Saponification: A Comparative Kinetic Study in a Batch Reactor

A thesis Submitted to the University of Khartoum in partial fulfillment of the requirement for the degree of M.Sc in Chemical Engineering

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قال تعالى :

(لاَ يُكَلِّفُ اللَّهُ نَفْساً إلاَّوُسْعَهَا لَهَا مَا كَسَبَتْ وَعَلَيْهَا مَا اكْتَسَبَتْ رَبَّنَا لاَ تُؤَاخِذْنَا إِن نَّسِينَا أَوْ أَخْطَأْنَا رَبَّنَا وَلاَ تَحْمِلْ عَلَيْنَا إِصْراً كَمَا حَمَلْتَهُ عَلَى الَّذِينَ مِن قَبْلِنَا رَبَّنَا وَلاَ تُحَمِّلْنَا مَا لاَ طَاقَةَ لَنَا بِهِ وَاعْفُ عَنَّا وَاغْفِرْ لَنَا وَارْحَمْنَا أَنتَ مَوْلاَنَا فَانصُرْنَا عَلَى الْقَوْمِ الْكَافِرِينَ)

سورة البقرة الآية (286)

Dedication

To the soul of my father

To my well – beloved mother

To my wife, brothers, sisters and extended family

To every body who contributed on this thesis directly or indirectly

,,,,,,,,,,,,,,,,,,,

Arman

Acknowledgement

I would like to thank the University of Khartoum and to express my sincere gratitude to my supervisor Dr. Mustafa Abbas Mustafa. I would like to acknowledge his unlimited efforts in guiding and following up the thesis progress, and specially his spirit – raising encouragement.

As many people have contributed constructively to this work. I would like to thank them all and in particular the people of University of Khartoum - Department of Chemical Engineering - Unit Operations lab, who provided me with the necessary information to rehabilitate the batch reactor. I owe special thanks to every body who contributed to this thesis directly or indirectly.

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Abstract

Knowledge of kinetic parameters is of extreme importance for the chemical engineer prior to design of chemical reactors. This research focuses on the study of the kinetics of the saponification reaction between sodium hydroxide and ethyl acetate in a batch reactor.

To achieve this, the batch reactor available at the unit operation laboratory (Department of Chemical Engineering, University of Khartoum) had been repaired and modified to suit the experimental procedures. The maintenance of the reactor includes change of bearing and bushes. The modification was made on the motion transmission from the electric motor to the agitator and on the temperature control system where a digital thermometer was used.

Prior to the kinetic study, two methods were tried for the temperature control. The first method used an electric heater plus a cooling jacket around the reactor but failed to precisely control the temperature. The second method used consists of a water bath of controlled temperature where the reactants are heated to the required temperature before they were fed to the reactor which was also heated to the same temperature using the water jacket. This method was successful in achieving a tight control of the temperature, thus ensuring isothermal conditions.

The reactions kinetics was studied through initially studying caustic soda concentrations dependency using an excess of ethyl acetate while maintaining isothermal conditions .Then the concentration dependency of ethyl acetate was evaluated using equal concentrations of reactants before operating at various condition to evaluate the temperature dependency.

Analytical mathematical and computer methods were used to analyze the experimental observations and data. The results obtained (of evaluated kinetic parameters) showed, a clear agreement with the values

from literature. Improved numerical accuracy has been shown in some cases to result as the use of polynomial fit relative to finite difference method.

It is recommended that future work focuses on fully automating the batch reactor using appropriate hardware and software (Labview) components.

مستخلص البحث

بالنسبة للمهندس الكيميائى من المهم معرفة المتغيرات الكينماتيكيه (حركية التفاعل) قبل الشروع فى تصميم المفاعل الكيميائى . يركز هذا البحث على دراسة حركية تفاعل التصبن ما بين هيدروكسيد الصوديوم واستات الإيثيل فى مفاعل الوجبه (الحله).

لإنجاز هذا، المفاعل الموجود فى معمل العمليات الموحد (قسم الهندسه الكيميائيه ،جامعة الخرطوم) تم إصلاحه وتعديله لملائمة طرق التجارب المستخدمه . الصيانة للمفاعل اشتملت على تغيير البلى والجلب . والتعديلات الخاصه بنقل الحركه من المحرك الكهربائى الى خلاط المفاعل وكذلك تغيير نظام التحكم فى درجة حرارة المفاعل حيث استخدم مقياس حراره رقمى .

