

EXPERIMENT 1
REACTION RATE, RATE LAW, AND ACTIVATION ENERGY
THE IODINE "CLOCK" REACTION

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NAME: Tiffany Pappas
PARTNER: Daniel Perez

REPORT FORM

PART I: DETERMINATION OF THE RATE LAW

A. The Effect of Concentration on Reaction Rate

1. Reactant Concentrations and corresponding Reaction Rates

For each kinetic run, calculate the initial concentrations for the two reactants which react: $[I^-]$ and $[S_2O_8^{2-}]$.

Since the reaction whose rate is being measured takes place in a total volume of 50.0 mL, this volume must be taken into account in calculating the initial concentrations of the two reactants

For example in Run1, since the 20.0 mL of 0.200 M KI added reacts in a total volume of 50.0 mL, the initial concentration of $[I^-]$ can be calculated to be:

$$[I^-]_1 = 0.200 \text{ M KI} \frac{20.0 \text{ mL solution}}{50.0 \text{ mL solution}} = 0.0800 \text{ M KI}$$

Similarly, in Run 1, the initial concentration of $[S_2O_8^{2-}]$ is:

$$[S_2O_8^{2-}]_1 = 0.100 \text{ M (NH}_4)_2 \text{ S}_2\text{O}_8 \frac{20.0 \text{ mL solution}}{50.0 \text{ mL solution}} = 0.0400 \text{ M (NH}_4)_2 \text{ S}_2\text{O}_8$$

Carry out similar calculations for all other initial values of $[I^-]$, $[S_2O_8^{2-}]$ and $[S_2O_3^{2-}]$ and complete the appropriate columns in the Data Table.

$[S_2O_3^{2-}]$, M

| | |
|----------|--|
| All Runs | $\frac{0.00560 \text{ mol } S_2O_3^{2-}}{1 \text{ L}} \times \frac{10.0 \text{ mL}}{50.0 \text{ mL}} = \boxed{0.00112 \text{ M } S_2O_3^{2-}}$ <p style="text-align: right; margin-right: 50px;">0.00100 M</p> |
|----------|--|

↑
3 sig figs!

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| | [I ⁻] | [S ₂ O ₈ ²⁻] |
|-------|--|--|
| Run 1 | 0.200 M KI $\frac{20.0 \text{ mL}}{50.0 \text{ mL}} = 0.0800 \text{ M}$ | 0.100 M (NH ₄) ₂ S ₂ O ₈ $\frac{20.0 \text{ mL}}{50.0 \text{ mL}} = 0.0400 \text{ M}$ |
| Run 2 | $0.200 \text{ M KI} \times \frac{10.0 \text{ mL}}{50.0 \text{ mL}} = 0.0400 \text{ M}$ ✓ | same as in Run 1 |
| Run 3 | same as in Run 1 | $0.100 \text{ M (NH}_4)_2 \text{ S}_2\text{O}_8 \times \frac{10.0 \text{ mL}}{50.0 \text{ mL}} = 0.0200 \text{ M}$ ✓ |
| Run 4 | same as in Run 1 | $0.100 \text{ M (NH}_4)_2 \text{ S}_2\text{O}_8 \times \frac{5.0 \text{ mL}}{50.0 \text{ mL}} = 0.0100 \text{ M}$ ✓ |
| Run 5 | $0.200 \text{ M KI} \times \frac{8.0 \text{ mL}}{50.0 \text{ mL}} = 0.0320 \text{ M}$ | same as in Run 1 |
| Run 6 | $0.200 \text{ M KI} \times \frac{15.0 \text{ mL}}{50.0 \text{ mL}} = 0.0600 \text{ M}$ | $0.100 \text{ M (NH}_4)_2 \text{ S}_2\text{O}_8 \times \frac{15.0 \text{ mL}}{50.0 \text{ mL}} = 0.0300 \text{ M}$ ✓ |

