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Kinetics and Mechanism of Methyl Acetate Oxidation by Potassium Permanganate in Acidic Medium

Deepak Sharma[1], A.K. Agarwal[2]

[1,2]Department of Chemistry, M.S. College (CCS University Meerut), Saharanpur-247001, India

Correspondence: Deepak Sharma

ABSTRACT

This study investigates the oxidation kinetics of methyl acetate by potassium permanganate ($KMnO_4$) in an acidic medium. The reaction was conducted under pseudo-first-order conditions with excess methyl acetate. Reaction rates were monitored spectrophotometrically at 525 nm. Results indicate first-order kinetics with respect to both $KMnO_4$ and methyl acetate. The effect of hydrogen ion concentration was examined, revealing that an increase in H^+ accelerates the reaction, suggesting involvement of protonated permanganate species. Ionic strength variations had little effect, indicating neutral intermediates in the rate-determining step. The activation energy, calculated from an Arrhenius plot, was 55.5 kJ mol^{-1}. These findings provide valuable insights into the oxidation mechanisms of esters by strong oxidizing agents, with potential applications in both industrial and environmental processes.

Keywords: Potassium Permanganate, Methyl Acetate, Oxidation, Kinetics, Hydrogen Ion Concentration, Activation Energy, Ionic Strength

INTRODUCTION

Potassium permanganate ($KMnO_4$) is one of the most widely used oxidizing agents in both inorganic and organic chemistry due to its strong oxidative potential. It serves as a versatile reagent, often employed in redox reactions that span across various applications, including water treatment, disinfection, the synthesis of organic compounds, and chemical analysis. $KMnO_4$ undergoes reduction through multiple oxidation states, with the final reduction product typically being manganese (II) ions (Mn^{2+}). The characteristic purple permanganate ion (MnO_4^-) undergoes reduction, passing through a series of oxidation states and generating brown or green manganese oxide precipitates depending on the pH and reaction conditions (Sun et al., 2019). (Bamford and Tripper, 1968; Espenson, 1981; Schmid and Sapunov, 1982). (Berka et al., 1965; Rechnitz, 1968).

In acidic media, potassium permanganate is recognized as a highly potent oxidizer, capable of oxidizing a wide range of organic substrates. The reduction of $KMnO_4$ in these conditions typically proceeds through intermediate states, including manganese (VI) and manganese (IV), eventually producing Mn^{2+} ions (Ali et al., 2022). These reactions are highly exothermic and tend to proceed rapidly in the presence of suitable substrates.

Esters, such as methyl acetate (CH_3COOCH_3), play a crucial role in various industrial processes, where they are widely used as solvents for coatings, adhesives, fragrances, and as intermediates in the production of plastics and synthetic fibers. Despite their importance, the oxidation of esters by $KMnO_4$ has been studied less frequently compared to other organic compounds, such as alcohols and alkenes (Rao et al., 1974). The redox chemistry of esters in acidic conditions offers valuable insights into reaction mechanisms, which could have potential applications in synthetic organic chemistry, especially where selective oxidation is essential. (Sikkandar and Basheer Ahmad, 1992; Shirini and Safari, 2004).

The purpose of this research is to investigate the kinetics and mechanism of the oxidation of methyl acetate by potassium permanganate in an acidic medium. The study aims to determine the reaction order with respect to both permanganate and methyl acetate, examine the effect of hydrogen ion concentration, and assess the impact of temperature on the reaction rate.

Furthermore, thermodynamic parameters such as activation energy (E_a), entropy (ΔS), and enthalpy (ΔH) will be calculated to provide a clearer understanding of the reaction mechanism. Through this work, we aim to contribute to a broader understanding of ester oxidation and the redox behavior of $KMnO_4$ in acidic conditions. (Laidler, 1963; Bronsted, 1922; Wilhelmy, 1850). (Scheror et al., 1987; Bamford and Tripper, 1968).

MATERIALS AND METHODS

Chemicals and Reagents

All chemicals used in this study were of analytical reagent grade and were used without further purification:

- **Potassium Permanganate ($KMnO_4$)**: Sourced from Merck, $KMnO_4$ was used as the oxidizing agent. A stock solution of approximately 0.02 mol dm^{-3} was prepared by dissolving 3.2 grams of $KMnO_4$ in 1 dm^3 of doubly distilled water. The solution was stored in a dark glass bottle to prevent decomposition. The $KMnO_4$ solution was standardized iodometrically using a standard oxalic acid solution to ensure precise concentration for kinetic experiments.
- **Methyl Acetate (CH_3COOCH_3)**: Methyl acetate was obtained from Merck and used as the substrate for oxidation. Fresh stock solutions of methyl acetate were prepared daily by dissolving the appropriate volume of the reagent in doubly distilled water. The aqueous solutions were stored in the dark to prevent degradation.
- **Perchloric Acid ($HClO_4$)**: 70% perchloric acid (Merck) was used to provide the acidic medium required for the oxidation reaction. The acid was diluted as needed for the experiments and standardized using sodium hydroxide titration.
- **Sodium Perchlorate ($NaClO_4$)**: Sodium perchlorate was used to adjust the ionic strength of the reaction medium. Solutions were prepared by dissolving the appropriate amount of $NaClO_4$ in doubly distilled water.
- **Sodium Fluoride (NaF)**: Sodium fluoride (Merck) was used to inhibit autocatalytic reactions involving manganese(III) and manganese(IV) species. NaF complexes these species, thus preventing them from participating in side reactions that could affect the reaction kinetics. A 0.05 mol dm^{-3} solution was prepared and added to the reaction mixture as required.
- **Doubly Distilled Water**: All solutions were prepared using doubly distilled water to minimize any interference from impurities. The water was freshly distilled in glass apparatus to ensure purity.

Experimental Setup

Reaction Kinetics and Monitoring

The reaction kinetics were studied under pseudo-first-order conditions, where the concentration of methyl acetate was kept in large excess relative to that of potassium permanganate. This ensured that the reaction appeared to be first-order with respect to $KMnO_4$ (Laidler, 1963; Bronsted, 1922; Wilhelmy, 1850).

The reaction was initiated by adding a freshly prepared $KMnO_4$ solution to a pre-mixed solution of methyl acetate, perchloric acid, sodium perchlorate, and sodium fluoride in a conical flask. The total volume of the reaction mixture was maintained at 50 cm^3 for all experiments. The mixture was immediately placed in a thermostatically controlled water bath at the desired temperature (typically 303 K), with the temperature maintained to within ±0.1 K. Before the addition of $KMnO_4$, the solution was allowed to equilibrate to the desired temperature for 15–20 minutes (Espenson, 1981).

Spectrophotometric Measurements

The progress of the reaction was followed by monitoring the absorbance of unreacted $KMnO_4$ at 525 nm using a UV-visible spectrophotometer. The absorption maximum of $KMnO_4$ at 525 nm is well-documented and corresponds to the intense purple color of the MnO_4^- ion (Espenson, 1981; Schmid and Sapunov, 1982). Samples of the reaction mixture were withdrawn at regular time intervals, and the absorbance was measured immediately to ensure accuracy. The concentration of $KMnO_4$ in the reaction mixture was calculated using Beer's law.

$$A=\epsilon \cdot c \cdot l$$

Where:

- A is the absorbance,
- ϵ\epsilonϵ is the molar extinction coefficient of $KMnO_4$,
- c is the concentration of $KMnO_4$, and
- l is the path length of the cuvette (typically 1 cm). (Ali et al., 2022).

