

PHYSICAL CHEMISTRY LABORATORY II

EXPERIMENT NUMBER: 6

NAME OF THE EXPERIMENT: Experimental Determination of the Reaction Rate

DATE OF THE EXPERIMENT: 27/4/2023

NAME OF THE ASSISTANT: Elif DEMİR ARABACI

GROUP NUMBER: 5

STUDENT NAME SURNAME: Elif Nazenin GİRAY

GROUP MEMBERS: Berkay Yapıcı & Alper İrez

SECTION: Thursday Afternoon

DATA SHEET

Table 1. Set 1 Data's

Set 1. 50°C K₂S₂O₈ + KI

Time(sec)	V _{titrant}
180 seconds	12,5 mL
420 seconds	18 mL
3600 seconds	19,2 mL

Table 2. Set 2 Data's

Set 2. 25°C K₂S₂O₈ + KI

Time (Sec)	V _{titrant}
180 seconds	7,2 mL
420 seconds	11,5 mL
600 seconds	15 mL
900 seconds	16,6 mL
1200 seconds	17 mL
1800 seconds	17,9 mL
2520 seconds	20,4 mL
3600 seconds	22,4 mL

Table 3. Set 3 Data's

K₂S₂O₈ + KI + KCl

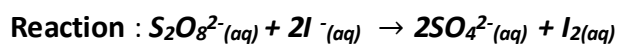
Time (Sec)	V _{titrant}
180 seconds	9 mL
420 seconds	16 mL
600 seconds	17,8 mL
900 seconds	19 mL
1200 seconds	19,3 mL
1800 seconds	20,5 mL
2520 seconds	21 mL
3600 seconds	22,2 mL

CALCULATION

Calculations for Set 2 and Set 3

FOR SET 2

→ Finding the concentration of S₂O₈²⁻ which taking from sample (from titration data)



Titration with $\text{Na}_2\text{S}_2\text{O}_3$ reaction is $\text{I}_{2(aq)} + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_2\text{O}_6^{2-}$

After all I_2 consumed by $2\text{S}_2\text{O}_3^{2-}$ titrant, analyte solution become colorless.

$$\text{Titrant} = n(\text{S}_2\text{O}_3^{2-}) = M_{\text{titrant}} \times V_{\text{titrant}}$$

$n(\text{I}_2)$ equal to $n(\text{S}_2\text{O}_3^{2-})/2$ and $n(\text{S}_2\text{O}_8^{2-})$

$$M(\text{S}_2\text{O}_8^{2-}) = \frac{n}{V} \quad V=10 \text{ mL (titrated analyte)}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{reacted}} = ((M_{\text{titrant}} \times V_{\text{titrant}}) / (2 \times 10 \text{ mL})) \Rightarrow (M_{\text{titrant}}) = 0,02 \text{ M}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{initial}} - [\text{S}_2\text{O}_8^{2-}]_{\text{reacted}} = [\text{S}_2\text{O}_8^{2-}]_{\text{unreacted}}$$

FOR SET 2 Calculation at 180 seconds,

$$M_{\text{titrant}} = 0.02 \text{ M} \quad V_{\text{titrant}} = 7,2 \text{ mL}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{Reacted}} = \frac{((0,02 \frac{\text{mol}}{\text{L}}) \times 7,2 \text{ mL})}{(2 \times 10 \text{ mL})} = 7,2 \times 10^{-3} \text{ M} \quad [\text{S}_2\text{O}_8^{2-}]_{\text{Initial}} = 0,036 \text{ M}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{Unreacted}} = ((0,036 - (7,2 \times 10^{-3})) = 0,0288$$

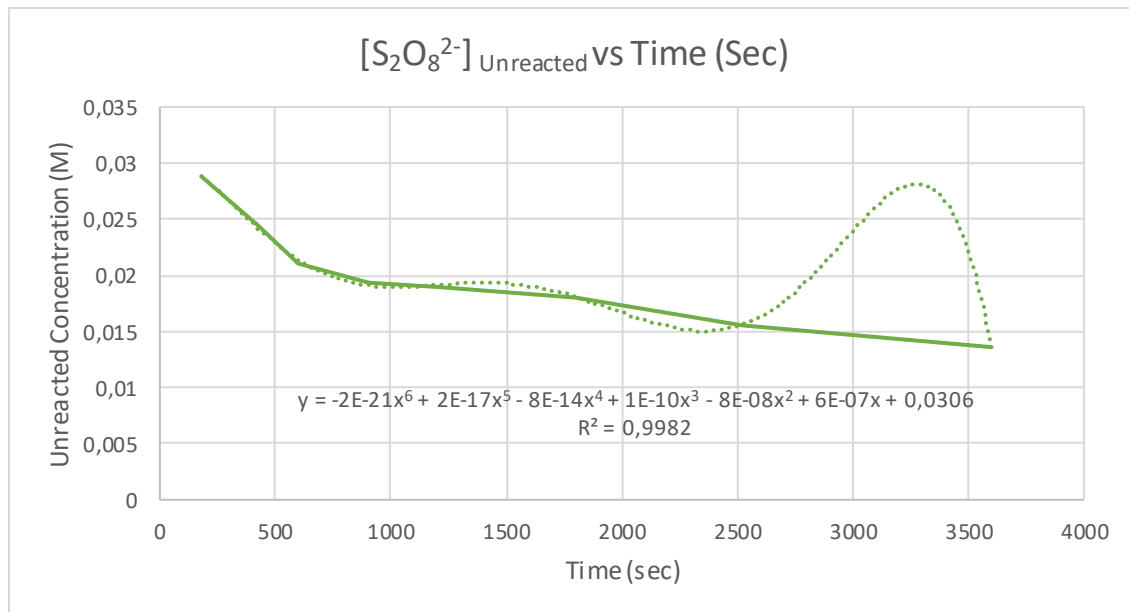
Set 2 for other steps(420,600,900,1200,1800,2520,3600 seconds) applying same calculations,

