Announcements – Lecture VIII – Thursday, Feb 15th

1. Exam 1: Saturday, February 24th, ISB 155/160 (General Chemistry Labs)

   Session I: 1:00-2:55, Last Name, A-J

   Session II: 3:00-4:55, Last Name, K-Z

   Anyone with extended time accommodation – go to Session I

   Make sure you bring your ID Card and place it on the desk for the duration of the exam.

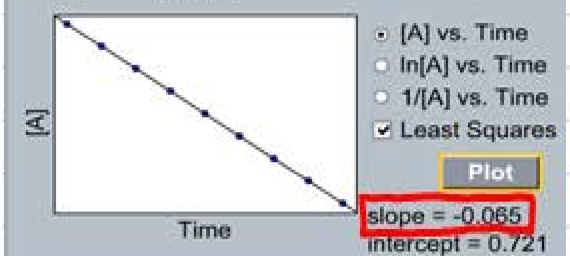
2. iClicker:  Pick any letter a-e

14.4 Concentration Changes over Time

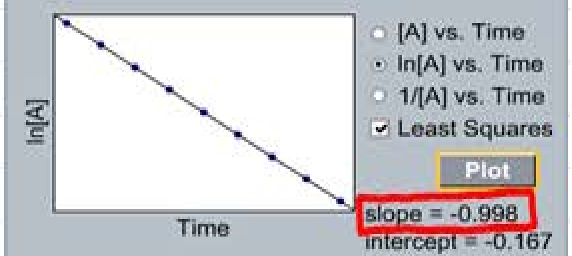
Graphical Determination of Reaction Order

Reaction Order	Integrated Rate Law	Rearranged Rate Law	Straight-Line Plot
Zero order	$[A]_t = [A]_0 - kt$	$[A]_t = -kt + [A]_0$ $y = mx + b$	$y = [A]_t$ $x = t$ slope $= -k$
First order	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\ln[A]_t = -kt + \ln[A]_0$ $y = mx + b$	$y = \ln[A]_t$ $x = t$ slope $= -k$
Second order	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ $y = mx + b$	$y = 1/[A]_t$ $x = t$ slope $= k$

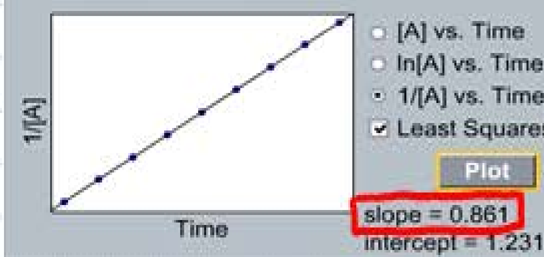
time, min	[A], mol/L	time, min	[A], mol/L
0	0.7210	5	0.3978
1	0.6563	6	0.3331
2	0.5917	7	0.2685
3	0.5271	8	0.2038
4	0.4624		



time, min	[A], mol/L	time, min	[A], mol/L
0	0.8466	5	0.0058
1	0.3121	6	0.0021
2	0.1151	7	0.0008
3	0.0424	8	0.0003
4	0.0156		



time, min	[A], mol/L	time, min	[A], mol/L
0	0.8126	5	0.1807
1	0.4782	6	0.1564
2	0.3387	7	0.1378
3	0.2623	8	0.1232
4	0.2140		



Rate $= k[A]^0 = k$
$= 0.065$

Rate $= k[A]^1$
$= 0.998[A]$

Rate $= k[A]^2$
$= 0.861[A]^2$

14.4 Concentration Changes over Time

Reaction Half-Life

Zero Order	First Order	Second Order
$t_{1/2} = \frac{[A]_o}{2k}$	* $t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_o}$
Directly proportional to $[A]_o$	Constant	Inversely proportional to $[A]_o$

$\ln[A]_t = -kt + \ln[A]_o$ @ $t_{1/2}$, $[A]_t = \frac{1}{2}[A]_o$

$$\ln(\tfrac{1}{2}[A]_o) = -kt_{1/2} + \ln[A]_o$$
$$-kt_{1/2} = \ln(\tfrac{1}{2}[A]_o) - \ln[A]_o$$
$$-kt_{1/2} = \ln\tfrac{1}{2} + \ln[A]_o - \ln[A]_o$$
$$-kt_{1/2} = \ln\tfrac{1}{2}$$
$$-kt_{1/2} = \ln 1 - \ln 2$$
$$-kt_{1/2} = 0 - \ln 2$$
$$-kt_{1/2} = -\ln 2$$

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

14.4 Concentration Changes over Time

Reaction Half-Life

Nitrogen-13 is used in tracers injected into the bloodstream for positron emission tomography (PET). The **half-life of nitrogen-13 is 10.0 minutes**. **How much time** is required for the mass of a sample of nitrogen-13 to fall to **6.25 percent** of its original value? Since the **decomposition is a radioactive decay** reaction, it is **first order**. ?0.0 min