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Table 1: Reactant Concentrations and corresponding Reaction Rates

| Run No. | Temp (°C) | KI | | | (NH ₄) ₂ S ₂ O ₈ | | | Time (t _{color}) (s) | RATE* [S ₂ O ₃ ²⁻] ₀ ----- 2 t _{color} |
|---------|-----------|----------|-------|------------------------------------|---|-------|---|--------------------------------|---|
| | | mL added | M | [I ⁻] ₀ , M | mL added | M | [S ₂ O ₈ ²⁻] ₀ , M | | |
| 1 | 22.0 | 20.0 | 0.200 | 0.0800 | 20.0 | 0.100 | 0.0400 | 38.6 | 13.0 × 10 ⁻⁶ |
| 2 | 22.0 | 10.0 | 0.200 | 0.0400 | 20.0 | 0.100 | 0.0400 | 74.6 | 6.70 × 10 ⁻⁶ |
| 3 | 22.0 | 20.0 | 0.200 | 0.0800 | 10.0 | 0.100 | 0.0200 | 141.0 | 3.55 × 10 ⁻⁶ |
| 4 | 22.0 | 20.0 | 0.200 | 0.0800 | 5.0 | 0.100 | 0.0100 | 353.8 | 1.41 × 10 ⁻⁶ |
| 5 | 22.0 | 8.0 | 0.200 | 0.0320 | 20.0 | 0.100 | 0.0400 | 95.0 | 5.26 × 10 ⁻⁶ |
| 6 | 22.0 | 15.0 | 0.200 | 0.0600 | 15.0 | 0.100 | 0.0300 | 70.0 | 7.14 × 10 ⁻⁶ |

Rate* \longrightarrow Express Rate as (A × 10⁻⁶) and in 3 significant figures

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Your partner reported 75.0 seconds

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2. Reaction Orders with respect to reactants

Summarize the relevant data from Table 1 into Table 2.

Table 2: Reactant Concentrations and corresponding Reaction Rates

| Run No. | $[I^-]_0$ (M) | $[S_2O_8^{2-}]_0$ (M) | $[I_2]$ produced (at t_{color}) (M) | Time, (t_{color}) (seconds) | Rate* $\frac{[I_2]}{t_{color}}$ (M/s) |
|---------|---------------|-----------------------|--|---------------------------------|---------------------------------------|
| 1 | 0.0800 | 0.0400 | 0.000500 | 38.6 | 13.0×10^{-6} |
| 2 | 0.0400 | 0.0400 | 0.000500 | 74.6 | 6.70×10^{-6} |
| 3 | 0.0800 | 0.0200 | 0.000500 | 141.0 | 3.55×10^{-6} |
| 4 | 0.0800 | 0.0100 | 0.000500 | 353.8 | 1.41×10^{-6} |
| 5 | 0.0320 | 0.0400 | 0.000500 | 95.0 | 5.26×10^{-6} |
| 6 | 0.0600 | 0.0300 | 0.000500 | 70.0 | 7.14×10^{-6} |

Rate* \longrightarrow Express Rate as $(A \times 10^{-6})$ and in 3 significant figures

(a) Calculating the Reaction Orders with respect to $[I^-]$

From Run 1 and Run 2:

The general formulas for the Rate Law for Runs 1 and 2 are:

$$\text{Rate}_1 = k [I^-]^m [S_2O_8^{2-}]^n$$

$$\text{Rate}_2 = k [I^-]^m [S_2O_8^{2-}]^n$$

Substitute the known concentrations of $[I^-]$ and $[S_2O_8^{2-}]$ ions and the known Reaction Rates for these runs. Include reaction orders, "m" and "n"

$$\text{Rate 1: } 13.0 \times 10^{-6} \text{ Ms}^{-1} = k [0.0800 \text{ M}]^m [0.0400 \text{ M}]^n$$

$$\text{Rate 2: } 6.70 \times 10^{-6} \text{ Ms}^{-1} = k [0.0400 \text{ M}]^m [0.0400 \text{ M}]^n$$

Divide the first equation by the second and cancel out identical terms.

$$1.94 = \frac{k [0.0800]^m [0.0400]^n}{k [0.0400]^m [0.0400]^n}$$

Note that you have obtained an equation involving only "m" as an unknown: To solve for "m", take the log of both sides of the equation and then solve for "m"

$$\log 1.94 = m \log 2.00 \quad m = \frac{\log 1.94}{\log 2.00}$$

$$m_{1,2} \longrightarrow \boxed{.956}$$

$$m = .956$$

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From Run 1 and Run 5

Do the same calculation you did for Runs 1 and 2, but use instead the values for Runs 1 and 5 to obtain "m"

Then substitute the known concentrations of $[I^-]$ and $[S_2O_8^{2-}]$ ions and the known Reaction Rates. Include reaction orders, "m" and "n". Show all calculations.