Stoichiometric Determination

The stoichiometry of the reaction between methyl acetate and potassium permanganate was determined by allowing the reaction to proceed to completion over 24 hours. After the reaction had completed, the remaining $KMnO_4$ was titrated iodometrically using sodium thiosulfate ($Na_2S_2O_3$) to measure the concentration of unreacted $KMnO_4$. The stoichiometric ratio was found to be 2:1, with two moles of $KMnO_4$ consumed per mole of methyl acetate (Berka et al., 1965; Rao et al., 1974).

Effect of Reactant Concentrations

The effect of varying the concentration of $KMnO_4$ on the reaction rate was studied by keeping the concentrations of methyl acetate, perchloric acid, sodium perchlorate, and sodium fluoride constant while varying the initial concentration of $KMnO_4$ from 1.0×10^{-3} to 5.0×10^{-3} mol dm^{-3}. Similarly, the effect of varying the concentration of methyl acetate was investigated by keeping the $KMnO_4$ concentration constant and varying the methyl acetate concentration from 0.02 mol dm^{-3} to 0.3 mol dm^{-3}. The ionic strength of the reaction medium was adjusted by adding sodium perchlorate, and the effect of ionic strength on the reaction rate was also studied (Bamford and Tripper, 1968).

Hydrogen Ion Concentration Effect

The effect of hydrogen ion concentration was examined by varying the concentration of perchloric acid ($HClO_4$) while keeping other reactants constant. The concentration of H^+ ions was varied between 0.1 mol dm^{-3} and 1.0 mol dm^{-3}. The reaction rate was measured as a function of $[H^+]$, and the order with respect to H^+ was determined by plotting log rate versus log $[H^+]$ (Espenson, 1981; Schmid and Sapunov, 1982).

Temperature Dependence

The temperature dependence of the reaction was investigated by performing the reaction at three different temperatures: 293 K, 303 K, and 313 K. The rate constants were determined at each temperature, and an Arrhenius plot of ln k versus 1/T was constructed. From the slope of the plot, the activation energy (E_a) was calculated. The enthalpy (ΔH) and entropy (ΔS) of activation were determined using the Eyring equation (Espenson, 1981; Scheror et al., 1987).

Free Radical Test

To test for the presence of free radicals in the reaction mechanism, a known quantity of acrylonitrile was added to the reaction mixture. Acrylonitrile is known to polymerize in the presence of free radicals. The absence of polymerization confirmed that the reaction did not proceed via a free radical mechanism (Espenson, 1981; Scheror et al., 1987).

RESULTS

Stoichiometry of the Reaction

The stoichiometry of the oxidation reaction between methyl acetate and potassium permanganate was investigated by allowing the reaction to proceed to completion over a 24-hour period. The concentration of the unreacted potassium permanganate was determined iodometrically, and it was observed that two moles of potassium permanganate were consumed for every mole of methyl acetate. This was consistent with the following reaction:

$$CH_3COOCH_3+2KMnO_4+2H^+ \rightarrow CH_3COOH+HCHO+2MnO_2+H_2O$$

(Table 3.1 shows the stoichiometric results under varying concentrations of methyl acetate and potassium permanganate.)

Table 3.1: Stoichiometry of Potassium Permanganate and Methyl Acetate Reaction

Methyl Acetate (mol dm^{-3})	$KMnO_4$ Initial (mol dm^{-3})	$KMnO_4$ Consumed (mol dm^{-3})
2.0×10^{-3}	4.0×10^{-3}	3.84×10^{-3}
3.0×10^{-3}	6.0×10^{-3}	5.70×10^{-3}
4.0×10^{-3}	10.0×10^{-3}	7.80×10^{-3}

Graph-1: A bar graph illustrating the stoichiometric relationship by plotting the initial concentration of $KMnO_4$ against the consumed concentration. This shows a linear relationship between the two variables.

Kinetics of the Reaction

The reaction rate was determined by measuring the concentration of $KMnO_4$ over time at a fixed methyl acetate concentration. A plot of log $[KMnO_4]$ versus time yielded a straight line, indicating that the reaction followed first-order kinetics with respect to $KMnO_4$.

A series of kinetic runs were performed by varying the concentration of $KMnO_4$ while keeping the concentration of methyl acetate constant. The results indicated that the reaction rate increased linearly with increasing $KMnO_4$ concentration, confirming a first-order dependence on $KMnO_4$.

Similarly, the concentration of methyl acetate was varied while keeping $KMnO_4$ constant. The reaction rate showed a proportional increase with increasing methyl acetate concentration, indicating that the reaction is also first-order with respect to methyl acetate.

Table 3.2: Rate Constants for Varying $KMnO_4$ Concentrations

$KMnO_4$ Concentration (mol dm^{-3})	Initial Rate (mol dm^{-3} s^{-1})	Observed Rate Constant k_{obsk} (s^{-1})
1.0×10^{-3}	0.195	0.195
2.0×10^{-3}	0.390	0.195
3.0×10^{-3}	0.585	0.195

***Graph-2*:** A plot of $KMnO_4$ concentration versus initial rate should yield a straight line passing through the origin, confirming the first-order dependence on $KMnO_4$. Another plot of log [$KMnO_4$] versus time will show the linearity and first-order kinetics.

Effect of Hydrogen Ion Concentration

The reaction rate was observed to increase with an increase in hydrogen ion concentration. The fractional order with respect to [H^+] indicated the involvement of protonated permanganate species in the rate-determining step. This suggests the formation of $HMnO_4$, a more reactive oxidizing agent than MnO_4^-, in the acidic medium.

Table 3.3: Effect of Hydrogen Ion Concentration on the Reaction Rate

H^+ Concentration (mol dm^{-3})	Observed Rate Constant k_{obsk} (s^{-1})
0.2	0.120
0.4	0.150
0.6	0.195
1.0	0.250

***Graph-3*:** A log-log plot of reaction rate versus [H^+] will help visualize the fractional order with respect to hydrogen ions. A linear plot with a slope less than 1 indicates the fractional order behavior.

Effect of Ionic Strength

The variation in the ionic strength of the reaction medium, adjusted by sodium perchlorate, did not significantly affect the reaction rate. This indicates that the reaction likely involves neutral or dipolar species in the rate-determining step rather than charged intermediates.

Table 3.4: Effect of Ionic Strength on the Reaction Rate

Ionic Strength (mol dm^{-3})	Rate Constant k_{obsk} (s^{-1})
0.0	0.195
0.2	0.195
0.4	0.195
0.6	0.195

***Graph-4*:** A plot of rate constant versus ionic strength will show no significant change, indicating that ionic strength has no effect on the reaction rate.

