}$$

$$y = mx + b$$

14.68

graphed data with Excell

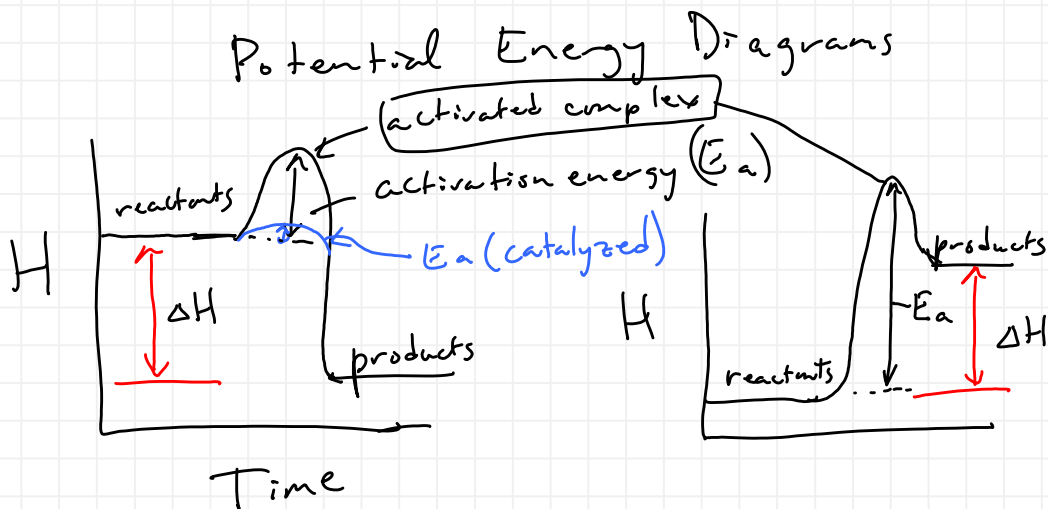
2nd order overall

$$\text{Rate} = k[A]^2$$

$$m = 11.513 \Rightarrow k = 11.5 \frac{\text{L}}{\text{mol} \cdot \text{min}}$$

$$k = \frac{\text{Rate}}{[A]^2} = \frac{\frac{\text{mol}}{\text{L} \cdot \text{min}}}{\left(\frac{\text{mol}}{\text{L}}\right)^2} = \frac{\text{L}}{\text{mol} \cdot \text{min}} \quad \boxed{k = 11.5 \frac{\text{L}}{\text{mol} \cdot \text{min}}}$$

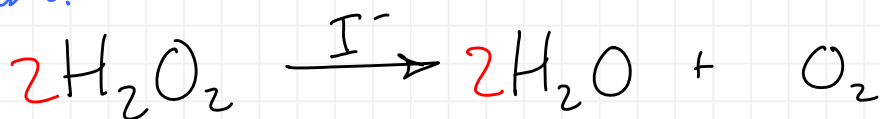
Activation Energy



exothermic
 $\Delta H = (-)$

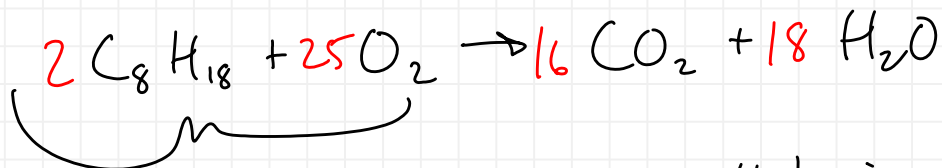
endothermic
 $\Delta H = (+)$

Demo!



Catalyst lowers activation energy by providing alternative pathway for the reaction

Consider:



implies 27 molecules that must collide in order to react. It won't happen.

This react must occur in a series of steps. Each step is limited to one,

two, or three molecules reacting at once.

Each step in process is called an elementary reaction. The combination of steps is the reaction mechanism.