

## Research Article

# Kinetics of Alkaline Hydrolysis of Ethyl Acetate by Conductometric Measurement Approach Over Temperature Ranges (298.15-343.15K)

Mukhtar A<sup>1\*</sup>, Shafiq U<sup>1</sup>, Qazi MO<sup>2</sup>, Qadir HA<sup>1</sup>, Qizilbash M<sup>2</sup> and Awan BA<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, NFC IE & FR Faisalabad, Pakistan

<sup>2</sup>Department of Chemical Engineering, Universitat Politècnica de Catalunya-UPC, Spain

<sup>3</sup>Institute of Chemical Engineering and Technology, University of the Punjab, Lahore, Pakistan

\*Corresponding author: Ahmad Mukhtar, Department of Chemical Engineering, NFC IE & FR Faisalabad, Pakistan

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## Abstract

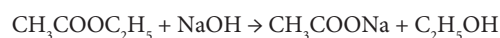
Industrial significance of the reaction product sodium acetate and ethanol demands for the process improvements in terms of maximum conversion and economical & environmental friendly usage of raw material. This research aims the kinetic study of ethyl acetate hydrolysis with sodium hydroxide at different temperatures and development of mathematical model for holding time in batch reactor. For this purpose the experiment is carried out in a batch type stirred tank reactor over different temperatures and change in concentrations (in terms of electrical conductivity) measured with time. Detail kinetic study has been investigated and concluded that this reaction is shifting order and cannot be expressed as 2<sup>nd</sup> order reaction kinetics also it has been found that the reaction is exothermic in nature and low reaction temperature favors the high conversion and high reaction rate. The average values of rate constant and activation energy are found to be 4.409 KJ/mole and 0.0243μs 0.3118s<sup>-1</sup> respectively which are agreed well with those of previous studies.

**Keywords:** Hydrolysis; Reaction Kinetics; Order of Reaction; Rate Constant; Conversion; Activation Energy

## Introduction

The chemical reactions taking place in a chemical reactor are considering the heart of a chemical process. Reaction kinetics is the translation of our understanding about chemical process into a mathematical rate expression that can be used in reactor design and rating. Because of the importance of the development of performance models to stimulate the reactor fundamental parameters, comprehensive reactor design chemical kinetics is a key aspect of research and development (R&D) in chemical process industries [1]. Chemical Kinetics is actually a part of physical chemistry deals with the study of reaction rates. Reaction rate can be defined as the changes in the number of molecules of reacting species per unit volume per unit time or how fast a reaction takes place [2]. The rate of chemical reactions is affected by a number of factors like greater the surface area of solid reactants greater will be the rate of reaction, high concentration of reactants high will be the rate of reaction, in case of gaseous reactants and products the rate of reactions directly proportional to the pressure, catalysts also increase the rate of reaction however negative catalysts can decrease the rate of chemical reactions, and high temperature usually favors high rate of reaction Saponification is the hydrolysis of carboxylic acid under alkaline conditions. Hydrolysis is the chemical decomposition involving the breaking of ester bond and releasing the fatty acid and glycerol in the presence of an alkali. Commercial importance of the reaction product sodium acetate which is not used specifically for cleaning purposes but has a wide range of industrial applications such as in pharmaceutical, paint and dying industry, as food additive, in electroplating industry, as meat preservative, photography and purification of glucose etc. whereas ethanol as a by-product can be used as a bio fuel. Despite the

commercial importance of no study has been found on the process improvements in terms of maximum conversion and economical & environmental friendly usage of raw material for this saponification reaction [3-6]. Saponification of ethyl acetate with sodium hydroxide proceeds through the direct attack of nucleophile (OH<sup>-1</sup>) on carbon atom of ethyl acetate [7-12]. Saponification of ethyl acetate with sodium hydroxide is the 2<sup>nd</sup> order overall, 1st order with respect to reactants furthermore reaction order decreases and become sequential rather than 2<sup>nd</sup> order when equimolecular concentrations of both reactants are used. This is a non-catalytic, homogeneous phase (liquid/liquid) and constant density system reaction. This reaction is mild exothermic in nature.



The hydrolysis of ethyl acetate with sodium hydroxide is one of the most well-known reactions in chemistry and it is represented as a model example of the 2<sup>nd</sup> order reaction in the literature dealing with chemical kinetics [13-15].

Previous research shows that equimolecular concentration of both reactants yield high conversion this can be also seen from the reaction stoichiometry. The addition of products actually retarded the overall reaction rate, but it is too much small to illustrate the deviation from 2<sup>nd</sup> order kinetics. Experimentally the deviation is more remarkable when the concentrations of ester and base are close. All the previous study shows that in continuous process increase in reactant flow rates cause decrease in residence time and due to which overall conversion decrease. On the other hand rate constant initially increase and then shows decline with the reactant flow rate. The dramatically decrease in conductivity can be observed with stirrer rate and results in

**Table 1:** Temperature vs. Concentration Data at Different Temperatures.

	Temperatures ( °C)									
	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C	70 °C
Time (min.)	Conductivity (µs)									
0	1001	974	1830	1743	1776	2010	2040	2110	1741	2030
1	480	529	1044	891	908	1019	1047	1045	809	947
2	443	486	1011	849	885	987	1037	1019	793	933
3	417	473	991	838	869	978	1026	1011	784	927
4	398	463	979	833	860	973	1020	1008	779	924
5	383	455	969	829	852	969	1015	1005	774	921
6	366	450	961	826	849	965	1013	1002	771	920
7	356	445	955	824	846	963	1011	999	768	918
8	350	442	949	822	845	961	1009	998	768	916
9	346	441	928	820	845	959	1008	998	768	916
10	325	441	919	820	845	953	1007	998	768	916

**Table 2:** Instantaneous Conversion based upon Initial Concentration.

	Temperatures ( °C)									
	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C	70 °C
Time (min.)	Instantaneous Conversion based upon Initial Concentration ( $X_{at}$ )									
0	0	0	0	0	0	0	0	0	0	0
1	0.52	0.45	0.42	0.48	0.48	0.49	0.48	0.5	0.53	0.53
2	0.55	0.5	0.44	0.52	0.5	0.5	0.49	0.51	0.54	0.54
3	0.58	0.51	0.45	0.52	0.51	0.51	0.49	0.52	0.54	0.54
4	0.6	0.52	0.46	0.53	0.51	0.51	0.5	0.52	0.55	0.54
5	0.61	0.53	0.47	0.52	0.52	0.51	0.5	0.52	0.55	0.54
6	0.63	0.53	0.47	0.52	0.52	0.51	0.5	0.52	0.55	0.54
7	0.64	0.54	0.47	0.52	0.52	0.52	0.5	0.52	0.55	0.54
8	0.65	0.54	0.48	0.52	0.52	0.52	0.5	0.52	0.55	0.54
9	0.65	0.54	0.49	0.53	0	0.52	0.5	0.52	0.55	0.54
10	0.67	0.54	0.49	0.53	0	0.52	0.5	0.52	0.55	0.54

