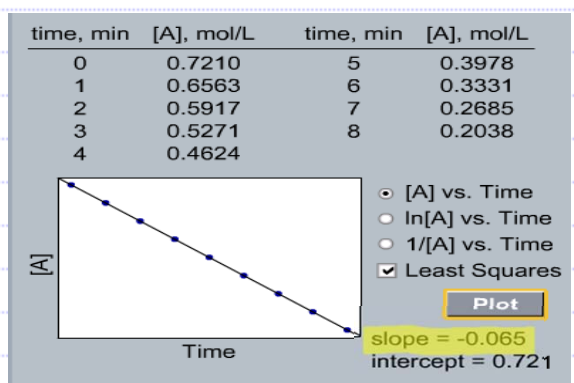


## 14.4 Concentration Changes over Time

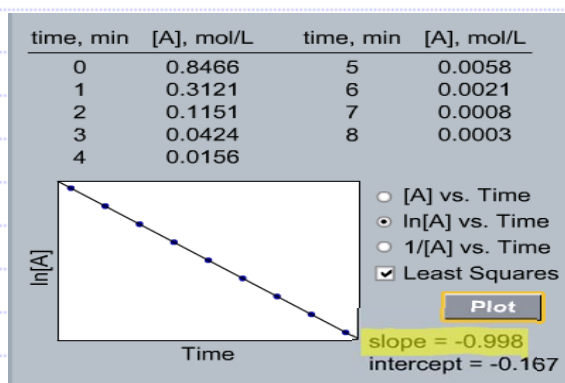
### Graphical Determination of Reaction Order

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 = $k$



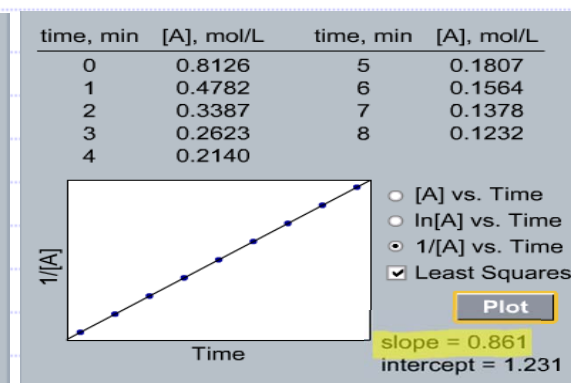
$$\begin{aligned} \text{Rate} &= k[A]^0 \\ &= k \\ &= 0.065 \end{aligned}$$

$$\text{Slope} = -k$$



$$\begin{aligned} \text{Rate} &= k[A] \\ &= 0.998[A] \end{aligned}$$

$$\text{Slope} = -k$$



$$\begin{aligned} \text{Rate} &= k[A]^2 \\ &= 0.861[A]^2 \end{aligned}$$

$$\text{Slope} = k$$

## 14.4 Concentration Changes over Time

### Reaction Half-Life

Zero Order	First Order	Second Order
$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Directly proportional to $[A]_0$	Constant	Inversely proportional to $[A]_0$

$$\ln [A]_t = -kt + \ln [A]_0 \quad ; \quad @ t_{1/2}, [A]_t = \frac{1}{2}[A]_0$$

$$\ln \left( \frac{1}{2}[A]_0 \right) = -kt_{1/2} + \ln [A]_0$$

$$\begin{aligned} -kt_{1/2} &= \ln \left( \frac{1}{2}[A]_0 \right) - \ln [A]_0 \\ &= \ln \frac{1}{2} + \ln [A]_0 - \ln [A]_0 \\ &= \ln \frac{1}{2} \\ &= \ln 1 - \ln 2 \\ &= 0 - \ln 2 \end{aligned}$$