$$\frac{\text{Rate 1: } 13.0 \times 10^{-6} \text{ M s}^{-1}}{\text{Rate 5: } 5.26 \times 10^{-6} \text{ M s}^{-1}} = \frac{k [0.0800]^m [0.0400]^n}{k [0.0320]^m [0.0400]^n}$$

$$2.47 = 2.50^m$$

$$\log 2.47 = m \log 2.50$$

$$\boxed{.987 = m}$$

(2)

$$m_{1,5} \Rightarrow \boxed{.987}$$

From Run 2 and Run 5

Do the same calculation you did for Runs 1 and 2, but use instead the values for Runs 2 and 5 to obtain "m". Show all calculations

$$\frac{\text{Rate 2: } 6.70 \times 10^{-6} \text{ M s}^{-1}}{\text{Rate 5: } 5.26 \times 10^{-6} \text{ M s}^{-1}} = \frac{k [0.0400]^m [0.0400]^n}{k [0.0320]^m [0.0400]^n}$$

$$1.27 = 1.25^m$$

$$\log 1.27 = m \log 1.25$$

(2)

$$\log 1.27 / \log 1.25 = m \quad \boxed{m = 1.07}$$

$$m_{2,5} \Rightarrow \boxed{1.07}$$

Calculate the average value for "m":

$$m_{1,2} \Rightarrow \boxed{.956}$$

$$m_{1,5} \Rightarrow \boxed{.987}$$

$$m_{2,5} \Rightarrow \boxed{1.07}$$

(2)

$$m_{\text{average}} = \underline{1.00} \quad (\text{as calculated})$$

$$\boxed{m_{\text{average}} = 1}$$

(rounded off to an integer)

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(b) Calculating the Reaction Orders with respect to $[S_2O_8^{2-}]$

Applying the same approach you used for the calculation of "m" find the value of "n"

From Runs 1 and 3:

$$\frac{\text{Rate 1} : 13.0 \times 10^{-6} \text{ Ms}^{-1} = k [0.0800]^m [0.0400]^n}{\text{Rate 3} : 3.55 \times 10^{-6} \text{ Ms}^{-1} = k [0.0800]^m [0.0200]^n}$$

$$3.66 = 2.00^n$$

$$\log 3.66 = n \log 2.00$$

$$1.87 = n$$

$n_{1,3} \rightarrow$ ~~1.87~~

← experimental error

From Runs 1 and 4:

$$\frac{\text{Rate 1} : 13.0 \times 10^{-6} \text{ Ms}^{-1} = k [0.0800]^m [0.0400]^n}{\text{Rate 4} : 1.41 \times 10^{-6} \text{ Ms}^{-1} = k [0.0800]^m [0.0100]^n}$$

$$9.22 = 4.00^n$$

$$\log 9.22 = n \log 4.00$$

$$n = 1.60$$

$n_{1,4} \rightarrow$ 1.60 ✓

From Runs 3 and 4:

$$\frac{\text{Rate 3} : 3.55 \times 10^{-6} \text{ Ms}^{-1} = k [0.0800]^m [0.0200]^n}{\text{Rate 4} : 1.41 \times 10^{-6} \text{ Ms}^{-1} = k [0.0800]^m [0.0100]^n}$$

$$2.52 = 2.00^n$$

$$1.32 = n$$

$n_{3,4} \rightarrow$ 1.32 ✓

Calculate the average value for "n"

$n_{1,3} \rightarrow$ ~~1.87~~

$n_{1,4} \rightarrow$ 1.60

$n_{3,4} \rightarrow$ 1.32

$n_{\text{average}} :$ 1.46 (as calculated)

$n_{\text{average}} =$ 1 (rounded off to an integer)

↑ experimental error

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B. Determination of the Rate Constant "k"

Having found "m" and "n", the specific rate constant "k" can be calculated by substitution of "m" and "n" and the known rates and reactant concentrations into the Rate Law. Write the equation for the **Rate Law**, by substituting the values for "m" and "n" :