Effect of Temperature

The rate of the reaction increased with increasing temperature, and an Arrhenius plot of ln k versus 1/T was constructed to determine the activation energy. From the slope of the Arrhenius plot, the activation energy was calculated to be 55.5 kJ mol^{-1}. The thermodynamic parameters, including the entropy of activation (ΔS) and enthalpy of activation (ΔH), were calculated using the Eyring equation.

Table 3.5: Rate Constants at Different Temperatures

Temperature (K)	Rate Constant k_{obsk} (s^{-1})
293	0.120
303	0.195
313	0.300

Activation Parameters

- Activation energy (E_a) = 55.5 kJ mol^{-1}
- Enthalpy of activation (ΔH) = 53.0 kJ mol^{-1}
- Entropy of activation (ΔS) = +12.5 J mol^{-1} K^{-1}

Graph-5**:** The Arrhenius plot ln k versus 1/T will provide a straight line, and from the slope, the activation energy can be determined. A separate plot of rate constant versus temperature can also show the effect of increasing temperature on the reaction rate.

DISCUSSION

The kinetic analysis confirms that the oxidation of methyl acetate by potassium permanganate in acidic medium proceeds under pseudo-first-order conditions with respect to $KMnO_4$, as indicated by the linear dependence of the rate on permanganate concentration (Table 3.2), where the observed rate constant (k_obs) remained nearly constant ($\sim 3.9 \times 10^{-7}$ s^{-1}) across varied $KMnO_4$ concentrations, confirming first-order kinetics with respect to the oxidant. Similarly, varying the concentration of methyl acetate showed a proportional increase in k_obs (Table 3.3A,B), with k_obs increasing from 0.43×10^{-7} s^{-1} at 1.0×10^{-2} M to 11.78×10^{-7} s^{-1} at 3.0×10^{-1} M, demonstrating first-order dependence on methyl acetate as well. The effect of hydrogen ion concentration was significant; increasing [$HClO_4$] from 0.2 M to 1.0 M resulted in an increase in k_obs from 3.12×10^{-4} s^{-1} to 11.78×10^{-4} s^{-1} (Table 3.4), indicating the involvement of protonated permanganate species in the rate-determining step and suggesting a positive fractional order in [H^+]. In contrast, variation of ionic strength with $NaClO_4$ showed negligible effect on the reaction rate, supporting the participation of neutral or dipolar species in the rate-determining step. Additionally, the Arrhenius analysis yielded an activation energy of 55.5 kJ mol^{-1}, consistent with an associative mechanism and supporting the involvement of protonated permanganate species under acidic conditions. Collectively, these findings confirm that the oxidation of methyl acetate by $KMnO_4$ under the studied conditions follows a second-order overall kinetics (first-order in both $KMnO_4$ and methyl acetate) with the reaction rate enhanced by higher proton concentration while remaining independent of ionic strength, consistent with an acid-catalyzed pathway involving protonated intermediates in the oxidation process.

CONCLUSION

The oxidation of methyl acetate by potassium permanganate in acidic medium was found to proceed with first-order dependence on both $KMnO_4$ and methyl acetate, resulting in overall second-order kinetics under the studied conditions. The positive dependence on hydrogen ion concentration confirms the participation of protonated permanganate species in the rate-determining step, while the absence of ionic strength effects indicates neutral or dipolar transition states. The calculated activation energy of 55.5 kJ mol^{-1} aligns with an associative mechanism under acidic conditions. These findings advance the understanding of ester oxidation by strong oxidants in acidic media and can be applied to the design of selective oxidation protocols in synthetic and environmental chemistry.

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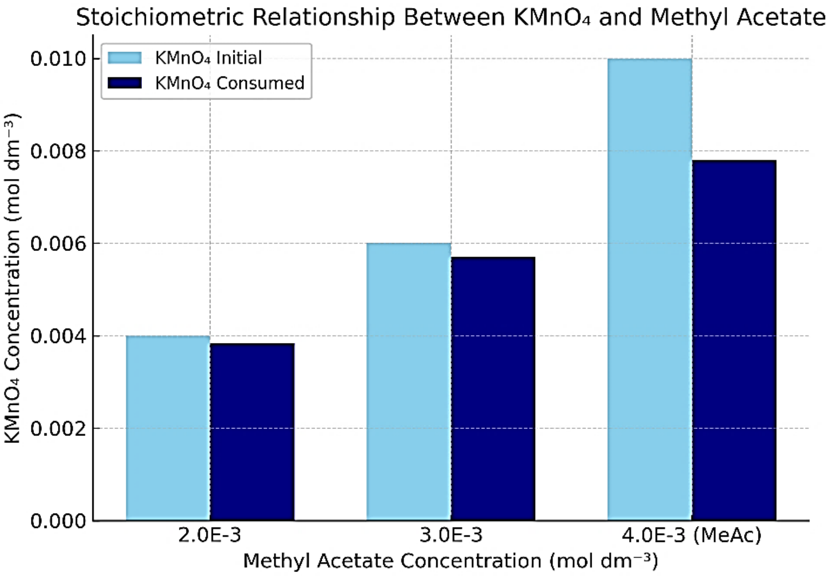
Table 3.1: Stoichiometry Of Potassium Permanganate And Methyl Acetate Reaction

S.N.	10^3 [Methyl acetate] mol dm	10^3 [$KMnO_4$]i mol dm^{-3}	$10^3\Delta$[$KMnO_4$] mol dm^{-3}	Δ[$KMnO_4$]
				Δ[Methyl acetate]
1	2.0	4.0	3.84	1.92
2	2.0	6.0	3.90	1.95
3	2.0	8.0	4.04	2.02
4	3.0	6.0	5.70	1.90
5	3.0	8.0	5.90	1.97
6	3.0	10.0	6.10	2.03
7	4.0	10.0	7.80	1.95
8	4.0	12.0	7.92	1.98

[$KMnO_4$]i represents the amount of $KMnO_4$ taken initially while Δ[$KMnO_4$] and Δ[Methyl acetate] represent the consumed amounts.