↳ 4

$$\ln \frac{[A]}{[A]_0} = -kt \qquad t_{1/2} = 10 \text{ min} \; ; \; \frac{[A]}{[A]_0} = 0.0625$$

$$k = \frac{\ln 2}{10.0 \text{ min}} = 6.930 \times 10^{-2} \text{ min}^{-1}$$

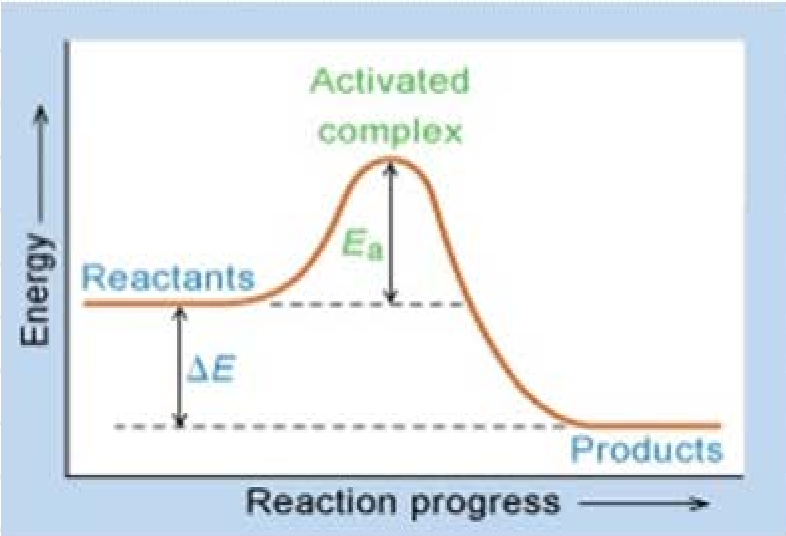
$$\ln \frac{[A]}{[A]_0} = -kt$$

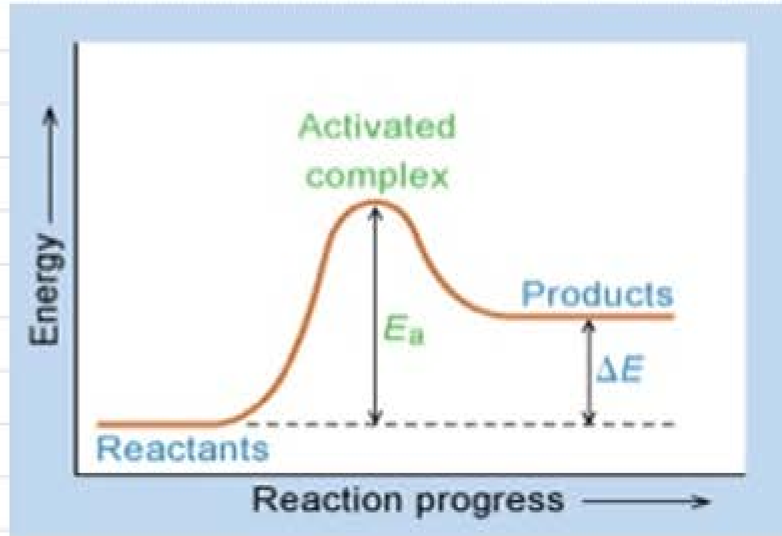
$$\ln(0.0625) = -6.930 \times 10^{-2}\, t$$

$$t = \frac{\ln(0.0625)}{-6.930 \times 10^{-2}} = 40 \text{ min}$$

14.5 Activation Energy and Temperature

Reaction Coordinate Diagrams





E_a = Activation Energy

$\Delta E = E_{products} - E_{reactants}$
< 0
Exothermic

E_a = Activation Energy

$\Delta E = E_{products} - E_{reactants}$
> 0
Endothermic

14.5 Activation Energy and Temperature

The Arrhenius Equation

$$k = Ae^{-\frac{E_a}{RT}}$$

k : Rate constant
A : Frequency factor
E_a : Activation Energy
R : Ideal Gas Constant
T : Temperature in K

A : Measure of the number of collisions that take place with the correct orientation.

$e^{-\frac{E_a}{RT}}$: Fraction of the collisions that occur with sufficient energy to overcome E_a.

a) $E_a \uparrow$, then $e^{-\frac{E_a}{RT}} \downarrow$, $k \downarrow$

b) $T \uparrow$, then $e^{-\frac{E_a}{RT}} \uparrow$, $k \uparrow$

$$k_1 = Ae^{-\frac{E_a}{RT_1}} \quad ; \quad k_2 = Ae^{-\frac{E_a}{RT_2}}$$

$$\ln k_1 = \ln\left(Ae^{-\frac{E_a}{RT_1}}\right) \quad ; \quad \ln k_2 = \ln\left(Ae^{-\frac{E_a}{RT_2}}\right)$$

$$\ln k_2 - \ln k_1 = \ln A + \ln e^{-\frac{E_a}{RT_2}} - \ln A - \ln e^{-\frac{E_a}{RT_1}}$$

$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right)$$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

14.5 Activation Energy and Temperature

The Arrhenius Equation

The **activation energy** for the gas phase decomposition of acetic anhydride is 144 kJ/mol.

$$(CH_3CO)_2O = CH_2{=}C{=}O + CH_3COOH$$

The **rate constant** for this reaction is $6.02 \times 10^{-4}\ s^{-1}$ at 495 K. What is the **rate constant** at 531 K?