قبل دراسة حركيه التفاعل ، اختبرت طريقتان للتحكم فى درجة حراره المفاعل .الطريقه الاولى استخدم سخان كهربائى بالاضافه الى قميص تبريد حول المفاعل ولكنها لم تنجح فى ضبط درجة المفاعل بالدقه المطلوبه .الطريقه الثانيه استخدم حمام مائى له درجة حراره ثابته حيث يتم فيه تسخين المواد المتفاعله ونفس الماء المتحكم فى درجة حرارتها تستخدم داخل القميص حول المفاعل . وهى طريقه ناجحه للحصول على درجة حراره ثابته.

تم دراسة حركية التفاعل الكيميائى بدراسة الإعتماد على تركيز الصودا الكاويه وإستخدام فائض من أستات الإيثيل وذلك عند ثبوت درجة الحراره. ثم دراسة الإعتماد على تركيز استات الإيثيل بإستخدام تراكيز متساويه من المادتين ومن ثم درس اعتماد التفاعل على درجة الحراره بتغير درجة الحراره .

استخدمت الطريقه الرياضيه للتحليل وطرق الحاسوب لتحليل نتائج الإختبارات المعمليه. النتائج المتحصل عليها(لقيم متغيرات حركية التفاعل) تتفق مع القيم الموجوده فى المراجع العلميه . كذلك استخدمت الطرق العددية للحصول على تطابق مع دوال القوى متعددة الحدود .

هذة الدراسة توصى مستقبلاً بإستخدام التحكم الأتوماتيكيى فى المفاعل وذلك عن طريق برامج الحاسوب وملحقاته .

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Abbreviations and Nomenclature

A	Frequency factor (litter/mol.sec)
C_A	Concentration of A after time t (mol/litter)
C_{A0}	Initial concentration of A (mol/litter)
CSTR	Continuous stripping tank reactor
E	Activity energy (J/mol or cal/mol)
EtAc	Ethyl acetate (Ethyl Acetate, $CH_3COOC_2H_5$)
F_j	Out flow of species j (mol/time)
F_{j0}	In flow of species j (mol/time)
G_j	Rate of generation of species j (mol/time)
HCl	Hydrochloric acid (HCl)
K	The reaction constant (litter/mol.sec)
MSDS	Material safety data sheet
M.W	Molecular weight (g/mol)
n	Order of reaction (dimensionless)
N_A	Number of moles of A remain in the reactor (mol)
N_{A0}	Number of moles of A initially in the reactor (mol)
N_j	Number of moles of species j (mol)
NaAc	Sodium acetate (CH_3COONa)
NaOH	Sodium hydroxide
PBR	Packed bed reactor
PFR	Plug flow reactor
R	Gas constant (R= 8.314 J/mol.^{0}K)
r_j	Rate of formation of species j (mol/litter. time)
t	Time (sec)
V	Volume (litter or ml)
V_{tit}	Volume of NaOH used in titration (ml)
X	Conversion (dimensionless)

CHAPTER ONE

INTRODUCTION

1.1. Background

A batch reactor may be described as a vessel in which any chemicals are placed to react. Batch reactors are normally used in studying the kinetics of chemical reactions, where the variation of a property of the reaction mixture is observed as the reaction progresses. Data collected usually consist of changes in variables such as concentration of a component, total volume of the system or a physical property like electrical conductivity. The data collected are then analyzed using pertinent equations to find desired kinetic parameters.

There is currently a pilot- scale batch reactor at the University of Khartoum - Department of Chemical Engineering - unit operations lab. One of the main objectives of this is thesis to rehabilitate and repair this reactor.

In order to validate this reactor a Saponification Reaction was chosen, because it is homogeneous (liquid phase reaction) in this case as constant volume reactor and Safety its reactants and products (Appendix A: Material Safety Data Sheet (MSDS)).

A saponification is a reaction between an ester and an alkali, such as sodium hydroxide, producing a free alcohol and an acid salt.

The stoichiometry of the saponification reaction between sodium hydroxide and Ethyl Acetate is:

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$ ------------- Eq(1.1)

Saponification is primarily used for the production of soaps.

1.2. Objectives

- The Repair of batch reactor in University of Khartoum - Department of Chemical Engineering - Unit Operations Lab.
- The validation of the repaired reactor by using a Saponification reaction and get experimental kinetic data, the values obtained was compared to values from Literature.