Table 4. Unreacted concentrations with Time

Time (Sec)	Unreacted Concentrations(M)
180 seconds	0,0288
420 seconds	0,0245
600 seconds	0,021
900 seconds	0,0194
1200 seconds	0,019
1800 seconds	0,018
2520 seconds	0,0156
3600 seconds	0,0136

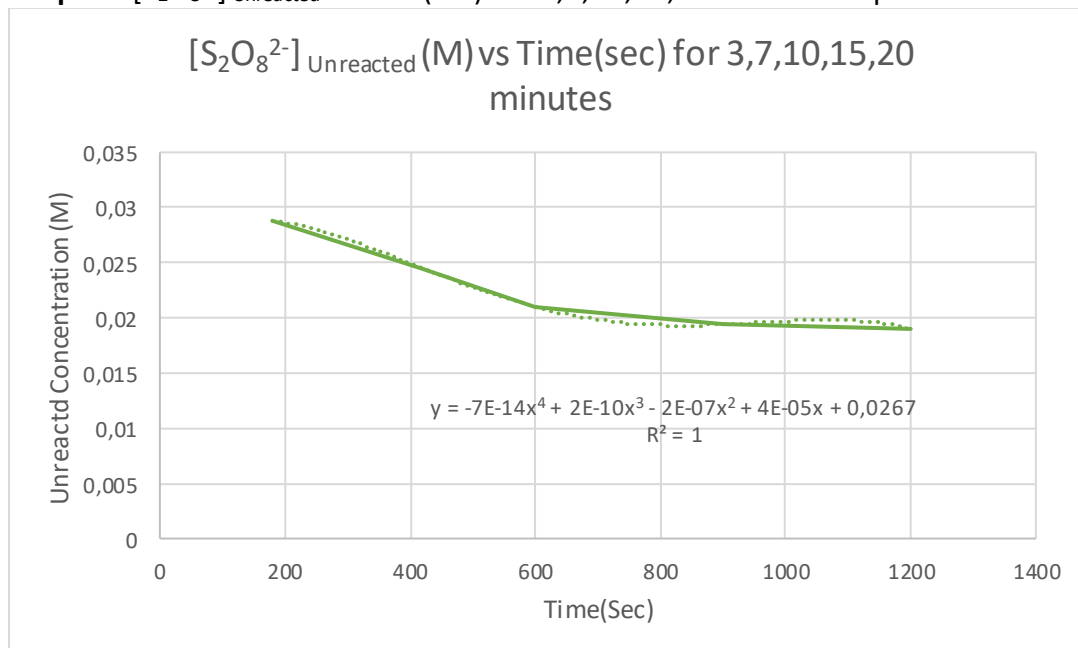
2) Plot $[S_2O_8^{2-}]_{\text{Unreacted}}$ vs time(sec) graph and fit the trend line as polynomial and choose the proper order.

Graph 1. $[S_2O_8^{2-}]_{\text{Unreacted}}$ vs Time (Sec) Graph



3) Plot the same graph $[S_2O_8^{2-}]_{\text{Unreacted}}$ vs time(sec), this time use only 3, 7, 10, 15, 20 minute data. Fit the trend line as polynomial and choose the proper order show the line equation.

Graph 2. $[S_2O_8^{2-}]_{\text{Unreacted}}$ vs Time(sec) for 3,7,10,15,20 minutes Graph



4. Take the derivative of the equation to find dc/dt .

→ From Graph 2.,

$$y = (-7 \times 10^{-14})x^4 + (2 \times 10^{-10})x^3 - (2 \times 10^{-7})x^2 + (4 \times 10^{-5})x + 0,0267 \text{ and } R^2 = 1 \text{ thus}$$

$$dc/dt = (-28 \times 10^{-14})x^3 + (6 \times 10^{-10})x^2 + (-4 \times 10^{-7})x + (4 \times 10^{-5})$$