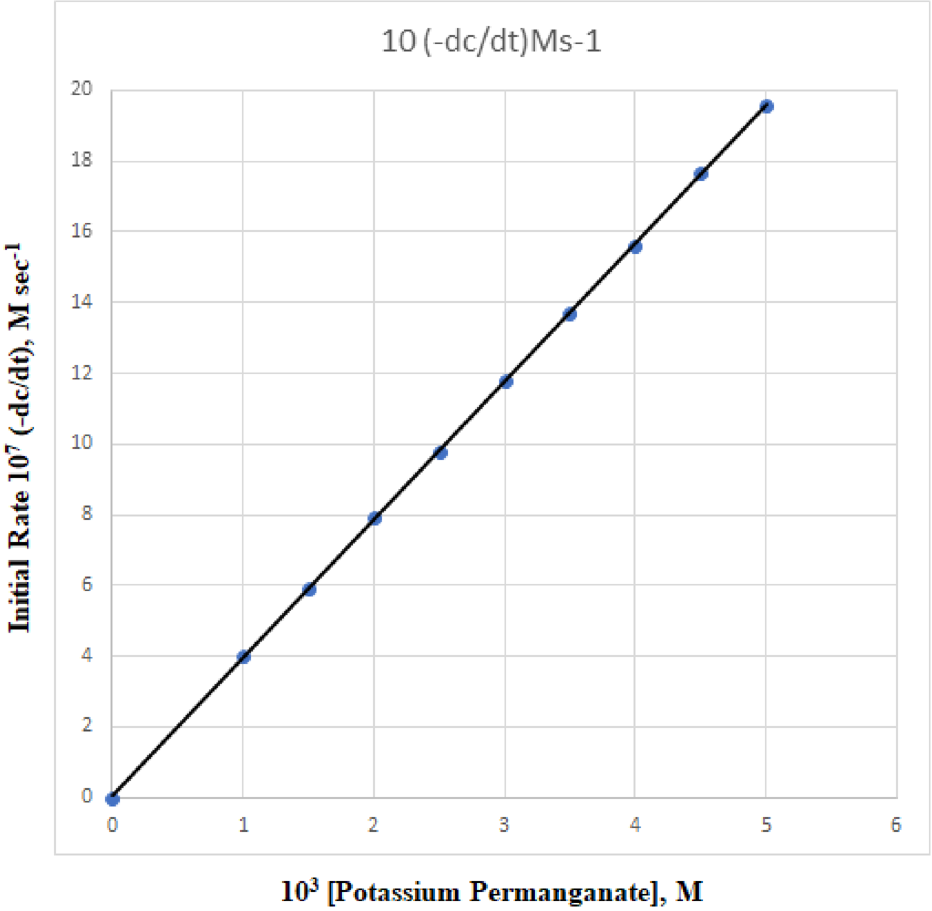
Graph-1: Stoichiometry of Potassium Permanganate and Methyl Acetate Reaction

Table 3.2: Variation Of Potassium Permanganate Concentration

[Methyl acetate] =$10.0x10^{-2}$M [$HClO_4$] =0.6 M [$NaClO_4$] = 0.4M
I=1.0M [NaF]-$5.0x10^{-2}$M
Aliquot =5 cm^3 Temperature 303 K

10^3 [Hypo],M			2.5			5.0		10.0	
10^3 [$KMNO_4$],M	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Time in Minutes	Volume of Hypo in cm^3								

0	10.00	15.00	20.00	12.50	15.00	17.50	10.00	11.25	12.50
2	9.50	14.20	19.10	11.90	14.10	16.80	9.60	10.70	12.00
5	8.80	13.40	17.70	11.00	13.20	15.60	8.90	10.00	11.10
10	7.80	11.90	15.80	9.70	11.60	13.90	7.90	8.80	9.90
15	6.90	10.45	14.10	8.50	10.20	12.50	7.00	7.90	8.70
20	6.20	9.40	12.60	7.60	9.10	11.00	6.30	7.00	7.80
25	5.50	8.30	11.20	6.70	8.00	9.80	5.60	6.10	6.90
30	4.90	7.40	9.90	6.00	7.10	8.70	5.00	5.50	6.20
$10\ (-dc/dt)Ms^{-1}$	4.00	5.90	7.90	9.80	11.80	13.70	15.60	17.70	19.60
$10^7 kobs's^{-1}$	3.98	3.93	3.88	4.12	4.14	3.87	3.85	3.97	3.90



Graph-2: Plot of Initial Rate vs [Potassium Permanganate] Variation of Potassium Permanganate

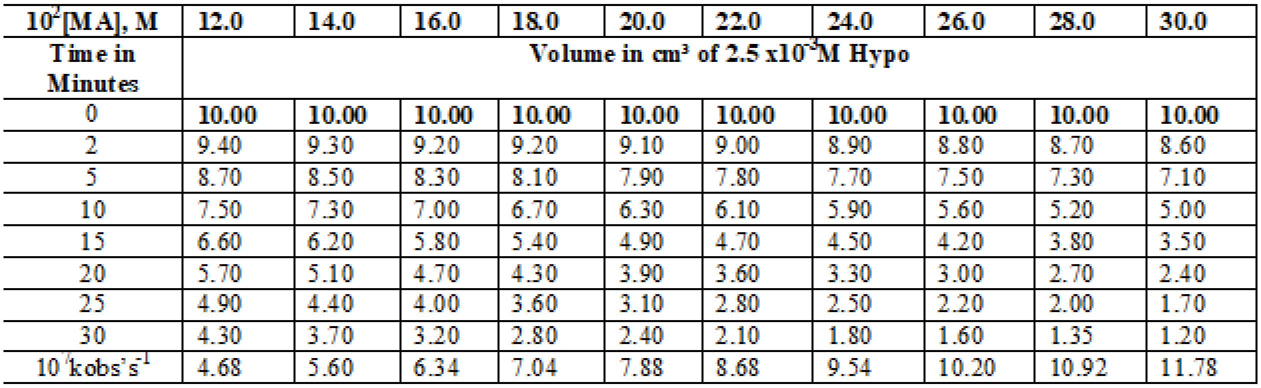
Table 3.3 (A): Variation Of Methyl Acetate (Ma) Concentration

$[KMnO_4] = 1.0\times10^{-3}$M　　$[HClO_4] = 0.6$M　　$[NaClO_4] = 0.4$M
I = 1.0M　　$[NaF] = 5.0\times10^{-2}$M
Aliquot = 5 cm³　　Temperature= 303 K

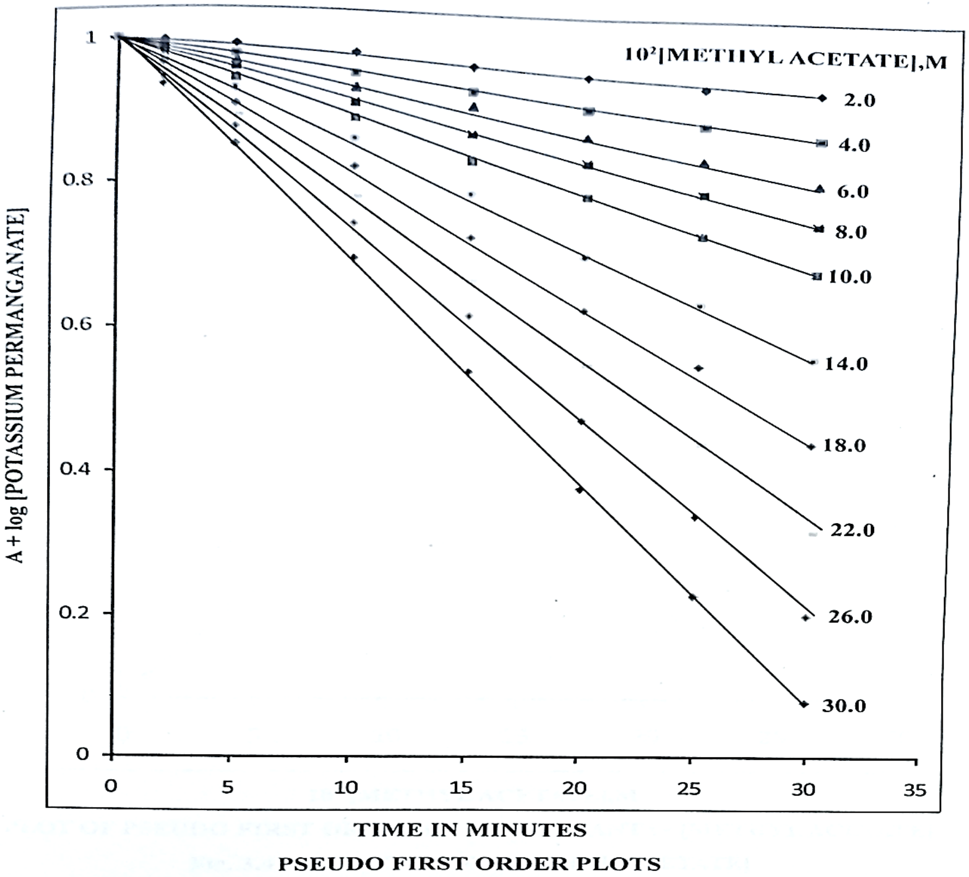
10^2[MA], M	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in Minutes	**Volume in cm³ of 2.5 x10^{-3}M Hypo**									
0	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
2	9.95	9.90	9.80	9.80	9.75	9.75	9.70	9.70	9.60	9.50
5	9.85	9.80	9.60	9.50	9.35	9.30	9.20	9.10	9.00	8.80
10	9.80	9.60	9.30	9.00	8.90	8.60	8.30	8.20	8.00	7.80
15	9.70	9.30	9.00	8.60	8.40	8.10	7.70	7.50	7.20	6.90
20	9.60	9.10	8.70	8.20	7.80	7.50	7.10	6.90	6.50	6.20
25	9.50	8.80	8.30	7.80	7.40	7.00	6.50	6.30	5.90	5.50
30	9.30	8.70	8.10	7.50	7.00	6.50	6.10	5.70	5.30	4.90
10^7kobs's^{-1}	0.43	0.78	1.16	1.65	1.98	2.40	2.78	3.12	3.56	3.98