CHAPTER TWO

LITERATURE REVIEW

2.1. Description of reactors.

2.1.1 Batch reactor

A batch reactor is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations. The reactor can be charged (i.e., filled) through the holes at the top (Figure 2.1). The batch reactor has the advantage and also has the disadvantages are shown in Table2.1.

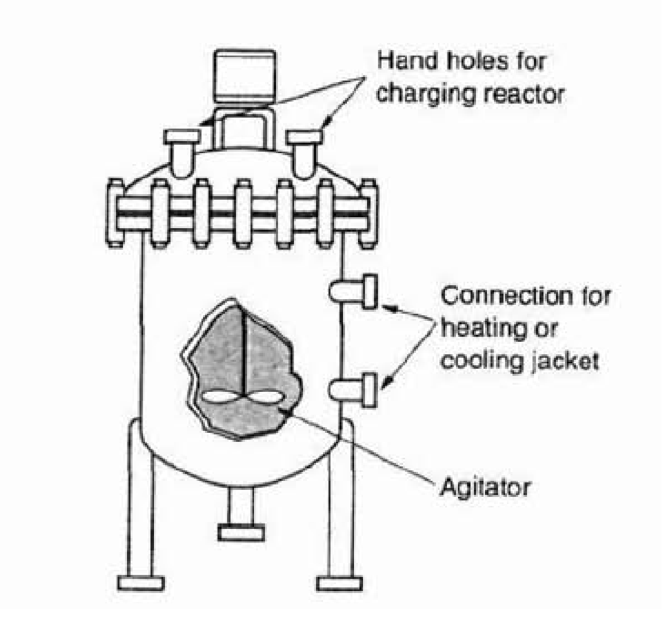


Figure 2.1: Simple batch homogeneous reactor

Table 2.1: Advantages and disadvantages of batch reactor

Advantages	disadvantages
High conversions can be obtained.	High cost of labor per unit of production.
Versatile, used to make many products.	Difficult to maintain large scale production.
Good for producing small amounts.	Long idle time (Charging & Discharging times) leads to periods of no production.
Easy to Clean	No instrumentation – Poor product quality

2.1.2 Continuous- Flow Reactors

Continuous flow reactors are almost always operated at steady state. We will consider three types, the continuous stirred tank reactor (CSTR), the plug flow reactor (PFR), and the packed bed reactor (PBR).

2.1.2.1 Continuous-Stirred Tank Reactor (CSTR)

A type of reactor used commonly in industrial processing is the stirred tank operated continuously (Figure 2.2). It is referred to as the continuous-stirred tank reactor (CSTR), or back mix reactor; and is used primarily for liquid phase reactions. It is normally operated at steady state and is assumed to be perfectly mixed. Consequently, there is no time dependence or position dependence of the temperature, the concentration, or the reaction rate inside the CSTR. That is, every variable is the same at every point inside the reactor. Because the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. Thus the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor.

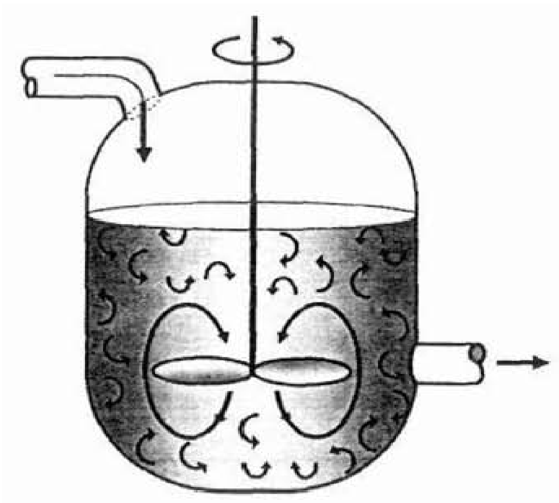


Figure 2.2: Continuous-Stirred Tank Reactor (CSTR)

The Continuous-Stirred Tank Reactor (CSTR) has advantages and the disadvantages as shown in Table 2.2.

Table 2.2: Advantages and disadvantages of CSTR

Advantages	disadvantages
Can be operated at temperatures between 20 and 450°F and at pressures up to 100 psi.	The conversion of reactant per volume of reactor is the smallest of the flow reactors. Consequently, very large reactors are necessary to obtain high conversions.
Can either be used by itself or as part of a series or battery of CSTRs	
Is relatively easy to maintain good temperature control since it is well mixed.	