At 180 seconds x equal to 0,0288 thus

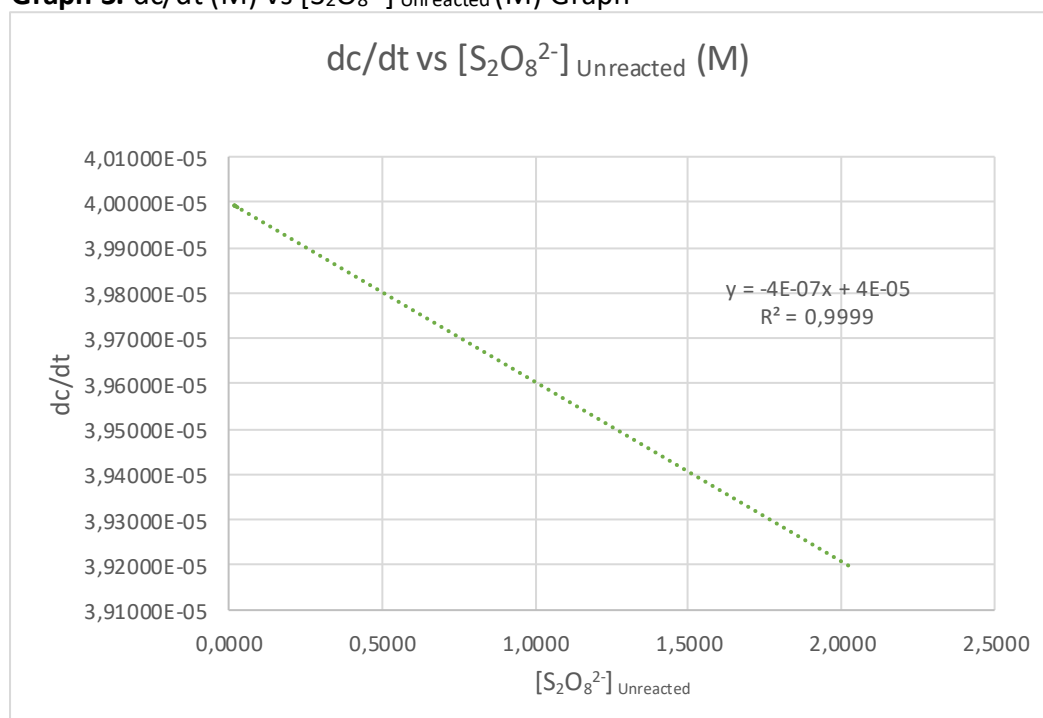
$$dc/dt = (-28 \times 10^{-14})(0,0288)^3 + (6 \times 10^{-10})(0,0288)^2 + (-4 \times 10^{-7})(0,0288) + (4 \times 10^{-5})$$

$$dc/dt = 3,9999885 \times (10^{-5})M$$

Table 5. Time(sec) with dc/dt values

Time(Sec)	$[S_2O_8^{2-}]_{\text{Unreacted}}$ (M)	Dc/dt (M)
180 seconds	0,0288	$3,99885 \times 10^{-5}$
420 seconds	0,0245	$3,99902 \times 10^{-5}$
600 seconds	0,021	$3,99916 \times 10^{-5}$
900 seconds	0,0194	$3,99922 \times 10^{-5}$
1200 seconds	0,019	$3,99924 \times 10^{-5}$

Graph 3. dc/dt (M) vs $[S_2O_8^{2-}]_{\text{Unreacted}}$ (M) Graph



5) Plot $\frac{d[A]}{dt}$ vs $[S_2O_8^{2-}]_{\text{Unreacted}}$ (M) for 3, 7, 10, 15, 20min data to find the rate constant, k.

$$\frac{d[A]}{dt} = -k[A] \text{ in there } [A] \text{ equal to } [S_2O_8^{2-}]_{\text{Unreacted}} \text{ thus,}$$

$\frac{d[S_2O_8^{2-}]_{\text{Unreacted}}}{dt} = -k[S_2O_8^{2-}]_{\text{Unreacted}}$ the slope of Graph 3 equal to negative of rate constant which is -k thus

$$k = 4 \times 10^{-7} \text{ s}^{-1}$$

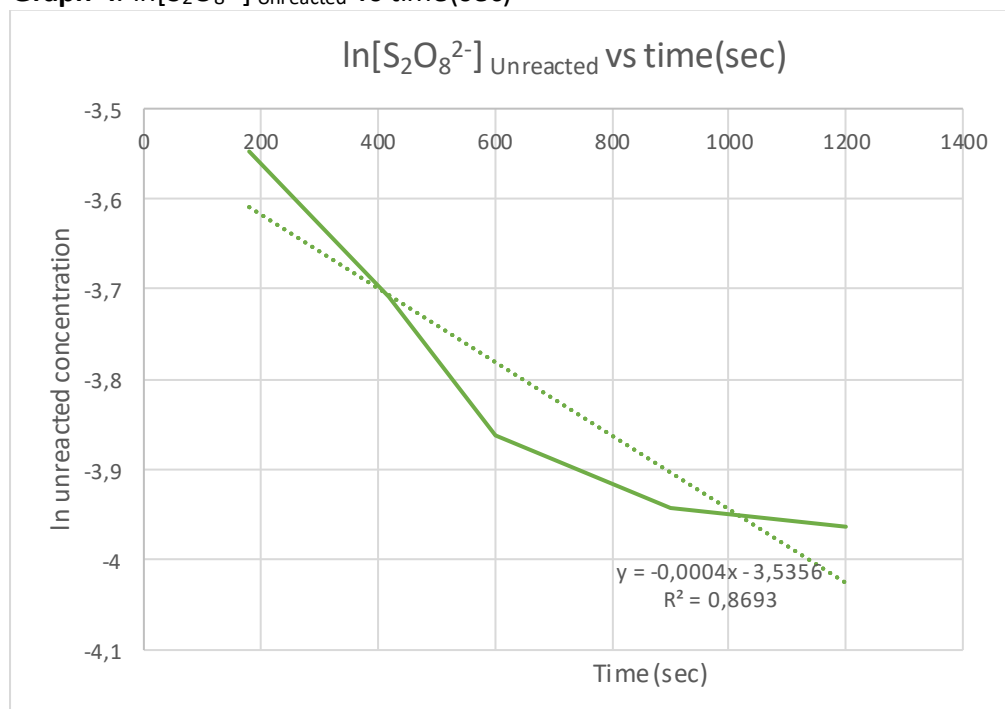
6) Plot $\ln[S_2O_8^{2-}]_{\text{Unreacted}}$ vs time(sec) for 3, 7, 10, 15, 20min data to find k.