**Table 3A:** Instantaneous Conversion based upon Variable Concentration.

	Temperatures ( °C)									
	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C	70 °C
Time (min.)	Instantaneous Conversion based upon Variable Concentration ( $X_{at}$ )									
0	0	0	0	0	0	0	0	0	0	0
1	0.52	0.45	0.42	0.48	0.48	0.49	0.48	0.5	0.53	0.53
2	0.07	0.08	0.03	0.04	0.02	0.03	0.009	0.02	0.01	0.01
3	0.05	0.02	0.01	0.01	0.01	0.009	0.01	0.007	0.01	0.006
4	0.04	0.02	0.01	0.005	0.01	0.005	0.005	0.002	0.006	0.003
5	0.03	0.01	0.01	0.004	0.009	0.004	0.004	0.002	0.006	0.003
6	0.04	0.01	0.008	0.003	0.003	0.004	0.001	0.002	0.003	0.001
7	0.02	0.01	0.006	0.002	0.003	0.002	0.001	0.002	0.003	0.002
8	0.01	0.006	0.006	0.002	0.001	0.002	0.001	0.002	0	0.002
9	0.01	0.002	0.02	0.002	0	0.002	0.0009	0.002	0	0
10	0.006	0	0.009	0.002	0	0.006	0.0009	0.002	0	0

**Table 3B:** Overall Reaction Conversion.

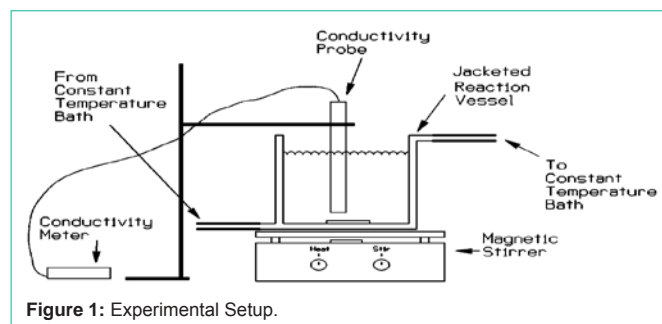
Sr. No.	Temperature (°C)	Overall Conversion ( $X_A$ )
1	25	67.53
2	30	54.72
3	35	49.78
4	40	52.95
5	45	52.42
6	50	52.28
7	55	50.63
8	60	52.7
9	65	55.88
10	70	54.87

**Table 4:** Fractional Life Method Data.

Sr. No.	$C_{A0}$	F (%)	$C_A = X_A C_{A0}$	$t_f$ (sec.)	$\log t_f$	$\ln C_{A0}$
1	1001	67.53	675.9753	210	2.32221	6.90875
2	974	54.72	532.9728	190	2.27875	6.88141
3	1830	49.78	910.974	170	2.23044	7.51207
4	1743	52.95	922.9185	140	2.14612	7.46336
5	1776	52.42	930.9792	130	2.11394	7.48211
6	2010	52.28	1050.828	110	2.04139	7.60589
7	2040	50.63	1032.852	70	1.84509	7.6207
8	2110	52.7	1111.97	60	1.77815	7.65444
9	1741	55.88	972.8708	60	1.77815	7.46221
10	2030	54.87	1113.861	40	1.60205	7.61579

achieving higher conversion as reaction proceeds. Therefore agitation is necessary to provide efficient mixing and uniform temperature distribution in reactor. The reaction conversion increases from 50.2% to 58.8% corresponding to a temperature change from 25°C to 30°C but for a reaction temperature more than 30°C a more sluggish behavior of change in reaction conversion can be observed [16-19]. As the previous research shows that the hydrolysis of ethyl acetate under alkaline conditions is 2<sup>nd</sup> order reaction, however during the experiments, we found that saponification of ethyl acetate with sodium hydroxide does not satisfy the 2<sup>nd</sup> order reaction kinetics. It was necessary to analyze the reaction more carefully. The previous works on this reaction did not analyze the reaction rate in details. Usually only the mean initial rate constant has been obtained. The deviation from the 2<sup>nd</sup> order rate equation has never been analyzed in detail kinetically. Therefore we study the kinetics and reaction rate of this reaction at different temperature careful in order to analyze the reaction kinetics.

This reaction has been studied by several researchers at different temperatures using a variety of measurement techniques in order to estimate the reaction order and activation energies [14,20]. Daniels et al [21]. And Levenson [22] use a volumetric titration method independently in which the composition of reaction mixture is analysed by withdrawal of samples after equal interval of time. The main disadvantages are the errors associated with the titration using color indicators. The 2<sup>nd</sup> technique is reported by Walker [15] based upon the composition measurement at any time using



Conductometric measurement method. These measurements are carried out manually. However the accuracy of results strongly depends upon the response time in Conductometric measurement. Another technique reported by Stead et al [23]. This is based upon the continuous flow systems and usually for large volumes of fluids. In this method the reactants are fed continuously to a stirred tank reactor at constant temperature. Jensen et al [24]. Used high frequency titrimetry. This method does not need the introduction of any electrodes or external indicator in the reaction vessel. But the precaution about the calibration of the equipment must be taken for the nonlinearity of the equipment. This method involves a number of manual operations in methodology as compared with the proposed method. Shui-Yuan et al. and Ge-Li et al. [25,26] used acidometry and micro calorimetry techniques respectively in order to estimate the rate constant of saponification of ester. However these latest techniques are not so simple as compared to proposed methods. Zhanjun et al. and Young-Tao et al. [27,28] focused their attention to online data using a Conductometric measurement technique in order to make the methodology much simpler.

## Experimental Work

For the batch experimentation equimolecular amounts of both reactants 0.1M of ethyl acetate ( $\text{CH}_3\text{COOC}_2\text{H}_5$ ) purchased from E. Merck KG and 0.1M of sodium hydroxide (NaOH) purchased from RdH Chemicals are introduced in a batch type stirred tank reactor. Agitation is provided with the help of a magnetic stirrer with a speed of (438rpm). Both reactants should be as close to same temperature as possible before starting the experiment. As the reaction proceeds to the forward direction hydroxide ions ( $\text{OH}^-$ ) are consumed and acetate ions ( $\text{CH}_3\text{COO}^-$ ) are produced. This change in ion concentration results in a conductivity change in the solution that is continuously measured by a conductivity meter and by the measurement of this conductivity we could ascertain the degree of hydrolysis. Note the conductivity of the reaction mixture after equal interval of times until the conductivity becomes constant. Repeat the experiment at different temperatures from (25°C-70°C). Heating is providing with the hot water circulation. The data obtained on the basis of key Component (NaOH) from the experiments are given in Table 1. The experimental setup is shown in Figure 1.