2.1.2.2 Tubular Reactor

The tubular reactor (i.e. plug-flow reactor [PFR]), consists of a cylindrical pipe and is normally operated at steady state, as is the CSTR. Tubular reactors are used most often for gas-phase reactions. In the tubular reactor, the reactants are continually consumed as they flow down the length of the reactor. In modeling the tubular reactor, we assume that the concentration varies continuously in the axial direction through the reactor. Consequently, the reaction rate, which is a function of concentration for all but zero-order reactions, will also vary axially. For the purposes of the material presented here, we consider systems in which the flow field may be modeled by that of a plug flow profile (e g. uniform velocity as in turbulent flow), as shown in (Figure 2.3). That is there is no radial variation in the reaction rate and the reactor is referred to as a plug-flow reactor (PFR).

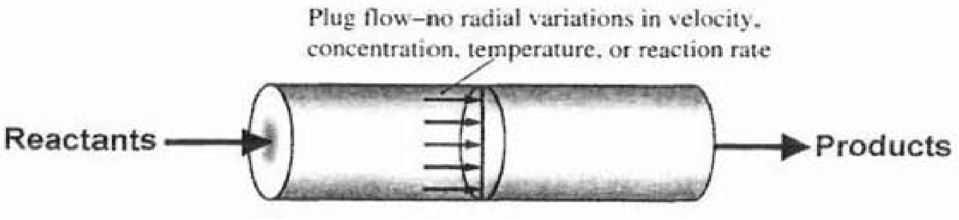


Figure 2.3: Plug-flow tubular reactor (PFR)

The tubular reactor (i.e. plug-flow reactor [PFR]), has advantages and disadvantages as showing in Table 2.3.

Table 2.3: Advantages and disadvantages of PFR

Advantages	disadvantages
Is relatively easy to maintain (no moving part)	It is difficult to control the temperature within the reactor. Furthermore hot spots can occur when the reaction is exothermic.
It usually produces the highest conversion per reactor volume of any of the flow reactors	

2.1.2.3 Packed-Bed Reactor

The principal difference between reactor design calculations involving homogeneous reactions and those involving fluid-solid heterogeneous reactions is that for the latter, the reaction takes place on the surface of the catalyst. Consequently, the reaction rate is based on mass of solid catalyst W, rather than on reactor volume V.

In the three idealized types of reactors just discussed (batch reactor, PFR, CSTR), the design equations (i.e... mole balances) were developed based on reactor volume. The derivation of the design equation for a packed-bed catalytic reactor (PBR) will be carried out in a manner analogous to the development of the tubular design equation, we simply replace the volume coordinate, with the catalyst weight coordinate W. shown in Figure 2.4.

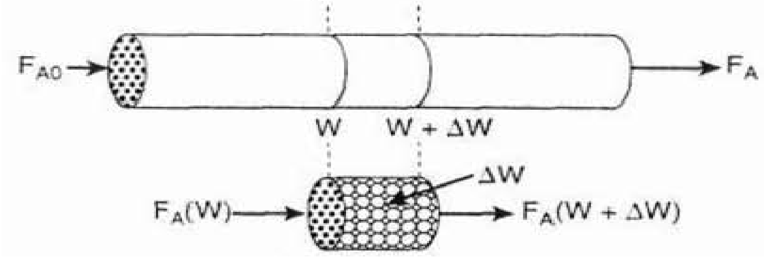


Figure 2.4: Packed-bed reactor (PBR)

2.2. The general mole balance equation

To perform a mole balance on any system, the system boundaries must first be specified. The volume enclosed by these boundaries is referred to as the system volume. We shall perform a mole balance on species j in a system volume, where species j represents the particular chemical species of interest, such as NaOH (Figure 2.5).