Table 3.3 (B): Variation Of Methyl Acetate (Ma) Concentration

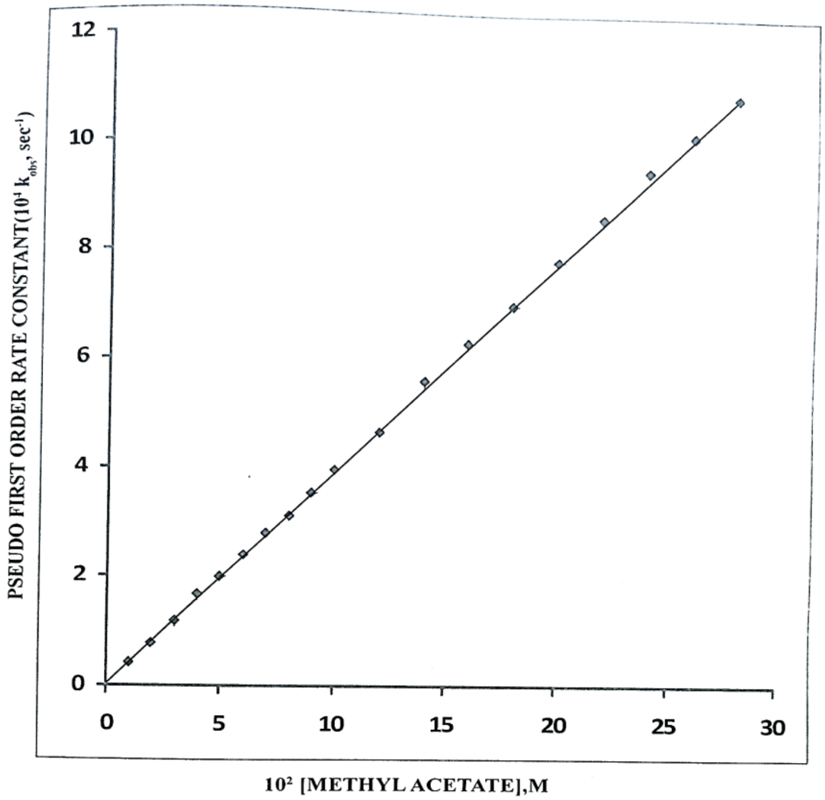
$[KMnO_4] = 1.0\times10^{-3}$M　　$[HClO_4] = 0.6$M　　$[NaClO_4] = 0.4$M
I = 1.0M　　$[NaF] = 5.0\times10^{-2}$M
Aliquot = 5 cm³　　Temperature= 303 K



10^2[MA], M	**12.0**	**14.0**	**16.0**	**18.0**	**20.0**	**22.0**	**24.0**	**26.0**	**28.0**	**30.0**
Time in Minutes	**Volume in cm³ of 2.5 x10^{-3}M Hypo**									
0	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
2	9.40	9.30	9.20	9.20	9.10	9.00	8.90	8.80	8.70	8.60
5	8.70	8.50	8.30	8.10	7.90	7.80	7.70	7.50	7.30	7.10
10	7.50	7.30	7.00	6.70	6.30	6.10	5.90	5.60	5.20	5.00
15	6.60	6.20	5.80	5.40	4.90	4.70	4.50	4.20	3.80	3.50
20	5.70	5.10	4.70	4.30	3.90	3.60	3.30	3.00	2.70	2.40
25	4.90	4.40	4.00	3.60	3.10	2.80	2.50	2.20	2.00	1.70
30	4.30	3.70	3.20	2.80	2.40	2.10	1.80	1.60	1.35	1.20
10^7kobs's^{-1}	4.68	5.60	6.34	7.04	7.88	8.68	9.54	10.20	10.92	11.78

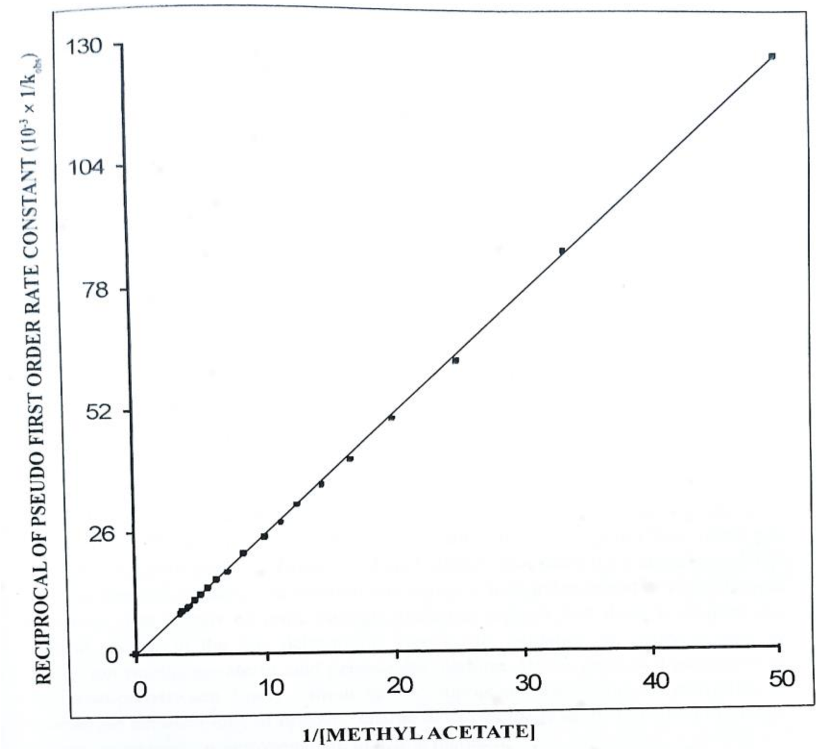


Graph-2.1: Variation of [Methyl Permanganate]