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$E_a = 144{,}000$ (Remember R is in J)

$T_1 = 495\ K$ $T_2 = 531\ K$

$k_1 = 6.02 \times 10^{-4}$ $k_2 = ?$

$R = 8.314\ J.mol^{-1}.K^{-1}$

$$\ln \frac{k_2}{6.02 \times 10^{-4}} = -\frac{144{,}000}{8.314}\left(\frac{1}{531} - \frac{1}{495}\right)$$

$$\ln k_2 - \ln(6.02 \times 10^{-4}) = -17320.2\left(\frac{1}{531} - \frac{1}{495}\right)$$

$$\ln k_2 + 7.4152 = 2.3722$$

$$\ln k_2 = 2.3722 - 7.4152$$

$$\ln k_2 = -5.043$$

$$k_2 = 6.45 \times 10^{-3}\ s^{-1}$$

14.5 Activation Energy and Temperature

Graphical Determination of Ea

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln k = \ln A + \ln e^{-\frac{E_a}{RT}}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + c$$

$\ln k$ vs $\frac{1}{T}$: slope $= -\frac{E_a}{R}$

The Arrhenius Equation

Question 1 of 3

The rate of the reaction

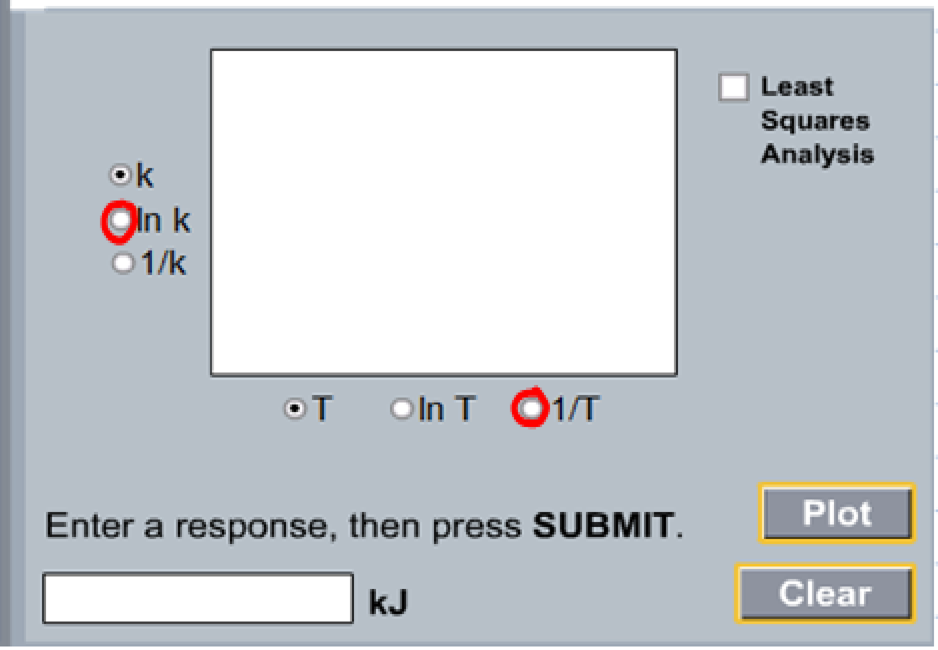
$$N_2O_5\,(g) \longrightarrow 2\,NO_2\,(g) + \tfrac{1}{2}O_2\,(g)$$

is measured at different temperatures, with the following rate constants, k, determined:

Temperature, K	k, s^{-1}
298	3.46×10^{-5}
328	1.5×10^{-3}
358	3.34×10^{-2}
378	0.21

What is the activation energy, E_a, for this reaction in units of kilojoules?

Submit



14.5 Activation Energy and Temperature

Graphical Determination of Ea

$\text{slope} = -1.23 \times 10^4$

$-E_a/R = -1.23 \times 10^4$

$-E_a = -1.23 \times 10^4 (8.314)$

$= -1.02 \times 10^5 \text{ J.mol}^{-1}$

$E_a = 1.02 \times 10^5 \text{ J.mol}^{-1}$

The Arrhenius Equation

Question 1 of 3

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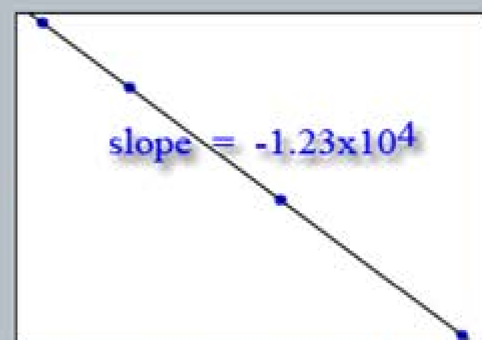
Submit

○ k
◉ ln k
○ 1/k



○ T ○ ln T ◉ 1/T

☑ Least Squares Analysis

Enter a response, then press **SUBMIT**.

102 kJ

Plot

Clear