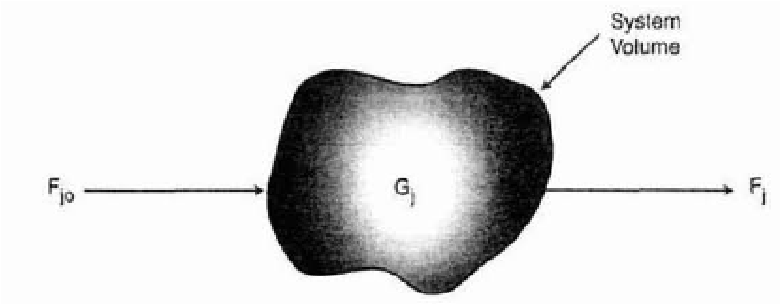


Figure 2.5: Balance in system volume

A mole balance on species j at any instant of time t, yields the following equation:

$$In - Out + Generation = Accumulation$$

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt} ----------------------------- Eq(2.1)$$

Where N_j represents the number of moles of species j in the system at time t, if all the system variables (e.g.. temperature. catalytic activity, concentration of the chemical species) are spatially uniform throughout the system volume, the rate of generation of species j , G_j is just the product of the reaction volume ,V. and the rate of formation of species j , r_j .

$$G_j = \int^{V} r_j.dv -------------------------------- Eq(2.2)$$

By its integral form Eq(2.2) to yield a form of the general mole balance equation Eq(2.1) for any chemical species j that is entering, leaving, reacting. and /or accumulating within any system volume V.

$$F_{j0} - F_j + \int^{V} r_j.dv = \frac{dN_j}{dt} -------------------------- Eq(2.3)$$

From this general mole balance equation we can develop the design equations for the various types of industrial reactors such as (Batch, PFR, and CSTR).

In a batch reactor has neither inflow nor outflow of reactants or products while the reaction is being carried out $F_{j0} = F_j = 0$ the resulting general mole balance on species j is:

$$\frac{dN_j}{dt} = \int^{V} r_j.dv ----------------------------- Eq(2.4)$$

If the reaction mixture is perfectly mixed so that there is no variation in the rate of reaction throughout the reactor volume. We can take r_j out of the integral, integrate and write the mole balance in the form.

$$\frac{dN_j}{dt} = r_j.V -------------------------------Eq(2.5)$$

2.3. Batch reactor design equation

In most batch reactors, the longer a reactant stays in the reactor, the more the reactant is converted to product until either equilibrium is reached or the reactant is exhausted. Consequently, in batch systems the conversion X is a function of the time the reactants spend in the reactor. If N_{A0} is the number of moles of A initially in the reactor. then the total number of moles of A that have reacted after a time t is $[N_{A0} \cdot X]$

$$[\text{Moles of A reacted (consumed)}] = [\text{Moles of A fed}].[\frac{\text{Moles of A reacted}}{\text{Moles of A fed}}]$$

$$[\text{mole of A reacted (consumed)}] = [N_{A0}].[X] ------- Eq(2.6)$$

Now, the number of moles of A that remain in the reactor after a time t, N_A can be expressed in terms of N_{A0} and X:

$$N_A = N_{A0} - N_{A0} \cdot X$$

The number of moles of A in the reactor after a conversion X has been achieved is :

$$N_A = N_{A0} - N_{A0} \cdot X = N_{A0}(1 - X) ------------Eq(2.7)$$

When no spatial variations in reaction rate exist, the mole balance on species A for a batch system is given by Eq(2.5):

$$\frac{dN_A}{dt} = r_A.V ----------------------------Eq(2.8)$$

This equation is valid whether or not the reactor volume is constant . In the general reaction. Reactant A is disappearing: therefore, we multiply both sides of Equation (2.8) by -1 to obtain the mole balance for the hatch reactor in the form:

$$-\frac{dN_A}{dt} = -r_A.V ----------------------------Eq(2.9)$$

For batch reactors, we are interested in determining how long to leave the

reactants in the reactor to achieve a certain conversion *X*. To determine this length of time, we write the mole balance Eq(2.8) in terms of conversion by differentiating Equation (2.7) with respect to time, remembering that N_{A0} is the number of moles of A initially present and is therefore a constant with respect to time.

$$\frac{dN_A}{dt} = 0 - N_{A0}\frac{dX}{dt}$$

Combining the above with Equation (2.8) yields

$$-N_{A0}\frac{dX}{dt} = r_A.V$$

For a batch reactor, the design equation in differential form is :

$$N_{A0}\frac{dX}{dt} = -r_A.V --------------------------Eq(2.10)$$

We call Equation (2.10) the differential form of the design equation for batch reactor because we have written the mole balance in terms of conversion ,the differential forms of the batch reactor mole balances Eq (2.5) and Eq(2.10) are often used in the interpretation of reaction rate data and for reactors with heat effects, respectively. Batch reactors are frequently used in industry for both gas-phase and liquid-phase reactions. Liquid-phase reactions are frequently carried out in batch reactors when small-scale production is desired or operating difficulties, rule out the use of continuous flow systems.