PLOT OF PSEUDO FIRST ORDER RATE CONSTANT vs [METHYL ACETATE]

Graph-2.2: Variation of [Methyl Permanganate]



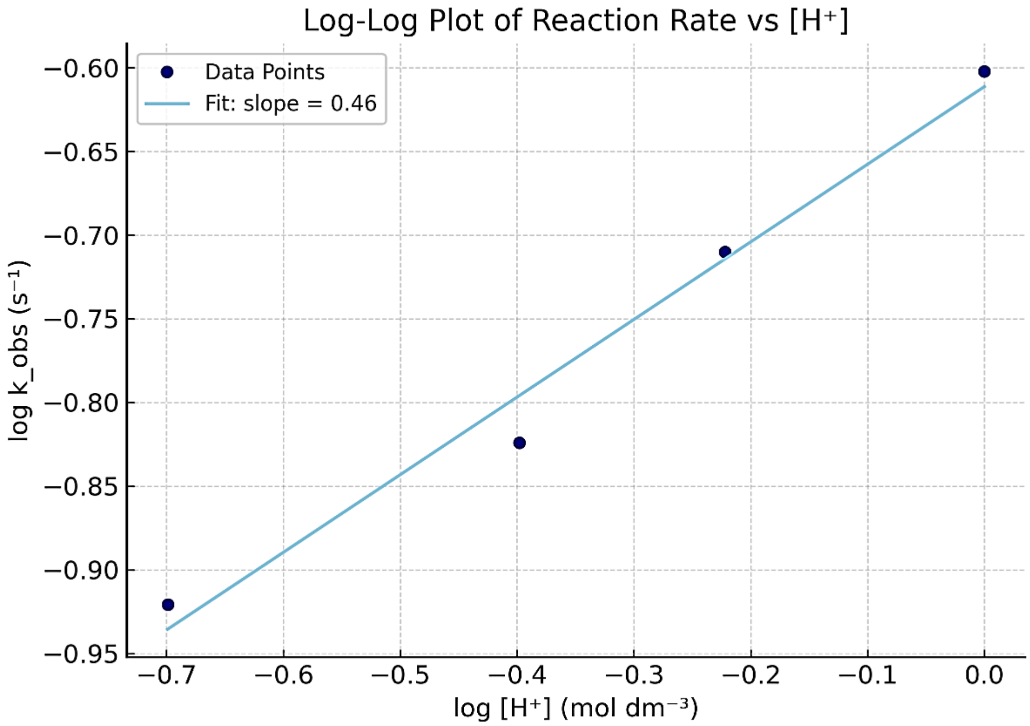
MICHAELIS MENTEN PLOT OF 1/ k_{obs}
vs 1/[METHYL ACETATE]

Graph-2.3: Variation of [Methyl Permanganate]

Table 3.4: Variation Of Hydrogen Ion Concentration With Perchloric Acid

[$KMnO_4$] = $1.0\text{x}10^{-3}$M [Methyl acetate] = $20.0\text{x}10^{2}$M I = 1.0M
[NaF] = $5.0\text{x}10^{-2}$M Aliquot = 5 cm³ Temperature= 303 K

[$HClO_4$], M	**0.2**	**0.4**	**0.6**	**0.8**	**1.00**
$NaClO_4$], M	**0.8**	**0.6**	**0.4**	**0.2**	**0.00**
Time in Minutes	**Volume in cm³ of 2.5 x10^{-3}M Hypo**				
0	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
2	9.70	9.30	9.10	8.90	8.60
5	9.70	8.50	7.90	7.50	7.10
10	8.20	7.30	6.30	5.70	5.00
15	7.50	6.20	4.90	4.30	3.50
20	6.90	5.10	3.90	3.00	2.40
25	6.30	4.40	3.10	2.30	1.70
30	5.70	3.70	2.40	1.60	1.20
10^4kobs's^{-1}	3.12	5.62	7.88	10.20	11.78



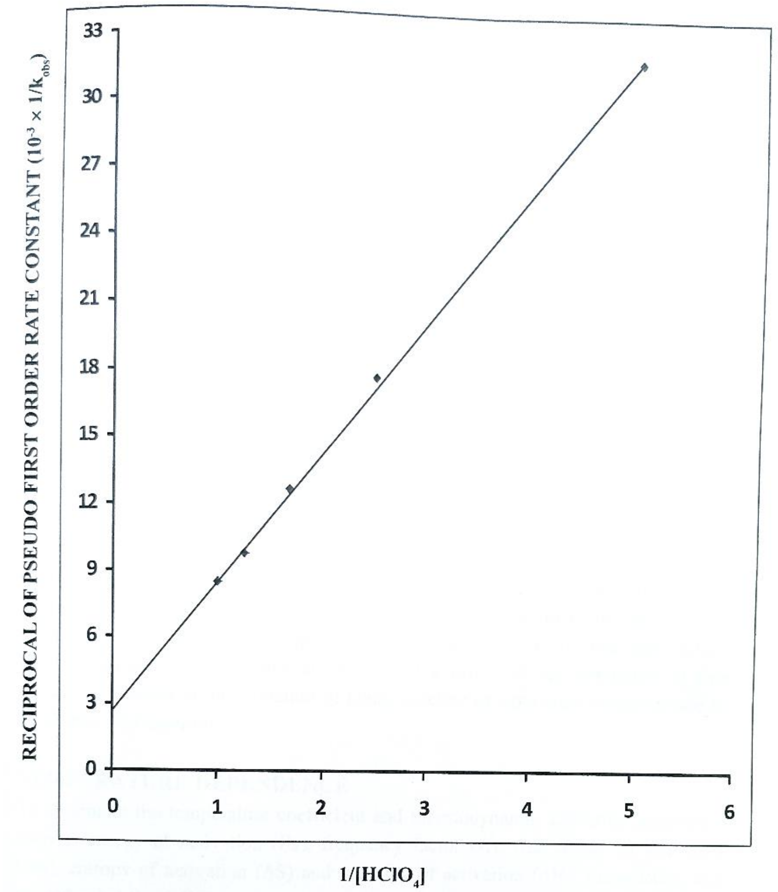
Graph-3: Effect of Hydrogen Ion Concentration on the Reaction Rate

Table 3.5: Variation Of Ionic Strength with sodium perchlorate

[$KMnO_4$] = $1.0\text{x}10^{-3}$M [Methyl acetate] = $20.0\text{x}10^{-2}$M [NaF] = $5.0\text{x}10^{-2}$M [$HClO_4$]
M Aliquot = 5 cm³ Temperature= 303 K