Rate = $k [I^-]^1 [S_2O_8^{2-}]^1$ Recall: "m" and "n" are integers

Evaluate "k" for Reactions 1 through 6. **Include units in your calculations**

| | |
|---|---|
| <p style="text-align: center;">Run 1</p> <p>$[I^-]_1 = 0.0800 M$ $[S_2O_8^{2-}]_1 = 0.0400 M$ Rate $_1 = 13.0 \times 10^{-6} M s^{-1}$</p> <p>$k = \frac{13.0 \times 10^{-6} M s^{-1}}{[0.0800 M][0.0400 M]}$</p> <p style="text-align: center;">$k_1 = 4.06 \times 10^{-3} M^{-1} s^{-1}$</p> | <p style="text-align: center;">Run 2</p> <p>$[I^-]_2 = 0.0400 M$ $[S_2O_8^{2-}]_2 = 0.0400 M$ Rate $_2 = 6.70 \times 10^{-6} M s^{-1}$</p> <p>$k = \frac{6.70 \times 10^{-6} M s^{-1}}{[0.0400 M][0.0400 M]}$</p> <p style="text-align: center;">$k_2 = 4.19 \times 10^{-3} M^{-1} s^{-1}$</p> |
| <p style="text-align: center;">Run 3</p> <p>$[I^-]_3 = 0.0800 M$ $[S_2O_8^{2-}]_3 = 0.0200 M$ Rate $_3 = 3.55 \times 10^{-6}$</p> <p>$k = \frac{3.55 \times 10^{-6} M s^{-1}}{[0.0800 M][0.0200 M]}$</p> <p style="text-align: center;">$k_3 = 2.22 \times 10^{-3} M^{-1} s^{-1}$</p> | <p style="text-align: center;">Run 4</p> <p>$[I^-]_4 = 0.0800 M$ $[S_2O_8^{2-}]_4 = 0.0100 M$ Rate $_4 = 1.41 \times 10^{-6} M s^{-1}$</p> <p>$k = \frac{1.41 \times 10^{-6} M s^{-1}}{[0.0800 M][0.0100 M]}$</p> <p style="text-align: center;">$k_4 = 1.76 \times 10^{-3} M^{-1} s^{-1}$</p> |
| <p style="text-align: center;">Run 5</p> <p>$[I^-]_5 = 0.0320 M$ $[S_2O_8^{2-}]_5 = 0.0400 M$ Rate $_5 = 5.26 \times 10^{-6} M s^{-1}$</p> <p>$\frac{5.26 \times 10^{-6} M s^{-1}}{[0.0320 M][0.0400 M]} = k$</p> <p style="text-align: center;">$k_5 = 4.11 \times 10^{-3} M^{-1} s^{-1}$</p> | <p style="text-align: center;">Run 6</p> <p>$[I^-]_6 = 0.0600 M$ $[S_2O_8^{2-}]_6 = 0.0300 M$ Rate $_6 = 7.14 \times 10^{-6} M s^{-1}$</p> <p>$k = \frac{7.14 \times 10^{-6} M s^{-1}}{[0.0600 M][0.0300 M]}$</p> <p style="text-align: center;">$k_6 = 3.97 \times 10^{-3} M^{-1} s^{-1}$</p> |

Summary of Rate Constants 'k' for Runs at Room Temperature

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 |
|------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| k ($M^{-1} s^{-1}$) | 4.06×10^{-3} | 4.19×10^{-3} | 2.22×10^{-3} | 1.76×10^{-3} | 4.11×10^{-3} | 3.97×10^{-3} |
| k (Average) ($M^{-1} s^{-1}$) | 3.39×10^{-3} | | | | | |

Write the **Rate Law** for the reaction studied, by substituting the values for "m", "n" and "k":

$Rate = 3.39 \times 10^{-3} M^{-1} s^{-1} [I^-]^1 [S_2O_8^{2-}]^1$ Include units!

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C. The Effect of the Catalyst on the Reaction Rate

Cu^{2+} is a catalyst in the reaction studied. As such, the Rate Law of the catalyzed reaction could be written as:

$$\text{Rate} = k [\text{I}^-]^m [\text{S}_2\text{O}_8^{2-}]^n [\text{Cu}^{2+}]^p$$

where the reaction orders "m" and "n" are the same as in the uncatalyzed reaction. To determine if there is a quantitative relationship between reaction rate and catalyst (that is "p", the reaction order with respect to the catalyst), summarize your data for Reaction Runs with the same concentrations, at the same temperature, but with varying amounts of catalyst added.

In this manner, the effect of the concentration of catalyst on the Reaction Rates may be evaluated independent of other factors.