For 180 second, $\ln[S_2O_8^{2-}]_{\text{Unreacted}} = \ln[0,0288] = -3,54738$ same calculation for other time values thus,

Table 6. $\ln[S_2O_8^{2-}]_{\text{Unreacted}}$ with time(sec) for 3, 7, 10, 15, 20min data

Time(Sec)	$[S_2O_8^{2-}]_{\text{Unreacted}}$ (M)	$\ln[S_2O_8^{2-}]_{\text{Unreacted}}$
180 seconds	0,0288	-3,54738
420 seconds	0,0245	-3,7091
600 seconds	0,021	-3,8632
900 seconds	0,0194	-3,9424
1200 seconds	0,019	-3,9633

Graph 4. $\ln[S_2O_8^{2-}]_{\text{Unreacted}}$ vs time(sec)



6) $\ln[A] = \ln[A]_0 - kt$ thus $\ln[S_2O_8^{2-}]_{\text{Unreacted}} = \ln[S_2O_8^{2-}]_0 - kt$ the slope of Graph 4 equal to $-k$,
 $-k = 0,004 \text{ s}^{-1}$

7. k_{av} ?

$$(0,004 + (4 \times 10^{-7})) / 2 = 2,002 \times 10^{-4} \text{ s}^{-1}$$

8) $t_{1/2}$?

Reaction is first order reaction then $t_{1/2} = \ln 2 / k$, $\ln 2 = 0,6931$ $k = k_{av}$

$$t_{1/2} = (0,6931) / 2,002 \times 10^{-4} \text{ s}^{-1} = 3462,27 \text{ seconds}$$

FOR SET 3

$$\text{Titrant} = n(S_2O_3^{2-}) = M_{\text{titrant}} \times V_{\text{titrant}}$$

$n(I_2)$ equal to $n(S_2O_3^{2-})/2$ and $n(S_2O_8^{2-})$

$$M(S_2O_8^{2-}) = \frac{n}{V} \quad V = 10 \text{ mL (titrated analyte)}$$

$$[S_2O_8^{2-}]_{\text{reacted}} = ((M_{\text{titrant}} \times V_{\text{titrant}}) / (2 \times 10 \text{ mL})) \Rightarrow (M_{\text{titrant}}) = 0,02 \text{ M}$$

$$[S_2O_8^{2-}]_{\text{initial}} - [S_2O_8^{2-}]_{\text{reacted}} = [S_2O_8^{2-}]_{\text{unreacted}}$$

For set 3 at 180 seconds

$$M_{\text{titrant}} = 0.02 \text{ M} \quad V_{\text{titrant}} = 9 \text{ mL}$$

$$[S_2O_8^{2-}]_{\text{Reacted}} = \frac{((0,02 \frac{\text{mol}}{\text{L}}) \times (9 \text{ mL}))}{(2 \times 10 \text{ mL})} = 9 \times 10^{-3} \text{ M} \quad [S_2O_8^{2-}]_{\text{Initial}} = 0,036 \text{ M}$$

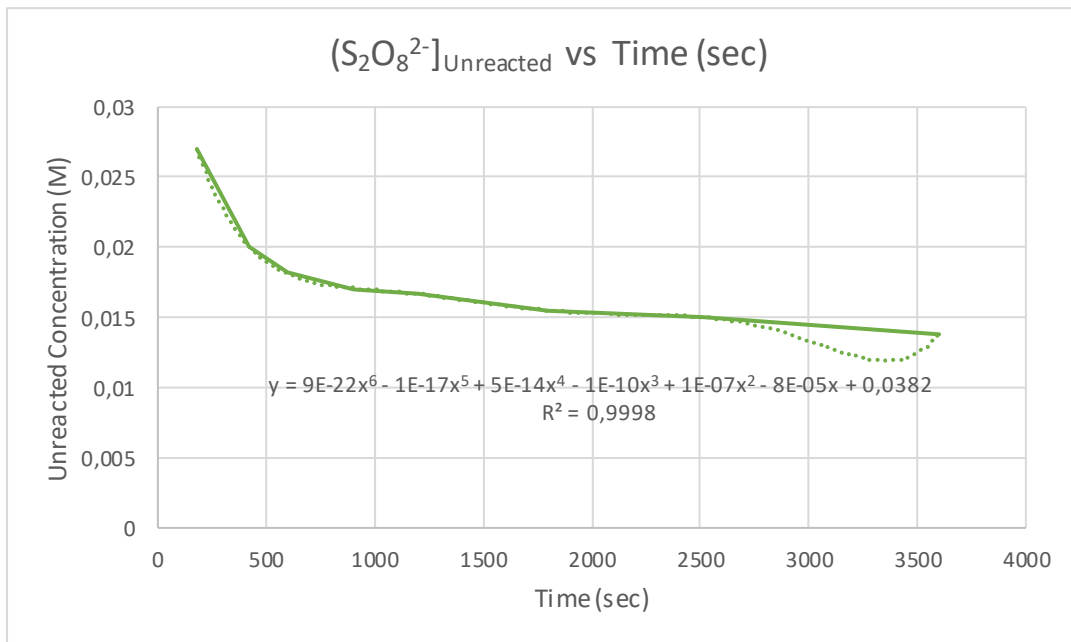
$$[S_2O_8^{2-}]_{\text{Unreacted}} = (0,036 - (9 \times 10^{-3})) = 0,027$$