## Results and Discussions

### Overall and instantaneous conversion

The Conversion of a chemical reaction is defined as in multi pass system the percentage transformation of reactants in to products in a single pass. The conversion is separated into instantaneous conversion

and overall conversion. For the continuous processes both have same meaning but for batch and semi-batch processes they have significant differences. The overall conversion, Instantaneous conversion based upon initial concentration, and Instantaneous conversion based upon variable concentration can be calculated by following equations. The results are tabulated in Table 2, Table 3, and Table 4.

$$X_A = 1 - \frac{C_{Af}}{C_{Ao}} \tag{1}$$

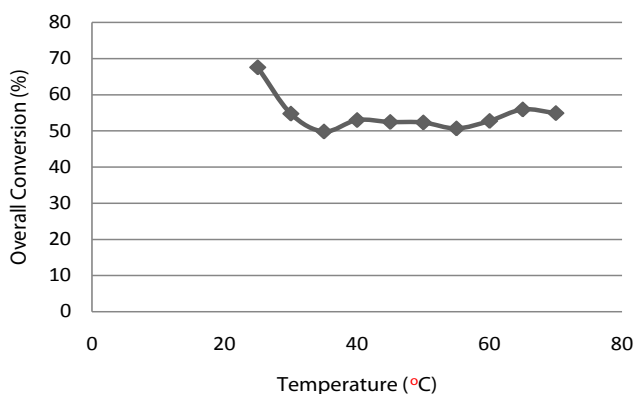
$$X_{A1} = 1 - \frac{C_{A1}}{C_{Ao}} \tag{2}$$

$$X_{A2} = 1 - \frac{C_{A2}}{C_{Ao}} \tag{3}$$

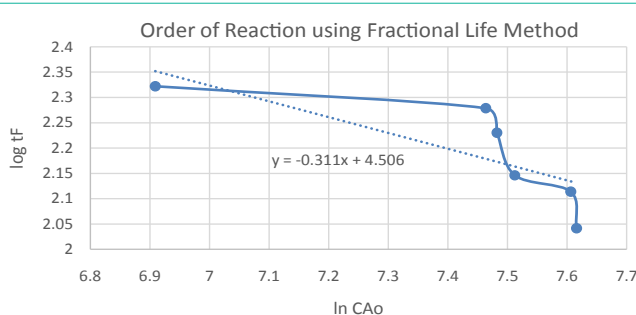
The effect of temperature on the overall conversion of reaction has been plotted shown in Graph 1: this shows that low temperature (25°C) favors the higher conversion (67.53%) and that is agreed well those of previous studies.

### Order of reaction

In chemical kinetics, the order of reaction with respect to a given substance (such as reactant, catalyst or product) is defined as the index, or exponent, to which its concentration term in the rate equation is raised. Order of reaction is a relationship between the concentrations of reactants, products, and rate of reaction. It gives detail about the stoichiometry of the rate determining step in the whole reaction. A reaction can have more than one order depending upon their different concentrations of reactants but order of reaction must be within a range of (+3,-3). It indicates that to what extent the concentration of reactants affects the rate of reaction as well as which component has highest effect. Let us plan to use the Fractional



Graph 1: Effect of Temperature on Overall Conversion.



Graph 2: Concentration vs. Time Graph for Order of Reaction.

Life Method in order to estimate the Order of Reaction. The basic equation of Fractional Life Method is given by.

$$t_F = \frac{(F)^{1-n} - 1}{k(n-1)} C_{Ao}^{1-n} \tag{4}$$

By taking the logarithm we get

$$\log t_F = \log \frac{(F)^{1-n} - 1}{k(n-1)} + (1-n) \log C_{Ao} \tag{5}$$

The calculation and data is tabulated in Table 04: for the calculation of the reaction order using fractional Life method. A Graph 2: is plotted between (ln C<sub>Ao</sub>) and (log t<sub>F</sub>) in order to estimate the order of reaction using Fractional Life Method. By comparing the equation (5) with the straight line equation obtained from the graph we found that the order of reaction is 1.3118. The previous research shows that this reaction follows the 2<sup>nd</sup> order reaction kinetics but we found the order of reaction 1.3118 so this reaction does not satisfactory expressed as a 2<sup>nd</sup> order reaction kinetics. Furthermore we will make the shifting order analyses in order to check that either 1.3118 is correct or not.

### Rate constant, frequency factor, and activation energy

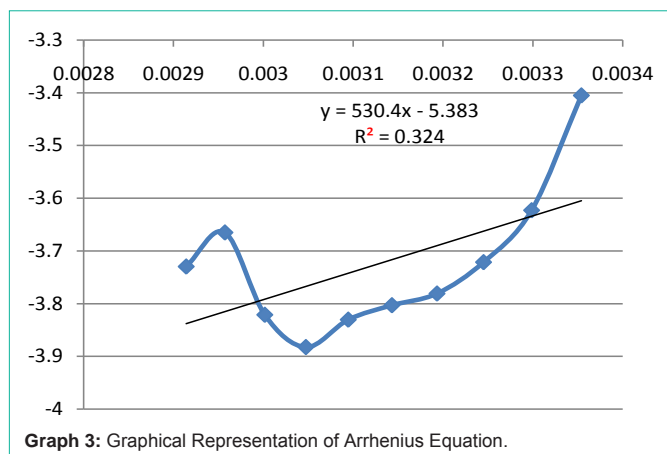
The rate equation shows the effect of changing concentrations of reactants on the rate of reaction. What about all the other things like temperature, pressure, and catalysts effect which also change the rate of reaction? Where do these fit into the rate equation? These

Table 5: Rate Constants at Different Temperatures.

Time (min.)	Temperatures (°C)									
	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C	70°C
0	0	0	0	0	0	0	0	0	0	0
1	0.0958	0.0789	0.0775	0.0730	0.0724	0.0707	0.0689	0.0723	0.0845	0.0802
2	0.0538	0.0455	0.0417	0.0394	0.0377	0.0372	0.0350	0.0376	0.0435	0.0410
3	0.0389	0.0316	0.0283	0.0268	0.0259	0.0251	0.0237	0.0253	0.0294	0.0275
4	0.0292	0.0245	0.0214	0.0203	0.0197	0.0190	0.0179	0.0191	0.0223	0.0207
5	0.0247	0.0201	0.0172	0.0163	0.0160	0.0153	0.0144	0.0153	0.0180	0.0167
6	0.0216	0.0168	0.0143	0.0136	0.0133	0.0128	0.0121	0.0128	0.0150	0.0139
7	0.0195	0.0148	0.0124	0.0117	0.0115	0.0110	0.0104	0.0110	0.0130	0.0119
8	0.0176	0.0131	0.0108	0.0103	0.0101	0.0096	0.0091	0.0097	0.0113	0.0105
9	0.0162	0.0117	0.0098	0.0092	0.0090	0.0086	0.0081	0.0086	0.0101	0.0093
10	0.0156	0.0105	0.0087	0.0083	0.0081	0.0078	0.0073	0.0077	0.0091	0.0084

Table 6: Average Values of Rate Constant at Different Temperatures and Arrhenius Parameters Data.