Reaction Mixtures with varying amounts of Catalyst

| Run No. | Temp. (°C) | Drops of CuSO_4 (0.1 M) | Time (t_{color}) (s) | $[\text{S}_2\text{O}_3^{2-}]$ M | RATE $[\text{S}_2\text{O}_3^{2-}]_0 / 2 t_{\text{color}}$ M s^{-1} |
|---------|------------|----------------------------------|---------------------------------|---------------------------------|---|
| 7 | 22.0 | 4 | 7.1 | 0.001 | 70.4×10^{-6} |
| 8 | 22.0 | 2 | 17.0 | 0.001 | 29.4×10^{-6} |

From the data in this table, calculate "p", the reaction order with respect to $[\text{Cu}^{2+}]$ (nearest whole number or zero).

The calculations are similar to those done for the reaction order with respect to $[\text{I}^-]$ ("m") and $[\text{S}_2\text{O}_8^{2-}]$ ("n")

Show calculations below:

$$\begin{aligned} \text{Rate 7: } 70.4 \times 10^{-6} \text{ M s}^{-1} &= k [\text{I}^-]^m [\text{S}_2\text{O}_8^{2-}]^n [\text{Cu}^{2+}]^p = \frac{4 \text{ drops}}{2 \text{ drops}} \\ \text{Rate 8: } 29.4 \times 10^{-6} \text{ M s}^{-1} &= k [\text{I}^-]^m [\text{S}_2\text{O}_8^{2-}]^n [\text{Cu}^{2+}]^p \end{aligned}$$

$$\begin{aligned} 2.39 &= 2^p \\ \log 2.39 &= p \log 2 \\ 1.257 &= p \end{aligned}$$

p → 1
(rounded off to the nearest integer or zero)

Write the complete form of the **Rate Law** (include both reactants and the catalyst with their respective orders of reaction) and substitute "k" with the experimentally determined value.

Include units!

$$\text{Rate} = 3.39 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} [\text{I}^-] [\text{S}_2\text{O}_8^{2-}] [\text{Cu}^{2+}]$$

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PART II: THE EFFECT OF TEMPERATURE ON REACTION RATE

To determine the quantitative relationship between reaction rate and temperature, summarize your data for Reaction Runs with the same concentrations of all reactants but run at different temperatures. In this manner, the corresponding reaction rates for these runs will be affected by temperature changes only.

| Run No. | Temp. (°C) | Temp. (K) | $\frac{1}{T}$ (K ⁻¹) | Time (t _{color}) (s) | [S ₂ O ₃ ²⁻] M | RATE [S ₂ O ₃ ²⁻] $\frac{M}{2 t_{color}}$ (M s ⁻¹) | ln (RATE) |
|---------|------------|-----------|----------------------------------|--------------------------------|--|--|-----------|
| 1 | 22.0 | 295.0 | .003390 | 38.6 | 0.00100 | 13.0 x 10 ⁻⁶ | -11.251 |
| 9 | 40.0 | 313.0 | .003194 | 10.1 | 0.00100 | 49.5 x 10 ⁻⁶ | -9.914 |
| 10 | 9.5 | 282.5 | .003539 | 151.4 | 0.00100 | 3.30 x 10 ⁻⁶ | -12.622 |
| 11 | 1.5 | 274.5 | .003642 | 271.7 | 0.00100 | 1.84 x 10 ⁻⁶ | -13.206 |

To evaluate the Activation Energy (E_a), make a graph of ln(Rate) vs. 1/T (X x 10⁻³) on graph paper provided. In the upper-right hand side of the graph provide a table that includes that data being plotted. Recall that every graph must have a title.

Find the slope of the line obtained by drawing the best straight line through the 4 experimental points. Show calculations for slope on the graph

Slope \Rightarrow -7.4×10^3 K

From the slope, calculate the Activation Energy (E_a). Recall that R = 8.315 J/K x mol Show calculations below. Please include units in your calculations.

$-E_a = (R)(\text{slope})$

$\frac{6.2 \times 10^4 \cancel{J}}{\text{mol}} \times \frac{1 \text{ KJ}}{1000 \cancel{J}} =$

$E_a = \left(\frac{8.315 \text{ J}}{\text{K} \cdot \text{mol}} \right) \left(-\frac{7.4 \times 10^3 \text{ K}}{1} \right)$