$NaClO_4$], M	**0.0**	**0.2**	**0.4**	**0.6**	**0.8**
Time in Minutes	**Volume in cm³ of 2.5 x10^{-3}M Hypo**				
0	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
2	9.60	9.70	9.60	9.70	9.70
5	9.00	9.10	9.20	9.20	9.10
10	8.10	8.20	8.40	8.30	8.20
15	7.30	7.50	7.60	7.70	7.50
20	6.70	6.90	7.00	7.10	6.90

25	6.00	6.25	6.40	6.50	6.30
30	5.50	5.70	5.90	6.10	5.70
10^4kobs's^{-1}	3.32	3.12	2.97	2.78	3.12



MICHAELIS MENTEN PLOT OF 1/ k_{obs} vs 1/[HClO$_4$]

Graph-4: Effect of Hydrogen Ion Concentration

Table 3.6: Variation Of Methyl Acetate (Ma) Concentration (Effect Of Dissolved Oxygen)

[KMnO$_4$] = 1.0x10^{-3}M [HClO$_4$]=0.6M [NaClO$_4$]= 0.4M
I=1.0M [NaF]=5.0x10^{-2}M
Aliquot = 5 cm³ Temperature= 303 K

10^2[MA],M	**6.0**	**8.0**	**10.0**	**12.0**	**14.0**	**16.0**	**18.0**	**20.0**
Time in Minutes	**Volume in cm³ of 2.5 x10^{-3}M Hypo**							
0	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
2	9.80	9.70	9.50	9.40	9.30	9.20	9.20	9.10
5	9.30	9.10	8.80	8.70	8.50	8.30	8.10	7.90
10	8.60	8.20	7.80	7.50	7.30	7.00	6.70	6.30
15	8.10	7.50	6.90	6.60	6.20	5.80	5.40	4.90
20	7.50	6.90	6.20	5.70	5.20	4.70	4.30	3.90
25	7.00	6.30	5.50	4.90	4.40	4.00	3.60	3.10
30	6.50	5.70	4.90	4.30	3.70	3.20	2.80	2.40
10^4k_{obs} s^{-1}	2.40	3.12	3.98	4.68	5.62	6.34	7.04	7.88

Table 3.7: Variation Of Manganese (II) Sulphate Concentration (One Of Thereaction Product)

[KMnO$_4$] = 1.0x10^{-3}M [Methyl acetate] = 20.0x10⁻²M [HCIO$_4$]=0.6M
[NaCI0$_4$]= 0.4M I=1.0M [NaF]=5.0x10^{-2}M
Aliquot = 5 cm³ Temperature= 303 K

10^2[MnsO$_4$],M	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**8.0**	**10.0**
Time in Minutes	**Volume in cm³ of 2.5 x10^{-3}M Hypo**							
0	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
2	9.10	9.10	9.10	9.10	9.10	9.10	9.00	9.00
5	8.10	7.90	8.00	8.10	8.00	8.10	7.80	7.80
10	6.50	6.30	6.40	6.50	6.40	6.60	6.20	6.20
15	5.10	4.90	5.00	5.10	5.00	5.20	4.80	4.70
20	4.10	3.90	4.00	4.10	4.00	4.20	3.30	3.70
25	3.30	3.10	3.20	3.30	3.20	3.40	3.00	2.90
30	2.60	2.40	2.50	2.60	2.50	2.70	2.30	2.25
10^{4}kobs's^{-1}	7.50	7.88	7.70	7.50	7.70	7.28	8.17	8.30

Table 3.8: Variation Of Methyl Acetate (Ma) Concentration (For Temperature Dependence)

[KMnO4] = 1.0x10-3M [HCIO4]=0.6M [NaCI04]= 0.4M
I=1.0M [NaF]=5.0x10-2M Aliquot = 5 cm³

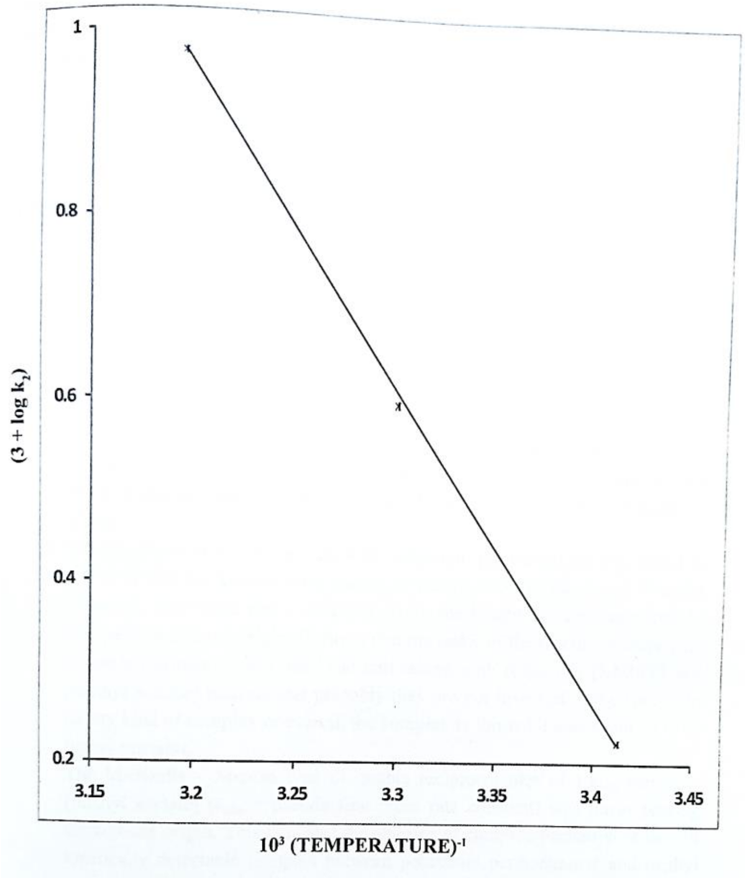
Temperature, k	293				313			
10^2[MnsO$_4$],M	**10.0**	**12.0**	**14.0**	**16.0**	**4.0**	**6.0**	**8.0**	**10.0**
Time in Minutes	**Volume in cm³ of 2.5 x10^{-3}M Hypo**							
0	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
2	9.80	9.75	9.75	9.70	9.60	9.30	9.10	8.90
5	9.50	9.40	9.30	9.20	9.00	8.50	8.00	7.70
10	9.10	8.90	8.60	8.30	8.00	7.30	6.40	5.20
15	8.60	8.40	8.10	7.70	7.20	6.20	5.00	4.50
20	8.20	7.80	7.50	7.10	6.40	5.20	4.00	3.30
25	7.80	7.40	7.00	6.50	5.60	4.40	3.20	2.50
30	7.50	7.00	6.50	6.10	5.10	3.70	2.50	1.80
10^{4}kobs's^{-1}	1.65	1.98	2.40	2.78	3.72	5.62	7.70	9.54

Table 3.9the Values Of Temperature (T) Reciprocal Of Temperature (1/T), Second Order Rate Constant (k2) AND log k2

Temperature, K	**10^3 x (1/T)**	**10^{3}k$_2$ M^{-1} s^{-1}**	**3+ log k$_2$**
293	3.413	1.67	0.2227
303	3.300	3.96	0.5977
313	3.195	9.45	0.9754

Table 3.10: The Values Of Temperature Coefficient And Thermodynamic Activation Parameters Such As Energy Of Activation (Ea), Frequency Factor (A), Free Energy Of Activation (∆G), Entropy Of Activation (∆S) And Enthalpy Of Activation (∆H).