Sr. No.	Temperature (°C)	Temperature (K)	1/T	K <sub>avg.</sub>	ln(K)
1	25	298.15	0.003354	0.0332	-3.4052
2	30	303.15	0.0032986	0.0267	-3.623
3	35	308.15	0.0032451	0.0242	-3.7214
4	40	313.15	0.0031933	0.0228	-3.7809
5	45	318.15	0.0031431	0.0223	-3.8031
6	50	323.15	0.0030945	0.0217	-3.8304
7	55	328.15	0.0030473	0.0206	-3.8824
8	60	333.15	0.0030016	0.0219	-3.8212
9	65	338.15	0.0029572	0.0256	-3.6651
10	70	343.15	0.0029141	0.024	-3.7297



Graph 3: Graphical Representation of Arrhenius Equation.

Table 7: Enthalpies and Gibbs Free Energies of Components.

Components	Enthalpies	Gibbs Free Energy
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	-480	-332.7
NaOH	-470	-419.2
CH <sub>3</sub> COONa	-709.32	-607.7
C <sub>2</sub> H <sub>5</sub> OH	-277.6	-168.3

are all included in the so-called rate constant. If you change the concentrations of reactants the rate constant will remain constant. But if you change the temperature, pressure, and catalysts the rate constants will change. The activation energy is the minimum amount of energy required by the reactant molecule in to make an effective collision for the occurrence of reaction. A couple of reasons are that in order to react. The 1<sup>st</sup> reason is that the molecules need energy to distort or stretch their bonds so that they break and now can form new bonds, and the 2<sup>nd</sup> reason is that the molecules need energy to overcome the steric and electron repulsive forces as they come close together. Frequency factor is a pre-exponential factor in the Arrhenius Equation which includes factors like the frequency of collision, and their orientation. It varies slightly with temperature although not much; it is often taken as constant across small temperature ranges.

When the mechanism of reaction is not known we often attempt to fit the data with a  $n^{\text{th}}$  order rate equation in the form given below.

$$-r_A = \frac{-d_{CA}}{d_t} = KC_A^n \quad (6)$$

This on separation and integration yields

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1)Kt \quad n \neq 1 \quad (7)$$

where

$$K = \frac{C_A^{1-n} - C_{A0}^{1-n}}{(n-1)t} \quad (8)$$

As we found that the order of reaction is  $(n=1.3118)$  so above equation can be modified in to this form given below.

$$K = \frac{C_A^{-0.3118} - C_{A0}^{-0.3118}}{(0.3118)t} \quad (9)$$

Above equation is used to calculate the rate constant at each temperature and concentration the results are tabulated in Table 5. Average values of rate constant at different temperatures and Arrhenius Parameters data is tabulated in Table 6.

The Arrhenius Equation is given by

$$k = k_0 e^{\frac{-E_a}{RT}} \quad (10)$$

Taking the natural log on both sides we get

$$\ln k = \ln k_0 + \ln e^{\frac{-E_a}{RT}} \quad (11)$$

$$\ln k = \ln k_0 + \frac{-E_a}{RT} \ln e \quad (12)$$

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln k_0 \quad (13)$$

Now by comparing it with the equation of straight line we get

$$y = mx + c \quad (14)$$

The graphical representation of the Arrhenius Equation is plotted in below Graph 3:

The results shows that

$$y = 530.4x - 5.3837 \quad (15)$$

Compare the above equation with the equation (13), (14), and (15) we found that the value of activation energy is 4.409KJ/mole and the value of frequency factor is 0.00459. The values of rate constant and activation energies are agreed well with that of previous studies. This finding leads to a general rule on the influence of activation energy. A high temperature favors the reaction with high activation energy and reaction will be more temperature sensitive while a low temperature favors the reaction with low activation energy and reaction will be less temperature sensitive.

### Equilibrium conversion and adiabatic reaction temperature

The highest conversion that can be achieved in a reversible reaction is the equilibrium conversion. For the endothermic reactions, the equilibrium conversion increases with increasing temperature up to a 1.0 and for exothermic reactions, the equilibrium conversion decreases with increasing temperature. The thermodynamic equilibrium constant is independent of pressure of system, presence or absence of inerts, kinetics of reaction, but dependent on temperature of system. Though the thermodynamic equilibrium constant is unaffected by the pressure of system, presence or absence of inerts, kinetics of reaction, but the equilibrium concentration of reactants and equilibrium conversion of reactants can be influenced by these variables.

To determine the maximum conversion that can be achieved in an exothermic reaction carried out adiabatically, we find the intersection of the equilibrium conversion as a function of temperature with temperature-conversion chart from the energy balance.

In order to find out the adiabatic reaction temperature and equilibrium reaction conversion it is need to be finding out the heat of reaction along with energy balance on the reaction and then precede the calculations as follows. The reaction is given by  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$

The values of enthalpy and Gibbs free energy of reactants and products are given in Table 7. The heat of reaction and Gibbs energy of the whole reaction is found given below.

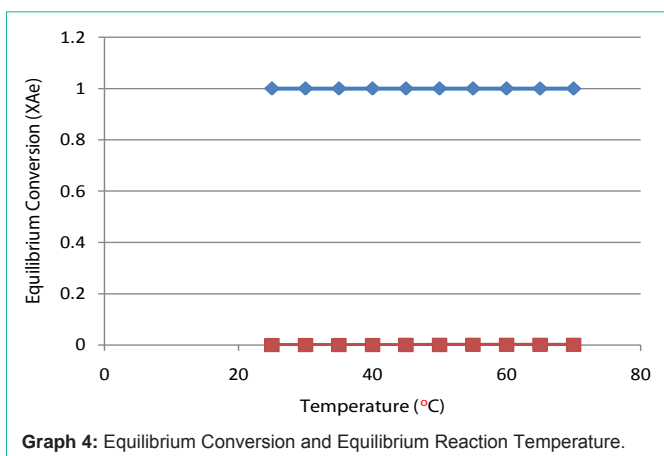
$$\Delta H_{298} = -36920 \frac{\text{KJ}}{\text{mole}} \quad (16)$$

$$\Delta G_{298} = -24100 \text{KJ} \quad (17)$$

Now for K298, K, equilibrium conversion X<sub>Ae</sub>, and adiabatic

**Table 8:** Equilibrium Conversion Data.

Temperature (K)	$K_{298}$	K	$X_{Ae}$	$X_{EB}$
298.15	-0.00581	16670.29	0.99994	0
303.15	-0.2514	13040.11	0.999923	8.07E-06
308.15	-0.4891	10280.18	0.999927	0.000163
313.15	-0.7192	8167.467	0.999877	0.000245
318.15	-0.9421	6535.986	0.999847	0.000329
323.15	-1.158	5266.683	0.99981	0.000413
328.15	-1.3674	4270.692	0.999765	0.000496
333.15	-1.5705	3485.971	0.999713	0.000581
338.15	-1.7676	2862.219	0.99965	0.000668
343.15	-1.9589	2364.223	0.999577	0.000753

**Graph 4:** Equilibrium Conversion and Equilibrium Reaction Temperature.**Table 9:** values of Shomate Constants for Sodium Hydroxide (NaOH) over Temperature Range of (298K-572K).