$$\begin{aligned} -kt_{1/2} &= -\ln 2 \\ kt_{1/2} &= \ln 2 \end{aligned}$$

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

## 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**.

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

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

$$10 = \frac{\ln 2}{k}$$

$$10k = \ln 2$$

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

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

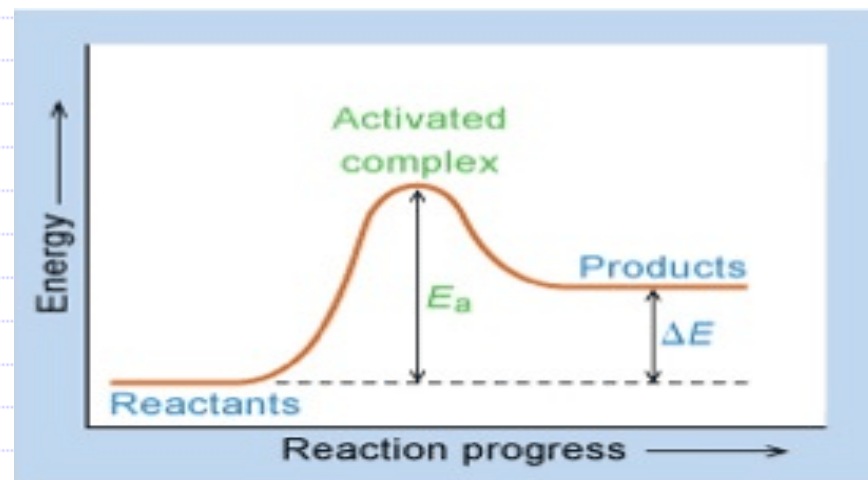
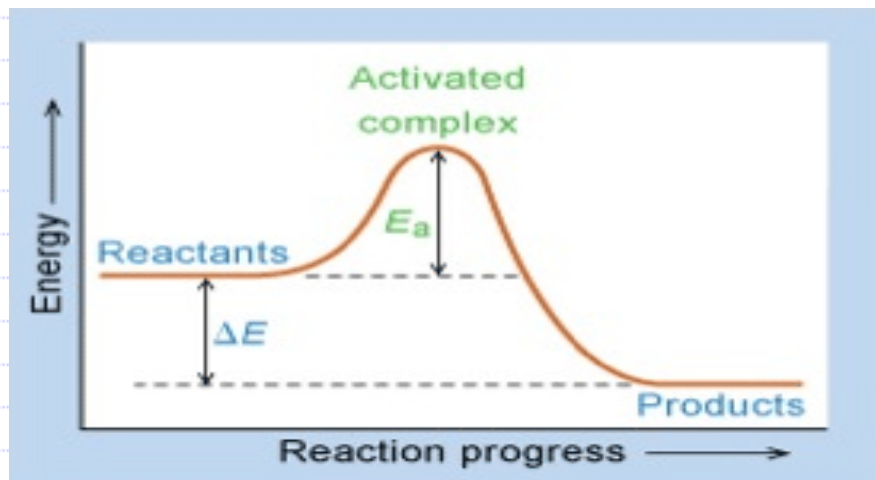
$$\ln (0.0625) = -6.930 \times 10^{-2} t$$

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

$$= 40 \text{ minutes}$$

## 14.5 Activation Energy and Temperature

### Reaction Coordinate Diagrams



$E_a$  = Activation Energy.

$$\Delta E = E_{\text{PRODUCTS}} - E_{\text{REACTANTS}}$$

$< 0$   
Exothermic

$$\Delta E = E_{\text{PRODUCTS}} - E_{\text{REACTANTS}}$$

$> 0$   
Endothermic

## 14.5 Activation Energy and Temperature

### The Arrhenius Equation

$$k = A e^{-\frac{E_0}{RT}}$$

$k$  : Rate constant.

$A$  : Frequency factor.

$E_0$  : Activation energy.

$R$  : Ideal Gas Constant.

$T$  : Temperature in K.