Set 3 for other steps (420, 600, 900, 1200, 1800, 2520, 3600 seconds) applying same calculations

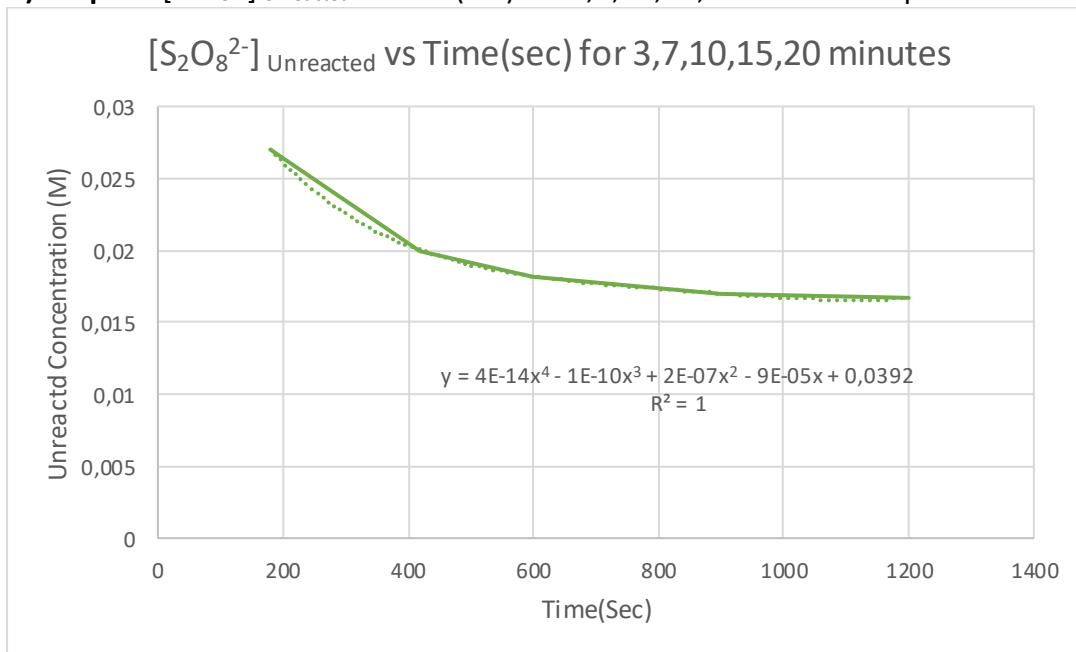
Table 7. $[S_2O_8^{2-}]_{\text{Unreacted}}$ with Time (sec) values

Time (Sec)	Unreacted Concentrations(M)
180 seconds	0,027
420 seconds	0,02
600 seconds	0,0182
900 seconds	0,017
1200 seconds	0,0167
1800 seconds	0,0155
2520 seconds	0,015
3600 seconds	0,0138

2) Graph 5. $[S_2O_8^{2-}]_{\text{Unreacted}}$ vs Time (sec) Graph



3) Graph 6. $[S_2O_8^{2-}]_{\text{Unreacted}}$ vs Time(sec) for 3,7,10,15,20 minutes Graph



4) From Graph 6,

$y = (-4 \times 10^{-14})x^4 + (1 \times 10^{-10})x^3 - (2 \times 10^{-7})x^2 + (-9 \times 10^{-5})x + 0,0392$ and $R^2 = 1$ thus