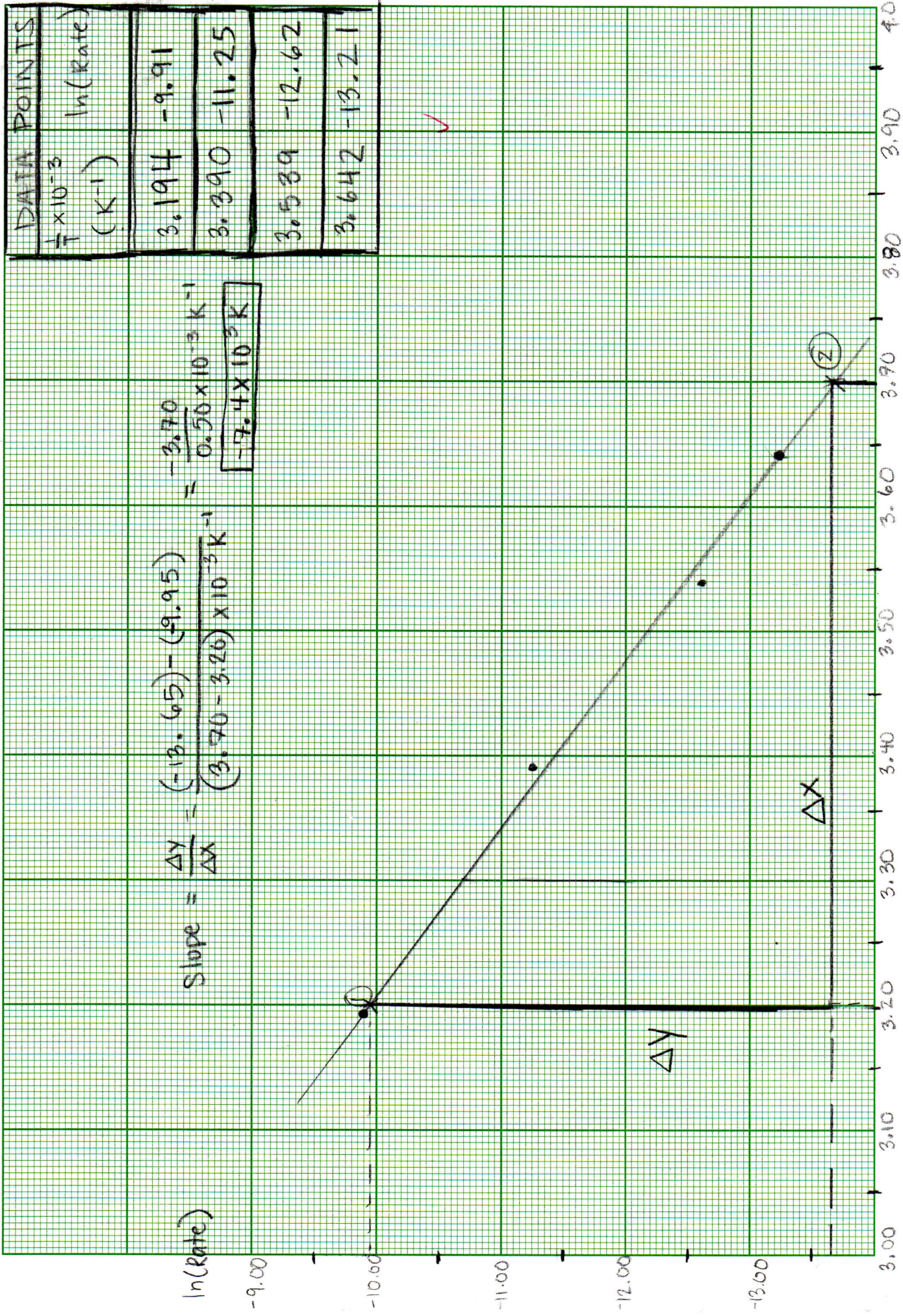
$E_a = 6.2 \times 10^4 \text{ J/mol}$

E_a \Rightarrow 6.2×10^4 J/mol

E_a \Rightarrow 62 kJ/mol

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GRAPHICAL REPRESENTATION OF $\ln(\text{Rate})$ vs. $\frac{1}{T}$ with Regards to the Iodine Clock Reaction



$$\text{Slope} = \frac{\Delta Y}{\Delta X} = \frac{(-13.65) - (-9.95)}{(3.70 - 3.26) \times 10^{-3} K^{-1}}$$

$$= \frac{-3.70}{0.50 \times 10^{-3} K^{-1}}$$

$$= \boxed{-7.4 \times 10^3 K}$$

$$\frac{1}{T} \times 10^{-3} (K^{-1})$$