For a constant-volume batch reactor $V = V_0$ Equation (2.8) can be arranged into the form Eq(2.11) :

$$\frac{1}{V_0}\frac{dN_A}{dt} = \frac{d(N_A/V_0)}{dt} = \frac{dC_A}{dt} = r_A ---------------------- Eq(2.11)$$

As previously mentioned. the differential form of the mole balance, Equation (2.11). is used for analyzing rate data in a batch reactor .

2.4. The reaction order and the rate law

The Reaction Order and the Rate Law In the chemical reactions considered in the following paragraphs, we take as the basis of calculation a species A, which is one of the reactants that is disappearing as a result of the reaction. The limiting reactant is usually chosen as our basis for calculation. The rate of disappearance of A $-r_A$ depends on temperature and composition. For many reactions it can be written as the product of a reaction, reaction rate constant k_A and a function of the concentrations of the various species involved in the reaction:

$$-r_A = [k_A(T)][fn(C_A, C_B, ...)] ------------- Eq(2.12)$$

The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or rate law**.** The specific rate of reaction (also called the rate constant k_A**,** like the reaction rate $-r_A$ always refers to a particular species in the reaction and normally should be subscripted with respect to that species.

2.4.1 Power law models

The dependence of the reaction rate . $-r_A$ on the concentrations of the species present. fn(C_j) is almost without exception determined by experimental observation. Although the functional dependence on concentration may be postulated from theory, experiments are necessary to confirm the proposed form. One of the most common general forms of this dependence is the power law model. Here the rate law 1s the product of concentrations of the individual reacting species. each of which is raised to a power. For example:

$$-r_A = k_A C_A^a C_B^b ---------------------- Eq(2.13)$$

The exponents of the concentrations in Equation (2.13) lead to the concept of reaction order. The order of a reaction refers to the powers to which the concentrations are raised in the kinetic rate law. In Equation (2.13), the reaction is a order with respect to reactant A. and b order with respect to reactant B. The overall order of the reaction, α

$$\alpha = a + b ---------------- Eq(2.14)$$

The units of $-r_A$ are always in terms of concentration per unit time while

the units of the specific reaction rate, k_A will vary with the order of the reaction.

2.4.2 The reaction rate constant

The reaction rate constant k is not truly a constant: it is merely independent of the concentrations of the species involved in the reaction. The quantity k is referred to as either the specific reaction rate or the rate constant. It is almost always strongly dependent on temperature. It depends on whether or not a catalyst is present, and in gas-phase reactions, it may be a function of total pressure. ln liquid systems it can also be a function of other parameters, such as ionic strength and choice of solvent. These other variables normally exhibit much Less effect on the specific reaction rate than temperature does with the exception of supercritical solvents, such as super critical water.

Consequently, for the purposes of the material presented here,it will be assumed that k_A, depends only on temperature. This assumption is valid in more laboratory and industrial reactions and seems to work quite well.

It was the great Swedish chemist Arrhenius who first suggested that the temperature dependence of the specific reaction rate, k_A, could be correlated by an equation of the type

$$k_A[T] = Ae^{\frac{-E}{RT}} ----------------------- Eq(2.15)$$

Where

A = frequency factor

E = activation energy. J/mol or cal/mol

R = gas constant = 8.3 14 J/mol .^{o}K = 1.987 cal/mol .^{o}K

T= absolute temperature, ^{o}K

Postulation of the Arrhenius equation, Equation (2.15), is determined experimentally calculation of the by carrying out the reaction at several different temperatures. After taking the natural logarithm of Equation (2.15) we obtain:

$$\ln k_A = \ln A - \frac{E}{R}(\frac{1}{T}) ----------------------- Eq(2.16)$$

and see that the activation energy can be found from a plot of $\ln k_A$ as a function of (1/T)