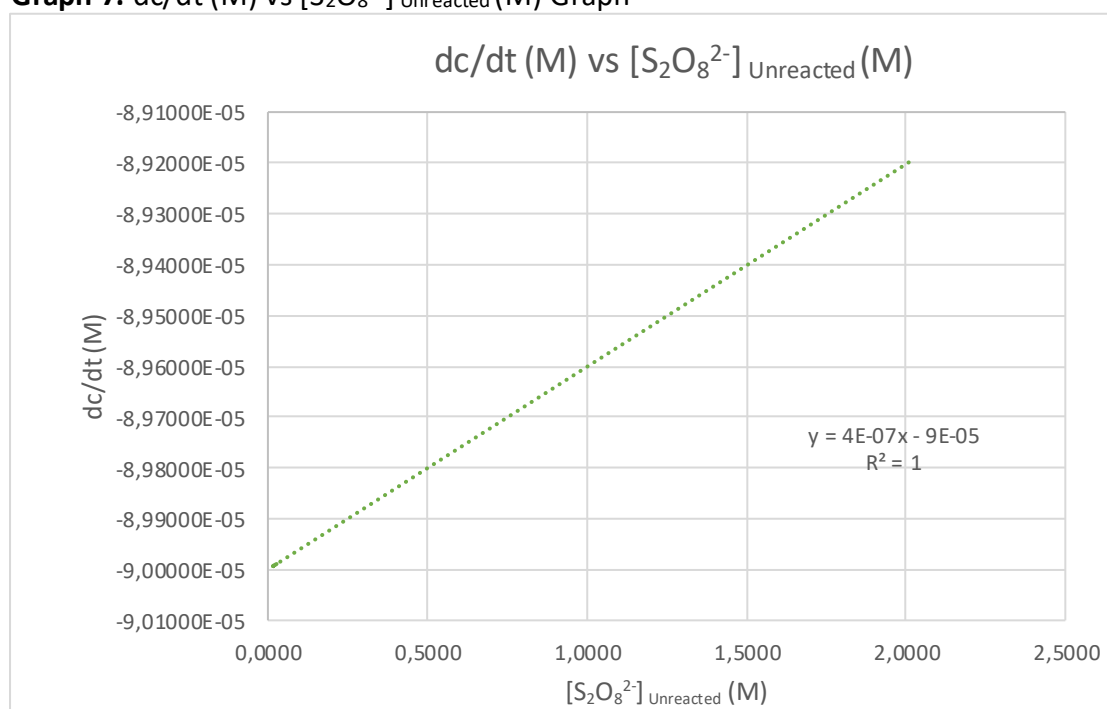
$$dc/dt = (-16 \times 10^{-14})x^3 + (3 \times 10^{-10})x^2 + (-9 \times 10^{-7})$$

At 180 seconds x equal to 0,027 thus

$$dc/dt = (-16 \times 10^{-14})(0,027)^3 + (3 \times 10^{-10})(0,027)^2(-9 \times 10^{-7}) = -8.9989 \times 10^{-3}$$

Table 8. Time(sec) with dc/dt values

Time(Sec)	$[S_2O_8^{2-}]_{\text{Unreacted}}$ (M)	Dc/dt (M)
180 seconds	0,027	$-8,9989 \times 10^{-5}$
420 seconds	0,0	$-8,9992 \times 10^{-5}$
600 seconds	0,0182	$-8,99927 \times 10^{-5}$
900 seconds	0,0194	$-8,99932 \times 10^{-5}$
1200 seconds	0,019	$-8,99933 \times 10^{-5}$

Graph 7. dc/dt (M) vs $[S_2O_8^{2-}]_{\text{Unreacted}}$ (M) Graph

5) $\frac{d[A]}{dt} = -k[A]$ in there [A] equal to $[S_2O_8^{2-}]_{\text{Unreacted}}$ thus,

$d[S_2O_8^{2-}]_{\text{Unreacted}} / dt = -k[S_2O_8^{2-}]_{\text{Unreacted}}$ the slope of Graph 7 equal to negative of rate constant which is -k thus

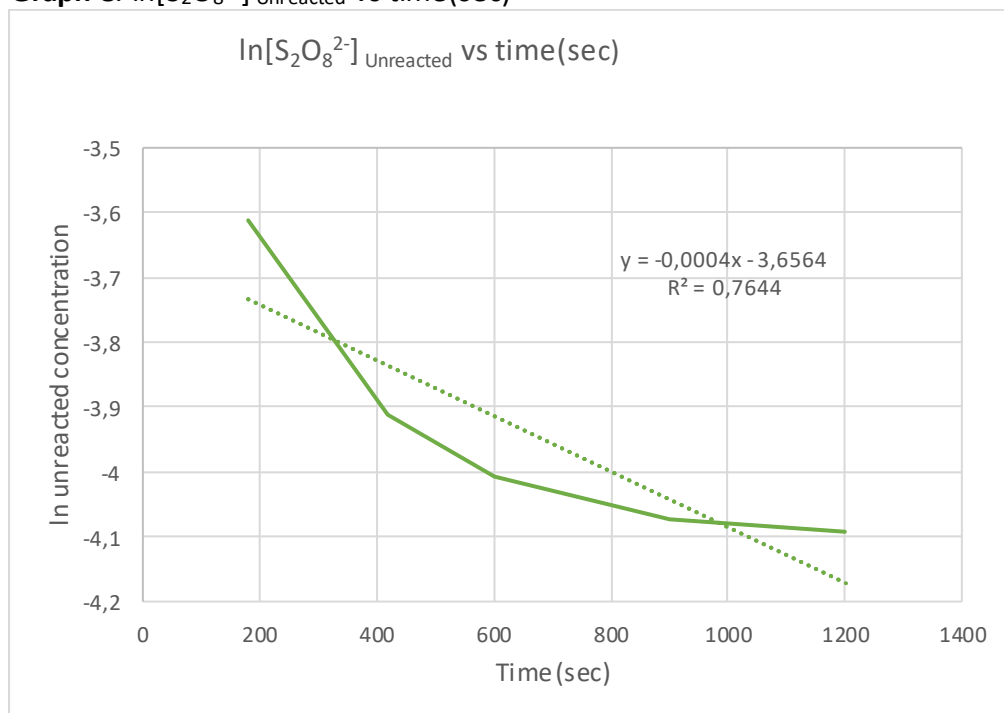
$$k = 4 \times 10^{-7} \text{ s}^{-1}$$

6) For 180 second, $\ln[S_2O_8^{2-}]_{\text{Unreacted}} = \ln[0,027] = -3,6119$ same calculation for other time values thus,