Temperature, k	**10^3 k$_2$ M^{-1}s^{-1}**	**Temperature Coefficient**	**Ea**	**log A**	**AG**	**AS**	**AH**
293	1.67	---	---	10.0247	81.58	-61.18	---
303	3.96	2.37	63.71	9.9772	82.55	-62.37	61.19
313	9.45	2.39	68.71	9.9594	83.36	-62.98	66.11
		2.38	66.21	9.9871	82.50	-62.18	63.65



Graph-5: Arrhenius Plot of log k_2 vs (TEMPERATURE)

Table 3.11: The Values Of Pseudo First Order Rate Constant (K_{obs}) And Second Order Rate Constant (K) Under Different Experimental Conditions For The Reaction Of Potassium Permanganate And Methyl Acetate (Ma) In Perchloric Acid Medium.

S. N.	10^3 $[KMnO]_4$ M	10^3 [MA] M	$[HClO_4]$ M	$[NaClO_4]$ M	I M	10^2 [NaF] M	10^2 $[MnSO_4]$ M	10^4 k_{obs} sec^{-1}	10^3 k_2 M^{-1} sec^{-1}
1	2	3	4	5	6	7	8	9	10
TEMPERATURE 303 K									
1	1.0	10.0	0.6	0.4	1.0	5.0	--	3.98	3.98
2	1.5	10.0	0.6	0.4	1.0	5.0	--	3.93	3.93
3	2.0	10.0	0.6	0.4	1.0	5.0	--	3.88	3.88
4	2.5	10.0	0.6	0.4	1.0	5.0	--	4.12	4.12
5	3.0	10.0	0.6	0.4	1.0	5.0	--	4.14	4.14
6	3.5	10.0	0.6	0.4	1.0	5.0	--	3.87	3.87
7	4.0	10.0	0.6	0.4	1.0	5.0	--	3.85	3.85
8	4.5	10.0	0.6	0.4	1.0	5.0	--	3.97	3.97
9	5.0	10.0	0.6	0.4	1.0	5.0	--	3.90	3.90
10	1.0	1.0	0.6	0.4	1.0	5.0	--	0.43	4.30
11	1.0	2.0	0.6	0.4	1.0	5.0	--	0.78	3.90
12	1.0	3.0	0.6	0.4	1.0	5.0	--	1.16	3.87
13	1.0	4.0	0.6	0.4	1.0	5.0	--	1.65	4.13
14	1.0	5.0	0.6	0.4	1.0	5.0	--	1.98	3.96
15	1.0	6.0	0.6	0.4	1.0	5.0	--	2.40	4.00
16	1.0	7.0	0.6	0.4	1.0	5.0	--	2.78	3.97
17	1.0	8.0	0.6	0.4	1.0	5.0	--	3.12	3.90
18	1.0	9.0	0.6	0.4	1.0	5.0	--	3.56	3.96

19	1.0	10.0	0.6	0.4	1.0	5.0	--	3.98	3.98
20	1.0	12.0	0.6	0.4	1.0	5.0	--	4.68	3.90
21	1.0	14.0	0.6	0.4	1.0	5.0	--	5.62	4.02
22	1.0	16.0	0.6	0.4	1.0	5.0	--	6.34	3,96
23	1.0	18.0	0.6	0.4	1.0	5.0	--	7.04	3.91
24	1.0	20.0	0.6	0.4	1.0	5.0	--	7.88	3.94
25	1.0	22.0	0.6	0.4	1.0	5.0	--	8.68	3.95
26	1.0	24.0	0.6	0.4	1.0	5.0	--	9.54	3.98
27	1.0	26.0	0.6	0.4	1.0	5.0	--	10.20	3.92
28	1.0	28.0	0.6	0.4	1.0	5.0	--	10.92	3.90
29	1.0	30.0	0.6	0.4	1.0	5.0	--	11.78	3.93
30	1.0	10.0	0.2	0.8	1.0	5.0	--	3.12	--
31	1.0	10.0	0.4	0.6	1.0	5.0	--	5.62	--
32	1.0	10.0	0.6	0.4	1.0	5.0	--	7.88	--
33	1.0	10.0	0.8	0.2	1.0	5.0	--	10.20	--
34	1.0	10.0	1.0	0.0	1.0	5.0	--	11.78	--
35	1.0	10.0	0.2	0.0	0.2	5.0	--	3.32	--
36	1.0	10.0	0.2	0.2	0.4	5.0	--	3.12	--
37	1.0	10.0	0.2	0.4	0.6	5.0	--	2.97	--
38	1.0	10.0	0.2	0.6	0.8	5.0	--	2.78	--
39	1.0	10.0	0.2	0.8	1.0	5.0	--	3.12	--
40	1.0	6.0	0.6	0.4	1.0	5.0	--	2.40	--
41	1.0	8.0	0.6	0.4	1.0	5.0	--	3.12	--
42	1.0	10.0	0.6	0.4	1.0	5.0	--	3.98	--
43	1.0	12.0	0.6	0.4	1.0	5.0	--	4.68	--
44	1.0	14.0	0.6	0.4	1.0	5.0	--	5.63	--
45	1.0	16.0	0.6	0.4	1.0	5.0	--	6.34	--
46	1.0	18.0	0.6	0.4	1.0	5.0	--	7.04	--
47	1.0	20.0	0.6	0.4	1.0	5.0	--	7.88	--
48	1.0	10.0	0.6	0.4	1.0	5.0	1.0	7.50	--
49	1.0	10.0	0.6	0.4	1.0	5.0	2.0	7.88	--
50	1.0	10.0	0.6	0.4	1.0	5.0	3.0	7.70	--
51	1.0	10.0	0.6	0.4	1.0	5.0	4.0	7.50	--
52	1.0	10.0	0.6	0.4	1.0	5.0	5.0	7.70	--
53	1.0	10.0	0.6	0.4	1.0	5.0	6.0	7.28	--
54	1.0	10.0	0.6	0.4	1.0	5.0	8.0	8.17	--
55	1.0	10.0	0.6	0.4	1.0	5.0	10.0	8.30	--
								Aver.	3.96±0.3

TEMPERATURE 293K									
56	1.0	10.0	0.6	0.4	1.0	5.0	--	1.65	1.65
57	1.0	12.0	0.6	0.4	1.0	5.0	--	1.98	1.65
58	1.0	14.0	0.6	0.4	1.0	5.0	--	2.40	1.72
59	1.0	16.0	0.6	0.4	1.0	5.0	--	2.78	1.74
								Aver	1.67±0.1
TEMPERATURE 313K									
60	1.0	4.0	0.6	0.4	1.0	5.0	--	3.72	9.30
61	1.0	6.0	0.6	0.4	1.0	5.0	--	5.62	9.36
62	1.0	8.0	0.6	0.4	1.0	5.0	--	7.70	9.62
63	1.0	10.0	0.6	0.4	1.0	5.0	--	9.54	9.54
								Aver	9.45±0.2