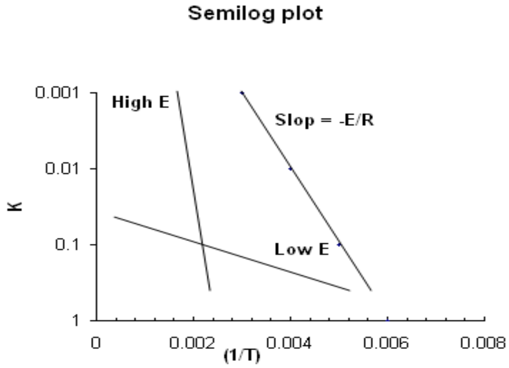


Figure 2.6: Calculation of the activation energy

One final comment on the Arrhenius equation ,Eq (2.15). It can be put in a most useful form by finding the specific reaction rate at a temperature T_o, that is:

$$k_A[T_o] = Ae^{\frac{-E}{RT_o}}$$

and at a temperature T

$$k_A[T] = Ae^{\frac{-E}{RT}}$$

and taking the ratio to obtain

$$k_A[T] = k_A[T_o]\ e^{\frac{E}{R}(\frac{1}{T_o}-\frac{1}{T})} -------------------- Eq(2.17)$$

This equation says that if we know the specific reaction rate $k_o(T_0)$ at a temperature T_0, and we know the activation energy, E. we can find the specific reaction rate $k(T)$ at any other temperature, T. for that reaction.

2.5. Examples of reaction rate laws

2.5.1. Zero Order Reaction:

- Rate low:

$$-r_A = -\frac{dC_A}{dt} = k$$

- Separate and integrate:

$$\int_{C_{A0}}^{C_A} -dC_A = \int_0^t k\ dt$$

$$C_{A0} - C_A = kt -------------------------------- Eq(2.18)$$

- Eq(2.18) in term of conversion :

  Where $C_A = C_{Ao}(1 - X_A)$

$$C_{A0}X_A = kt$$

- Plot Eq(2.18):

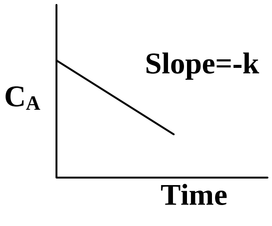


Figure 2.7: Zero Order Reaction

2.5.2. **First Order Reaction: A → Products**

- Rate low:

$$-r_A = -\frac{dC_A}{dt} = kC_A$$

- Separate and integrate:

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A} = \int_0^t k\ dt$$

$$\ln(C_{A0}/C_A) = kt \text{ ------------------------------- } Eq(2.19)$$

- Eq(2.19) in term of conversion :

  Where $C_A = C_{Ao}(1 - X_A)$, $-\ln(1 - X_A) = kt$

- Plot Eq(2.19):

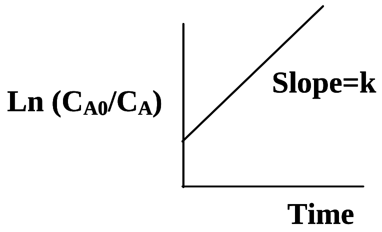


Figure 2.8: First Order Reaction

2.5.3. **Second Order Reaction:**

1. 2A→Product, A + B → Products $C_{A0} = C_{B0}$

- Rate low:

$$-r_A = -\frac{dC_A}{dt} = kC_A^2$$

- Separate and integrate :

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A^2} = \int_0^t k\ dt$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \text{ ----------------------------------- } Eq(2.20)$$

- Eq(2.20) in term of conversion :

Where $C_A = C_{Ao}(1 - X_A)$, $\frac{X_A}{1 - X_A} = kC_{A0}t$

- Plot Eq(2.20):

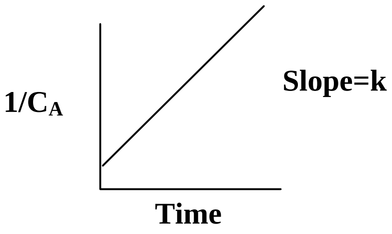


Figure 2.9: Second Order Reaction equal molar

2. A + B → Products $C_{A0} \neq C_{B0}$

- Rate low:

$$-r_A = -\frac{dC_A}{dt} = kC_AC_B$$

- Separate and integrate :

$$\ln\left(\frac{M - x_A}{1 - x_A}\right) = \ln\left(\frac{C_BC_{A0}}{C_{B0}C_A}\right) = (C_{B0} - C_{A0})kt - - - - - - - - - - - - - - - - - - - Eq(2.21)$$

Where $C_A = C_{Ao}(1 - X_A), M = \frac{C_{B0}}{C_{A0}}$

- Plot Eq(2.21):