Table 9. $\ln[S_2O_8^{2-}]_{\text{Unreacted}}$ with time(sec) for 3, 7, 10, 15, 20min data

Time(Sec)	$[S_2O_8^{2-}]_{\text{Unreacted}} \text{ (M)}$	$\ln[S_2O_8^{2-}]_{\text{Unreacted}}$
180 seconds	0,0288	-3,6119
420 seconds	0,02	-3,9120
600 seconds	0,0182	-4,0063
900 seconds	0,017	-4,0745
1200 seconds	0,0167	-4,0923

Graph 8. $\ln[S_2O_8^{2-}]_{\text{Unreacted}}$ vs time(sec)



6) $\ln[A] = \ln[A]_0 - kt$ thus $\ln[S_2O_8^{2-}]_{\text{Unreacted}} = \ln[S_2O_8^{2-}]_0 - kt$ the slope of Graph 8 equal to $-k$,
 $-k = 0,004 \text{ s}^{-1}$

7) k_{av} ?

$$(0,004 + (4 \times 10^{-7})) / 2 = 2,002 \times 10^{-4} \text{ s}^{-1}$$

8) $t_{1/2}$?

Reaction is first order reaction then $t_{1/2} = \ln 2 / k$, $\ln 2 = 0,6931$ $k = k_{av}$

$$t_{1/2} = (0,6931) / 2,002 \times 10^{-4} \text{ s}^{-1} = 3462,27 \text{ seconds}$$

SET 1 CALCULATIONS

$$9) \text{ Titrant} = n(\text{S}_2\text{O}_3^{2-}) = M_{\text{titrant}} \times V_{\text{titrant}}$$

$$n(I_2) \text{ equal to } n(\text{S}_2\text{O}_3^{2-})/2 \text{ and } n(\text{S}_2\text{O}_8^{2-})$$

$$M(\text{S}_2\text{O}_8^{2-}) = \frac{n}{V} \quad V=10 \text{ mL (titrated analyte)}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{reacted}} = ((M_{\text{titrant}} \times V_{\text{titrant}}) / (2 \times 10 \text{ mL})) \Rightarrow (M_{\text{titrant}}) = 0,02 \text{ M}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{initial}} - [\text{S}_2\text{O}_8^{2-}]_{\text{reacted}} = [\text{S}_2\text{O}_8^{2-}]_{\text{unreacted}}$$

$$\text{For Set 1 at 180 seconds, } V_{\text{titrant}} = 12,5 \text{ mL, } M_{\text{titrant}} = 0.02 \text{ M}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{Reacted}} = \frac{\left((0,02 \frac{\text{mol}}{\text{L}}) \times (12,5 \text{ mL})\right)}{(2 \times 10 \text{ mL})} = 0,0125 \text{ M}$$

$$\text{For Set 1 at 420 seconds, } V_{\text{titrant}} = 18 \text{ mL, } M_{\text{titrant}} = 0.02 \text{ M}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{Reacted}} = \frac{\left((0,02 \frac{\text{mol}}{\text{L}}) \times (18 \text{ mL})\right)}{(2 \times 10 \text{ mL})} = 0,018 \text{ M}$$

$$\text{For Set 1 at 3600 seconds, } V_{\text{titrant}} = 19,2 \text{ mL, } M_{\text{titrant}} = 0.02 \text{ M}$$

$$[\text{S}_2\text{O}_8^{2-}]_{\text{Reacted}} = \frac{\left((0,02 \frac{\text{mol}}{\text{L}}) \times (19,2 \text{ mL})\right)}{(2 \times 10 \text{ mL})} = 0,0195 \text{ M}$$

$R = \Delta c / \Delta t$ thus,

→ For 180 seconds,

$$R = (0,0125 - 0) \text{ M} / (180 - 0) \text{ s} = 6,94 \times 10^{-5} \text{ M/s}$$

→ For 420 seconds,

$$R = (0,018 - 0,0125) \text{ M} / (420 - 180) \text{ s} = 2,292 \times 10^{-5} \text{ M/s}$$

→ For 3600 seconds,

$$R = (0,0195 - 0,018) \text{ M} / (3600 - 420) \text{ s} = 4,717 \times 10^{-7} \text{ M/s}$$

10. Compare the reaction rate with 3rd min data for (set2) 25 °C and (set1) 50 °C,

FOR SET 2 at 180 seconds, at 25 °C

$$[\text{S}_2\text{O}_8^{2-}]_{\text{Reacted}} = \frac{\left((0,02 \frac{\text{mol}}{\text{L}}) \times 7,2 \text{ mL}\right)}{(2 \times 10 \text{ mL})} = 7,2 \times 10^{-3} \text{ M} \quad \text{firstly no reacted happen thus a at } 0^{\text{th}} \text{ min } 0 \text{ M thus}$$

$$R = (7,2 \times 10^{-3} - 0) \text{ M} / (180 - 0) \text{ s} = 4,0 \times 10^{-5} \text{ M/s}$$

FOR SET 1 at 180 seconds, at 50 °C

$$R = (0,0125 - 0) \text{ M} / (180 - 0) \text{ s} = 6,94 \times 10^{-5} \text{ M/s}$$

As the temperature increased, it was observed that the reaction rate increased, as shown in the calculations, which shows that the reaction is endothermic.