Constants	Values
A	419.4837
B	-1717.75
C	2953.573
D	-1597.22
E	-6.04688

equilibrium conversion we have following equations (18-22).

$$K_{298} = \exp\left(\frac{\Delta G_{298}}{RT}\right) \quad (18)$$

$$K = K_{298} \left[ \left( \frac{HR_{298}}{R} \right) \left( \frac{1}{T} - \frac{1}{298} \right) \right] \quad (19)$$

$$X_{Ae} = \frac{K}{K+1} \quad (20)$$

After that an energy balance is made on this reaction. For this reaction carried out adiabatically, the energy balance for key component reduces to.

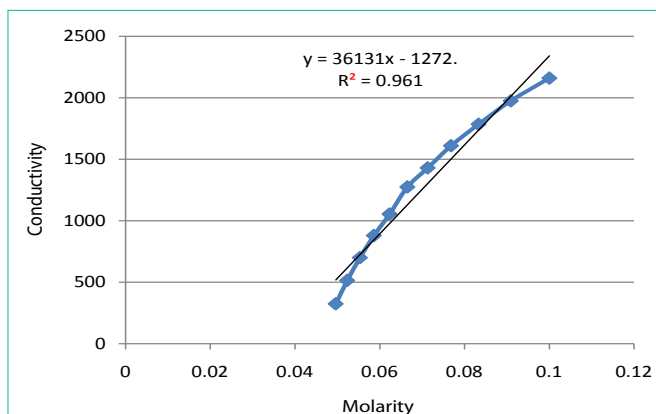
$$X_{EB} = \frac{\sum \theta_i C_{pi} (T - T_0)}{-\Delta H_{RX}} = \frac{C_{pA} (T - T_0)}{-\Delta H_{RX}} \quad (21)$$

The solid phase heat capacity values of key component sodium hydroxide (NaOH) are calculated from the Shomate Equation (22) and the values of Shomate constant are found from National Institute of Standard and Technology (NIST) and presented in Table 09.

$$C_p = A + BT + CT^2 + DT^3 + \frac{E}{T^2} \quad (22)$$

**Table 10:** Standard Curve Data for Key Component (NaOH).

Volume	Conductivity	Molarity
200	2160	0.1
220	1975	0.0909
240	1785	0.0833
260	1610	0.0768
280	1430	0.0713
300	1275	0.0665
320	1055	0.0623
340	880	0.0586
360	700	0.0553
380	515	0.0523
400	325	0.0496

**Graph 5:** Standard Curve for Key Component (NaOH).

Where temperature is in  $T/1000$  (kelvin) and the values of equilibrium conversion and adiabatic equilibrium conversion are tabulated in Table 8 and its graphical presentation shows in Graph 4. From this graph it has been clearly seen that both lines are far away and not intersect each other so from this finding it has been proved that reaction is purely irreversible and it is not possible to find out the equilibrium conversion and temperature because it is only for reversible reactions.

### Shifting order analysis

In searching for a kinetic equation it may be found that the data are well fitted by one reaction order at high concentrations but by another reaction order at low concentrations. Consider the reaction rate equation for such case.

$$-r_A = \frac{-dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} \quad (23)$$

By separation and integration of above equation we get.

$$\ln\left(\frac{C_{A0}}{C_A}\right) + k_2(C_{A0} - C_A) = k_1 t \quad (24)$$

To linearize and rearrange we get following two different forms.

$$\frac{C_{A0} - C_A}{\ln\left(\frac{C_{A0}}{C_A}\right)} = \frac{-1 + k_1}{k_2} + \frac{k_1}{k_2} \left( \frac{t}{\ln\left(\frac{C_{A0}}{C_A}\right)} \right) \quad (25)$$

$$\frac{\ln\left(\frac{C_{A0}}{C_A}\right)}{C_{A0} - C_A} = -k_2 + \frac{-k_1 t}{C_{A0} - C_A} \quad (26)$$

**Table 11:** Shifting Order Calculation Data at 25°C and 30°C.

Time	Shifting Order Analysis at 25°C				Shifting Order Analysis at 30°C			
	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$
0	1001	0.063	$\infty$	$\infty$	974	0.0622	$\infty$	$\infty$
1	480	0.0486	69.4444	18.0138	529	0.0499	81.3008	18.0999
2	443	0.0475	129.0322	18.2129	486	0.0487	148.1481	18.1185
3	417	0.0468	185.1851	18.3456	473	0.0484	217.3913	18.1739
4	398	0.0463	239.5209	18.4371	463	0.0481	283.6879	18.2269
5	383	0.0459	292.3976	18.5146	455	0.0479	349.6503	18.2657
6	366	0.0454	340.909	18.6079	450	0.0477	413.7931	18.2965
7	356	0.0451	391.0614	18.6684	445	0.0476	479.452	18.3219
8	350	0.045	439.5604	18.6888	442	0.0475	544.2176	18.3333
9	346	0.0448	494.5054	18.7252	441	0.0475	612.2448	18.3333
10	325	0.0443	534.7593	18.8288	441	0.0475	680.2721	18.3333

**Table 12:** Shifting Order Calculation Data at 35°C and 40°C.

Time	Shifting Order Analysis at 35°C				Shifting Order Analysis at 40°C			
	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$
0	1830	0.0859	$\infty$	$\infty$	1743	0.0835	$\infty$	$\infty$
1	1044	0.0641	45.8715	13.422	891	0.0599	42.3728	14.072
2	1011	0.0632	88.1057	13.5154	549	0.0588	80.9716	14.1943
3	991	0.0627	129.3103	13.5689	838	0.0585	120	14.228
4	979	0.0623	169.4915	13.6101	833	0.0583	158.73	14.2539
5	969	0.0621	210.084	13.626	829	0.0582	197.628	14.2648
6	961	0.0619	250	13.65	826	0.0581	236.22	14.2755
7	955	0.0617	289.2561	13.6694	824	0.0581	275.59	14.2755
8	949	0.0615	327.8688	13.6926	822	0.058	313.725	14.2862
9	928	0.0609	360	13.756	820	0.058	352.941	14.2862
10	919	0.0607	396.8253	13.7777	820	0.058	392.1568	14.2862

