

Chemistry 146 Lecture Problems Arrhenius Equation

The Arrhenius Equation

$$k = A \cdot e^{-\frac{E_a}{R \cdot T}}$$

From Example 21.8 in Kisk and Rawn

$$A := 1.0 \cdot 10^{14} \cdot \text{sec}^{-1}$$

$$E_a := 75 \cdot 10^3 \cdot \frac{\text{joule}}{\text{mole}}$$

$$R := 8.314 \cdot \text{joule} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

At 27 C:

$$T := (273 + 27) \cdot \text{K}$$

$$k := A \cdot e^{-\frac{E_a}{R \cdot T}}$$

$$k = 8.72707 \text{ sec}^{-1}$$

At 37 C:

$$T := (273 + 37) \cdot \text{K}$$

$$k := A \cdot e^{-\frac{E_a}{R \cdot T}}$$

$$k = 23.02134 \text{ sec}^{-1}$$

Calculate the change in the rate constant at different temperatures (for a known activation energy)

The Arrhenius expression at T_1 and T_2 :

$$k_1 = A \cdot e^{-\frac{E_a}{R \cdot T_1}} \quad k_2 = A \cdot e^{-\frac{E_a}{R \cdot T_2}}$$

Divide the two expressions:

$$\frac{k_1}{k_2} = \frac{A \cdot e^{-\frac{E_a}{R \cdot T_1}}}{A \cdot e^{-\frac{E_a}{R \cdot T_2}}}$$

$$\frac{k_1}{k_2} = \frac{e^{-\frac{E_a}{R \cdot T_1}}}{e^{-\frac{E_a}{R \cdot T_2}}}$$

Cancel A

$$\frac{k_1}{k_2} = e^{-\left(\frac{E_a}{R \cdot T_1}\right) - \left(-\frac{E_a}{R \cdot T_2}\right)}$$

Rearrange exponents (dividing numbers, subtract exponent)

$$\frac{k_1}{k_2} = e^{\left(\frac{E_a}{R \cdot T_2}\right) - \left(\frac{E_a}{R \cdot T_1}\right)}$$

Rearrange

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

Extract activation energy from expression:

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

Take the natural log

Determine change in reaction rate constant from 273 K to 284 K for different activation energies:

Given:

$$T_1 := 273 \cdot \text{K}$$

$$T_2 := 283 \cdot \text{K}$$

$$k_2 := 1$$

Set k_2 as 1, and will calculate k_1 (will show relative rate constant)

$$E_a = 1 \text{ kJ mole}^{-1}$$

$$E_a := 1 \cdot 10^3 \frac{\text{joule}}{\text{mole}}$$

$$k_1 := e^{\left(\frac{E_a}{R}\right) \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \cdot k_2$$

$$k_1 = 0.98455 \cdot k_2$$

$$E_a = 10 \text{ kJ mole}^{-1}$$

$$E_a := 10 \cdot 10^3 \frac{\text{joule}}{\text{mole}}$$

$$k_1 := e^{\left(\frac{E_a}{R}\right) \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \cdot k_2$$

$$k_1 = 0.85583 \cdot k_2$$

$$E_a = 100 \text{ kJ mole}^{-1}$$

$$E_a := 100 \cdot 10^3 \frac{\text{joule}}{\text{mole}}$$

$$k_1 := e^{\left(\frac{E_a}{R}\right) \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \cdot k_2$$

$$k_1 = 0.2108 \cdot k_2$$

Calculating the activation energy from the rate constant at two different temperatures

The expression from above:

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

Rearrange and solve for the activation energy:

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

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

Calculate the activation energy for the reaction: $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ (data from Kask and Rawn)

Given

$$k_1 := 7.78 \cdot 10^{-7} \quad T_1 := 273 \cdot \text{K}$$

$$k_2 := 3.46 \cdot 10^{-5} \quad T_2 := 298 \cdot \text{K}$$

Solve for the activation energy:

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

$$E_a = 1.02671 \cdot 10^5 \text{ joule} \cdot \text{mole}^{-1}$$

Graphical determination of the activation energy

$$k = A \cdot e^{-\frac{E_a}{R \cdot T}}$$

The Arrhenius Equation

$$\ln(k) = \ln\left(A \cdot e^{-\frac{E_a}{R \cdot T}}\right)$$

Take the natural log

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

Expand expression (multiplied inside log so add)

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

Expand expression (power in log so multiply)

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

This has the form $y = mx + b$ where
 x axis is $1/T$
 y axis is $\ln(k)$
 y intercept is $\ln(A)$
 slope is $-E_a/R$

Calculate the activation energy and the pre-exponential factor from the following data:

Data Set $N := 5$ $i := 0, 1.. N - 1$

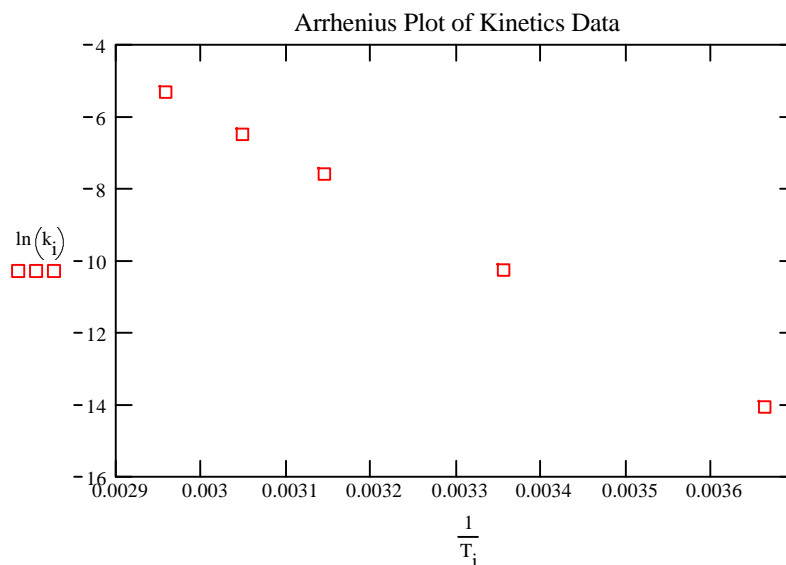
Temp (K) Rate Constant (sec-1)

$T_i :=$

$k_i :=$

273
298
318
328
338

$7.78 \cdot 10^{-7}$
$3.46 \cdot 10^{-5}$
$4.98 \cdot 10^{-4}$
$1.50 \cdot 10^{-3}$
$4.87 \cdot 10^{-3}$



Regression Analysis:

$$x_i := \frac{1}{T_i} \quad y_i := \ln(k_i)$$

Calculation of line:

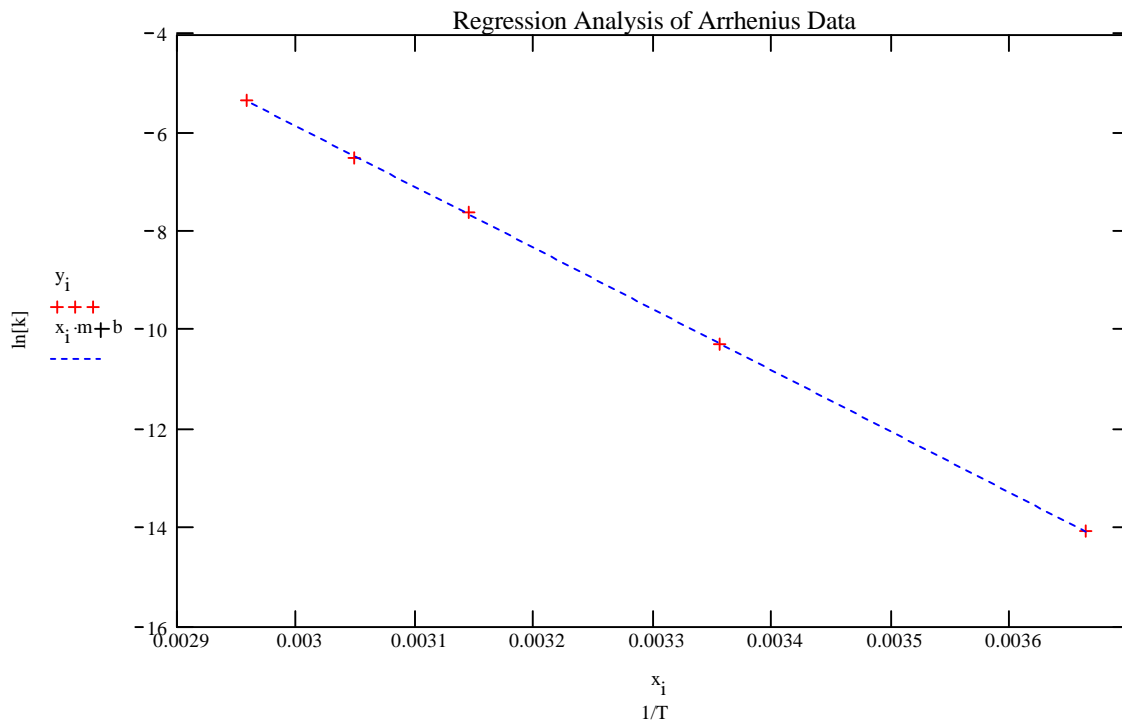
$$\text{Slope:} \quad m := \text{slope}(x, y) \quad m = -1.23912 \cdot 10^4$$

$$\text{Intercept:} \quad b := \text{intercept}(x, y) \quad b = 31.32107$$

Calculation of Activation Energy and Collision Frequency

$$E_a := -m \cdot R \cdot K \quad E_a = 1.03021 \cdot 10^5 \text{ joule} \cdot \text{mole}^{-1}$$

$$A := e^b \cdot \text{sec}^{-1} \quad A = 4.00467 \cdot 10^{13} \text{ sec}^{-1}$$



$$\text{Slope of regression line} \quad m = -1.23912 \cdot 10^4$$

$$\text{Slope of plot} \quad m = -\frac{E_a}{R}$$

$$\text{Activation Energy} \quad E_a := -m \cdot R$$

$$E_a = 1.03021 \cdot 10^5 \text{ mole}^{-1} \text{ joule} \cdot \text{K}^{-1}$$