QUESTIONS

- 1) During the experiment, cold water was added to prevent the reaction from proceeding before the titration because theoretically, the reaction was known to be endothermic in our experiment. As a result of the $R = \Delta c / \Delta t$ process in calculation number 10 this theory has been proven to be correct. It is known that the temperature increase will increase the reaction rate because this is an endothermic reaction.
- 2) The ionic strength between the ions is expected to increase if the presence of ions increases, and on the other hand, if the ions have charges with the same sign the increasing ionic strength is expected to increase the rate constant but if the ions have different charges it will decrease the rate constant^[1]. In Set2 and Set3 the effect of the increasing ion interaction on the reaction rate to examine it we added KCl to Set3 and thus increased the number of ions. As a result of the increase in the number of ions in the experiment and the interaction brought by it was expected that the rate constant would increase for Set3 however, in the calculations made for Set2 and Set3 in the calculation part of the report, it was observed that the reaction rate did not increase for Set3.
- 3) $aA + bB \longrightarrow \text{Product}$

Suppose we have a reaction above.

The formula for the rate of this reaction is with stoichiometric values,

$$\text{Rate} = -\frac{1}{b} \frac{[B]}{dt} = -\frac{1}{a} \frac{[A]}{dt}$$

OR

$$v = k \times [A]^a [B]^b$$

$a+b=0 \rightarrow$	Zero order
$a+b=1 \rightarrow$	First order
$a+b=2 \rightarrow$	Second order

k is the rate constant and finding the order of reaction, the "a" and "b" must be summarized.^[2]

→ Reactants may have different concentrations in reactions. In a situation where the order of the reaction is unknown, there may be concentrations that vary according to the rate it has. By doing the reverse operation, we can find the reaction order by comparing the reaction rates where the changing concentrations of a reaction whose order we do not know are equal.^[2]

For instance,

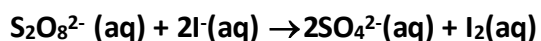


$$v = k \times [A]^a [B]^b \quad k = 1,8 \times 10^{-5} \quad v = 180 \times 10^{-5} \quad [A] = 10 \text{ M} \quad [B] = 1 \text{ M} \Rightarrow 10^2 = 100$$

then order of reaction is 2.

DISCUSSION

To examine how the reaction rate is affected by the temperature at which the reactions take place and their ionic strengths, the solutions were discussed at different temperatures and the effectiveness of different ionic strengths in the environment. For these purposes, three sets of experiments were established for the solutions. Set1 and Set2 were appointed to investigate the effect of temperature on the reaction rate reaction used in these two sets is:



In Set 1, this reaction occurred at 50°C; in Set 2, this reaction occurred at 25°C.

To examine the effect of the ionic power created by the ions on the reaction rate, the Set2 and Set3 stages were established in the experiment. The reactions in Set2 and Set3 occurred at the same temperature, but KCl was added to Set3 differently than Set2. Measurements were taken at certain times to compare the reaction rates in different conditions prepared in the experiment. Titration into solutions before applying the process, we wanted to stop the progress of the reaction with 200 mL of distilled water because we theoretically knew that the reaction, we were working on was endothermic.

$\text{Na}_2\text{S}_2\text{O}_3$ and Starch were used to titrate the solutions in the experiment. The titration process was used to determine the concentrations of the reactants before and after the reaction. Starch was used because it decomposes in case of excess iodine ions. Since the reaction is endothermic, the reaction rate is expected to increase as the temperature rises. As a result of the data taken from Set1 and Set2 and the calculations made afterwards, the reaction rate increased, proving the theory. On the other hand, in the calculations made for Set2 and Set3, it was not observed that the reaction rate increased despite the increasing ion effect.

Some errors may have occurred during the titration that causes to same rate constant values for Set2 and Set3. Among the main reasons, there may have been problems in the thermal equilibrium of the water bath because the lid could not be closed. Time errors may have occurred. The temperature of the environment may have affected the experiment. The volumes spent during titration may have been misread. Na_2SO_3 may have been used too much. Using more Starch than requested may have caused an error.

References

- [1] Liu, Y., Sheaffer, R. L., & Barker, J. R. (2003). Effects of temperature and ionic strength on the rate and equilibrium constants for the reaction $I^{\bullet}aq + i-aq \leftrightarrow I2^{\bullet}-aq$. *The Journal of Physical Chemistry A*, 107(48), 10296–10302.
<https://doi.org/10.1021/jp036126a>
- [2] Atkins, P. W., & Paula, J. D. (2014). Chapter 20 Chemical Kinetics. In *Atkins' physical chemistry* (pp. 819–878). essay, Oxford University Press.