**Table 13:** Shifting Order Calculation Data at 45°C and 50°C.

Time	Shifting Order Analysis at 45°C				Shifting Order Analysis at 50°C			
	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$
0	1776	0.0844	$\infty$	$\infty$	2010	0.0909	$\infty$	$\infty$
1	908	0.0604	41.6661	13.9375	1019	0.0635	36.4963	13.0875
2	885	0.0598	81.3008	14.004	987	0.0626	70.6713	13.1766
3	869	0.0593	119.5219	14.0597	978	0.0623	104.8951	13.2062
4	860	0.0591	158.1027	14.079	973	0.0622	139.3728	13.216
5	852	0.0588	195.3125	14.1132	969	0.0621	173.6111	13.2256
6	849	0.0588	234.375	14.1132	965	0.062	207.6124	13.2387
7	846	0.0587	272.3735	14.1284	963	0.0619	241.3793	13.2448
8	845	0.0586	310.0775	14.1356	961	0.0619	275.862	13.2448
9	845	0.0586	348.8372	14.1356	959	0.0618	309.2783	13.2577
10	845	0.0586	387.5968	14.1356	953	0.0616	343.6426	13.3676

By similar reasoning to the above we can show that the general rate forms where order shifts from m to n.

$$-r_A = \frac{-d_{CA}}{d_t} = \frac{k_1 C_A^m}{1 + k_2 C_A^n} \quad (27)$$

In order to make a shifting order analyses it is necessary to convert the concentration values in terms of conductivity into molarity units. For this purpose a batch experiment is separately performed and by using molarity-volume relationship equation (28) conductivity

**Table 14:** Shifting Order Calculation Data at 55°C and 60°C.

Time	Shifting Order Analysis at 55°C				Shifting Order Analysis at 60°C			
	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$
0	2040	0.0917	$\infty$	$\infty$	2110	0.0936	$\infty$	$\infty$
1	1047	0.0642	36.3636	12.96	1045	0.0642	40.1606	12.8197
2	1037	0.064	72.2021	12.9819	1019	0.0635	66.4451	12.887
3	1026	0.0636	106.7615	13.0177	1011	0.0632	98.6842	12.9177
4	1020	0.0635	141.8439	13.0283	1008	0.0632	131.5789	12.9177
5	1015	0.0633	176.0563	13.0457	1005	0.0631	163.9344	12.9245
6	1013	0.0633	211.2676	13.0457	1002	0.063	196.0784	12.9346
7	1011	0.0632	245.614	13.0561	999	0.0629	228.013	12.9446
8	1009	0.0632	280.7017	13.0561	998	0.0629	260.5863	12.9446
9	1008	0.0632	315.7894	13.0561	998	0.0629	293.1596	12.9446
10	1007	0.0631	349.6503	13.0664	998	0.0629	325.7328	12.9446

**Table 15:** Shifting Order Calculation Data at 65°C and 70°C.

Time	Shifting Order Analysis at 65°C				Shifting Order Analysis at 70°C			
	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$	C	M	$t/C_{A_0}-C_A$	$\ln(C_{A_0}/C_A)/C_{A_0}-C_A$
0	1741	0.0834	$\infty$	$\infty$	2030	0.0914	$\infty$	$\infty$
1	809	0.0576	38.7596	14.3449	947	0.0615	33.4448	13.2474
2	793	0.0572	76.3358	14.3893	933	0.0611	66.0066	13.2904
3	784	0.057	113.6363	14.4128	927	0.0609	98.3606	13.3081
4	779	0.0568	150.3759	14.4398	924	0.0608	130.7189	13.3169
5	771	0.0566	186.5671	14.4589	921	0.0607	162.8664	13.3289
6	768	0.0565	223.0483	14.4758	920	0.0607	195.4397	13.3289
7	768	0.0565	260.223	14.4758	918	0.0607	228.013	13.3289
8	768	0.0565	297.3977	14.4758	916	0.0606	259.742	13.3409
9	768	0.0565	334.5724	14.4758	916	0.0606	292.2077	13.3409
10	768	0.0565	371.7472	14.4758	916	0.0606	324.6753	13.3409

curve for key component sodium hydroxide (NaOH) is obtained and then by using the equation straight line required conductivity values are converted into molarity units. The data of conductivity-molarity values of batch experiment are presented in Table 10 and it is graphically presented in Graph 5.

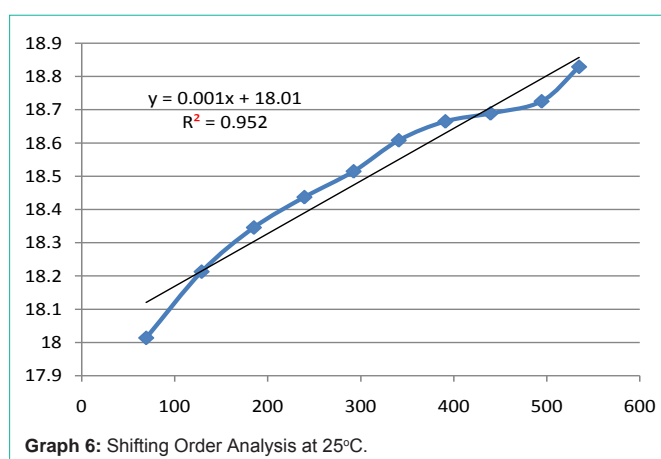
$$M_2 = \frac{M_1 V_1}{V_2} \quad (28)$$

The shifting order is confirmed by proving the equation (26) by a straight line graph when it is plotted. The shifting order analyses calculations for different temperatures and their graphical presentation are shown in Tables 11-15 and Graphs 6-15 and only those values of concentrations are plotted when there is change in concentration is observed with time and excluded when concentrations become constant with time.

The results show that all graphs are almost straight lines and hence it is proved that this reaction is shifting order whose order is shifted from 2 to 1.3118 and cannot be expressed as a 2<sup>nd</sup> order reaction specifically when equimolar concentrations of both reactants are used.