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

$e^{-\frac{E_0}{RT}}$  : Fraction of the collisions that occur with sufficient energy to overcome  $E_0$ .

a)  $E_0 \uparrow$ , then  $e^{-\frac{E_0}{RT}} \downarrow$ ,  $k \downarrow$

b)  $E_0 \downarrow$ , then  $e^{-\frac{E_0}{RT}} \uparrow$ ,  $k \uparrow$

$$k_1 = A e^{-\frac{E_0}{RT_1}} \quad : \quad k_2 = A e^{-\frac{E_0}{RT_2}}$$

$$\ln k_1 = \ln \left( A e^{-\frac{E_0}{RT_1}} \right) \quad : \quad \ln k_2 = \ln \left( A e^{-\frac{E_0}{RT_2}} \right)$$

$$\ln k_2 - \ln k_1 = \ln A + \ln e^{-\frac{E_0}{RT_2}} - \ln A - \ln e^{-\frac{E_0}{RT_1}}$$

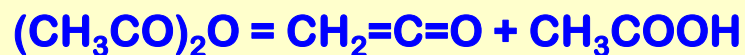
$$\ln k_2 - \ln k_1 = -\frac{E_0}{RT_2} - \left( -\frac{E_0}{RT_1} \right)$$

$$\ln \frac{k_2}{k_1} = -\frac{E_0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

## 14.5 Activation Energy and Temperature

### The Arrhenius Equation

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



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

$$\ln \frac{k_2}{k_1} = -\frac{E_0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$E_0 = 144,000 \text{ J} \quad (\text{Remember, } R \text{ is in J})$$

$$T_1 = 495 \text{ K} \quad T_2 = 531 \text{ K}$$

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

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

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

$$\ln k_2 - \ln(6.02 \times 10^{-4}) = -17320.2 (-1.3696 \times 10^{-4})$$

$$\ln k_2 + 7.4152 = 2.3722$$

$$\ln k_2 = 2.3722 - 7.4152$$

$$\ln k_2 = -5.043$$

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

## 14.5 Activation Energy and Temperature

### Graphical Determination of $E_a$

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

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

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

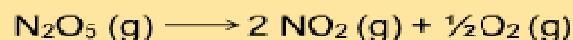
$$y = mx + c$$

$$\ln k \text{ vs } 1/T \text{ plot, slope} = -\frac{E_a}{R}$$

### The Arrhenius Equation

#### Question 1 of 3

The rate of the reaction



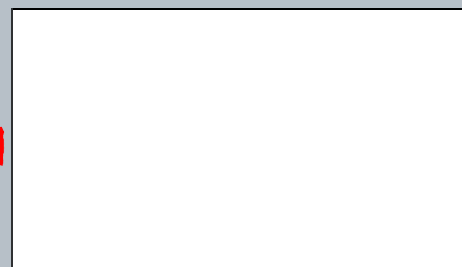
is measured at different temperatures, with the following rate constants,  $k$ , determined:

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

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

Submit

- $k$   
  $\ln k$   
  $1/k$



- $T$      $\ln T$      $1/T$

Least Squares Analysis

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

kJ

Plot

Clear

## 14.5 Activation Energy and Temperature

### Graphical Determination of $E_a$

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

$$-\frac{E_a}{R} = -1.23 \times 10^4$$

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

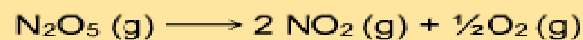
$$E_a = 1.02 \times 10^5 \text{ J. mol}^{-1}$$

OR  
 $102 \text{ kJ. mol}^{-1}$

## The Arrhenius Equation

### Question 1 of 3

The rate of the reaction



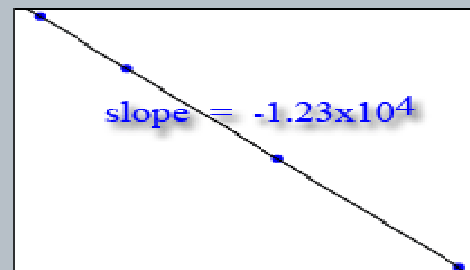
is measured at different temperatures, with the following rate constants,  $k$ , determined:

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

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

Submit

- $k$
- $\ln k$
- $1/k$



- T
- $\ln T$
- $1/T$

Least Squares Analysis

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

Plot

102 kJ

Clear