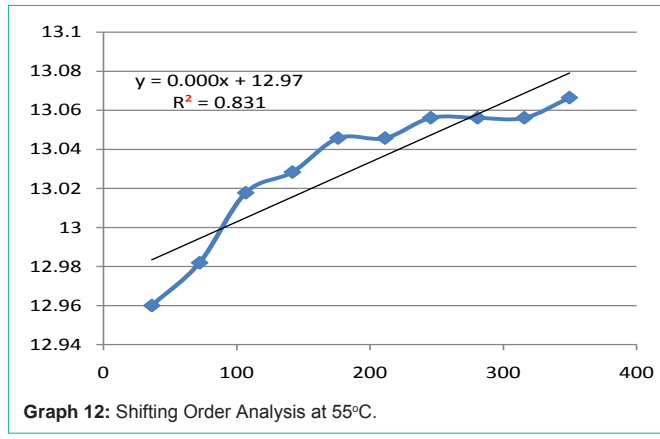
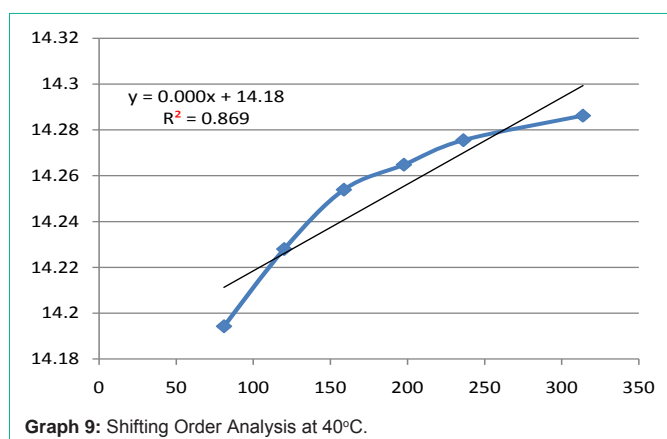
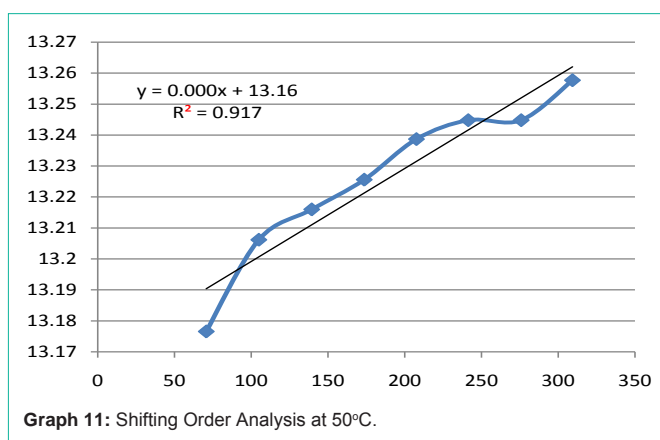
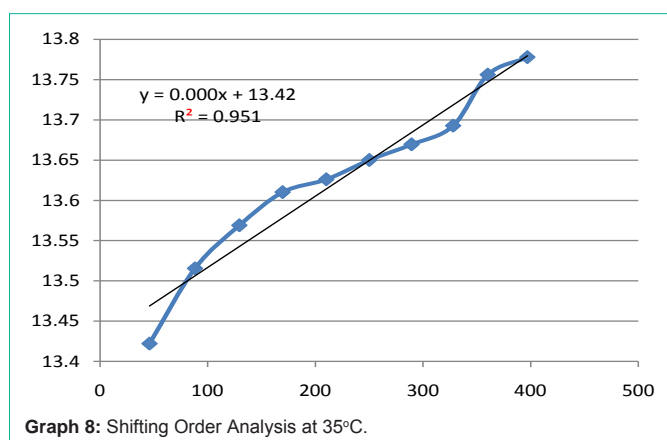
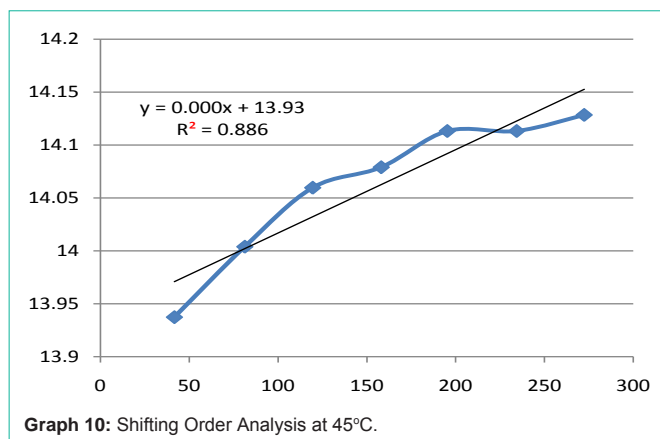
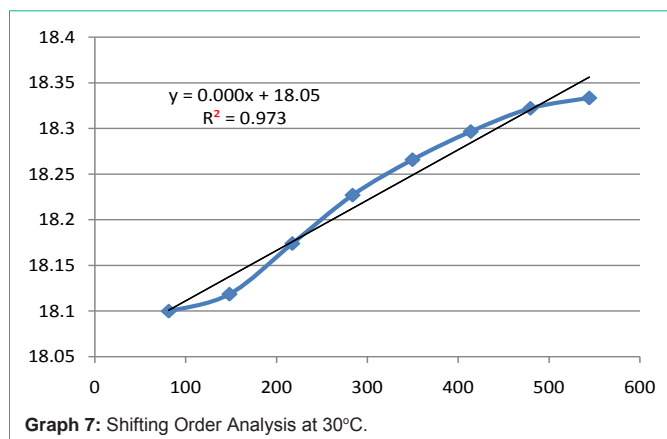
### Temperature effect on rate of reaction

The rate of reaction at each temperature and each concentration



has been calculated using equation (27) using the value of  $m$  is 2 and the value of  $n$  is 1.3118 as reaction order shifts from 2 to 1.3118. The results are presented in Table 16 and graphically are Graph 16. We found that rate of reaction increases with increasing temperature and goes to a peak value at a temperature of 70°C. A temperature effect on the temperature sensitivity of the reaction has been already explained

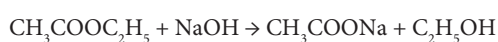




in previous section, the determination of Arrhenius Parameters.

### Mathematical model for holding time

Here we tried to develop a mathematical model for the holding time in a batch reactor for this reaction. The reaction is given by.



Whereas NaOH is the key component and also limiting reactant the material balance on this key component in the batch reactor is.

$$-r_A = \frac{-1}{V_R} \frac{dN_A}{dt} \quad (29)$$

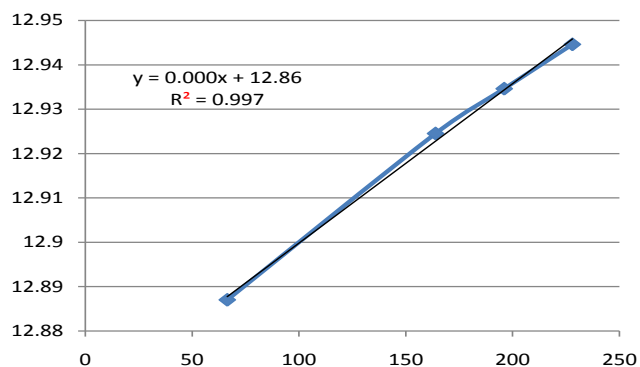
Where  $C_A = N_A/V_R$  so equation (29) becomes.

$$-r_A = \frac{dC_A}{dt} = KC_{\text{NaOH}}^n \quad (30)$$

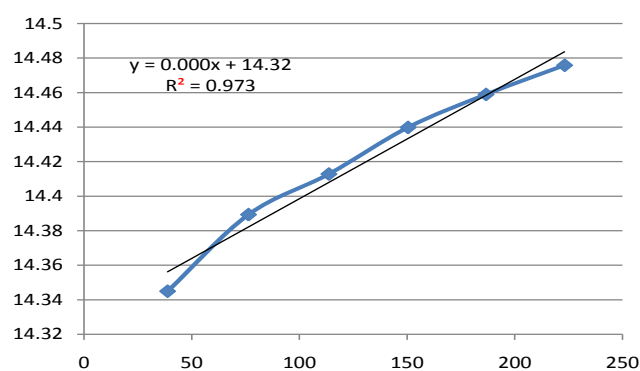
As all the data we collect from experimental runs at different temperatures are based upon the key component and 2<sup>nd</sup> component involvement in this study is ignored therefore above rate model is written in the form of key component only. The concentration of NaOH can be expressed in the terms of fractional conversion and the stoichiometry of the reaction is shown in Table 17. From the stoichiometry we have.

$$C_{A0} - C_A = C_{B0} - C_B \quad (31)$$

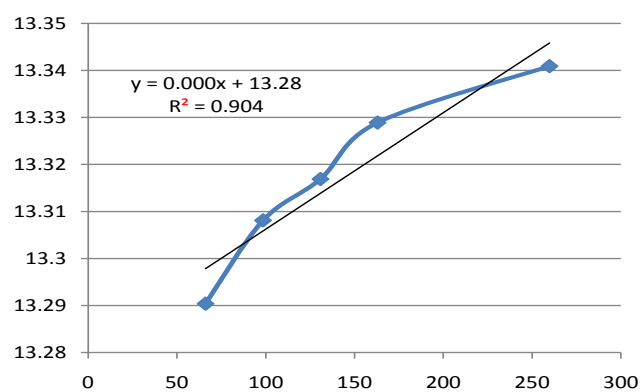
The concentration of B is expressed in



Graph 13: Shifting Order Analysis at 60°C.



Graph 14: Shifting Order Analysis at 65°C.



Graph 15: Shifting Order Analysis at 70°C.

$$C_{Bo} = C_{Bo} - C_{Ao} + C_A \quad (32)$$

Using the fractional conversion  $X_A$  at constant volume we have.

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}} \quad (33)$$

Therefore the amount reacted we have.

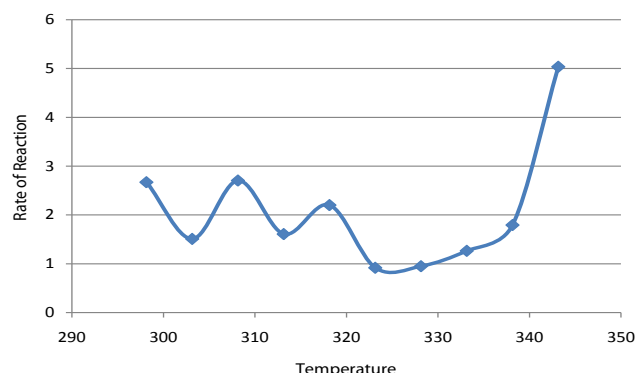
$$C_{Ao} - C_A = X_A C_{Ao} \quad (34)$$

Or

$$C_A = C_{Ao}(1 - X_A) \quad (35)$$

Differentiation of equation (34) gives.

$$-dC_A = C_{Ao} dX_A \quad (36)$$



Graph 16: Temperature Effect of Rate of Reaction .

Table 16: Temperature Effect on Rate of Reaction.

Temperature	Rate of Reaction
298.15	$2.6702 \times 10^{-6}$
303.15	$1.5094 \times 10^{-6}$
308.15	$2.7045 \times 10^{-6}$
313.15	$1.0679 \times 10^{-6}$
318.15	$2.2015 \times 10^{-6}$
323.15	$0.9180 \times 10^{-6}$
328.15	$0.9496 \times 10^{-6}$
333.15	$1.2649 \times 10^{-6}$
338.15	$1.7930 \times 10^{-6}$
343.15	$5.0339 \times 10^{-6}$

Table 17: Stoichiometry of the Reaction.

Component	A
At Time $t = 0$	$C_{Ao}$
At Time $t = t$	$C_A$
Amount Reacted	$C_{Ao} - C_A$

Put the values from equations (32, 35 and 36) in equation (30) we get.

$$C_{Ao} \frac{dX_A}{dt} = K [C_{Ao} (1 - X_A)]^{1.3118} \quad (37)$$

The value of  $n=1.3118$  used as we previously find that this reaction is shifting order with order 1.3118 not 2<sup>nd</sup> order. Upon the rearranging and applying the integral sign and limits on equation (37) we get the form.

$$\int_0^{X_{Af}} \frac{dX_A}{(1 - X_A)^{1.3118}} = KC_{Ao}^{0.3118} \int_0^{t_{HoldingTime}} dt \quad (38)$$

After integration and solving the limits we get the equation for holding time for batch reactor.

$$t_{HoldingTime} = \frac{3.2071 [1 - (1 - X_{Af})^{0.3118}]}{(1 - X_{Af})^{0.3118} KC_{Ao}^{0.3118}} \quad (39)$$

This is the final form of the mathematical model that can be used for the holding time calculations under these conditions as described in this research.

## Conclusion

It has been concluded that the alkaline hydrolysis of ethyl acetate has an overall reaction order 1.3118 and cannot be expressed

satisfactorily as a 2<sup>nd</sup> order reaction specially when equimolecular concentrations of both reactants are used. The low reaction temperature favors the high overall conversion, low energy barrier for reactant molecules to make an effective collision and less temperature sensitive. The reaction has no change in equilibrium conversion as well as adiabatic equilibrium conversion that shows that the reaction is irreversible and exothermic in nature (-ve heat of reaction) the rate of reaction increases with increasing temperature so at high temperature (70°C) the reaction has high reaction rate.

## Symbols

A, B, C, D, E: Shomate Constants;  $C_{A0}$ : Initial Concentration;  $C_{Af}$ : Final Concentration;  $C_{pA}$ : Heat Capacity; E: Activation Energy; F: Fraction; G: Gibbs free energy;  $H_R$ : Heat of Reaction;  $k_0$ : Frequency Factor; K: Rate Constant; m, n: Reaction Orders; M: Molarity;  $-r_A$ : Rate of Reaction; R: General Gas Constant; t: Time; T: Temperature; V: Volume;  $X_A$ : Overall Conversion;  $X_{AE}$ : Equilibrium Conversion;  $X_{EB}$ : Adiabatic Equilibrium Conversion

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