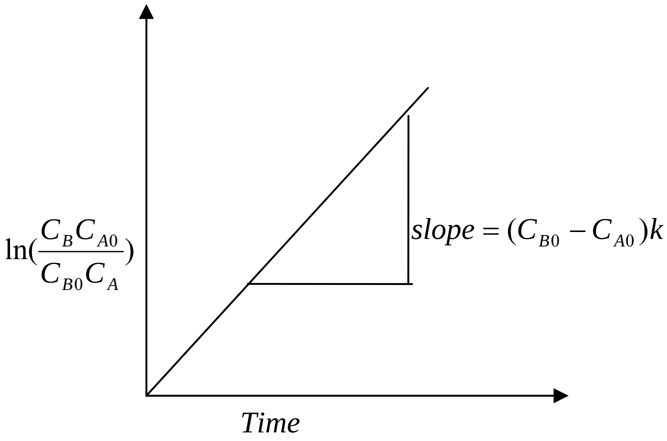


Figure 2.10: Second Order Reaction non equal molar

2.6. Collection and analysis of rate data

Assume that the rate law is of the form

$$-r_A = k_A C_A^{\alpha} --------- Eq(2.22)$$

Batch reactors are used primarily to determine rate law parameters for homogeneous reactions. This determination is usually achieved by measuring concentration as a function of time and then using either the differential, integral method of data analysis to determine the reaction order, α, and specific reaction rate constant, k_A.

However, by utilizing the method of excess, it is also possible to determine the relationship between $-r_A$ and the concentration of other reactant That is for the irreversible reaction below Equation :

$$A + B \rightarrow \text{Products}$$

With the rate law Eq(2.13)

$$-r_A = k_A C_A^a C_B^b ---------------------- Eq(2.13)$$

where a and b are both unknown, the reaction could first be run in an excess of B so that C_B remains essentially unchanged during the course of the reaction and :

$$-r_A = k_A C_A^a C_B^b = k_A C_B^b C_A^a = k' C_A^a ------------------ Eq(3.23)$$

Where

$$k' = k_A C_B^b \approx k_A C_{B0}^b --------------------------- Eq(3.24)$$

After determining a, the reaction is carried out in an excess of A, or equal molar to get overall reaction order .

$$-r_A = k C_A^a C_B^b = k'' C_A^{(a+b)} = k'' C_A^{\alpha}$$

Where , α overall reaction order.

2.6.1. Differential method of analysis

To outline the procedure used in the differential method of analysis. we consider a reaction carried out isothermally in a constant-volume batch reactor and the concentration recorded as a function of time. By combining (the mole balance with the rate low given by (Eq 2.22).

$$-\frac{dC_A}{dt} = k_A C_A^{\alpha} ---------- Eq(2.22)$$

After taking the natural logarithm of both sides of Equation (2.22)

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(k_A) + \alpha \ln(C_A) ---------- Eq(2.25)$$

Observe that the slope of a plot of $\ln\left(-\frac{dC_A}{dt}\right)$ as a function of $\ln(C_A)$ is the reaction order, α (Figure 2.8).

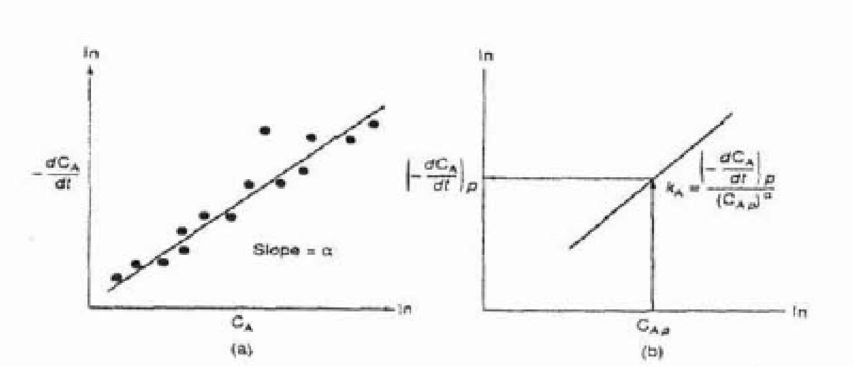


Figure 2.11: Differential method to determine reaction order

Figure 2.11 (a) shows a plot of [- (dC_A/dt)] versus [CA] on log-log paper (or use Excel to make the plot) where the slope is equal to the reaction order α .The specific reaction rate k_A can be found by first choosing a concentration in the plot , say C_{AP}, and then finding the corresponding value of [- (dC_A/dt)] as shown in Figure 2.8 (b). After raising C_{AP} to the α power, we divide it in to [- (dC_A/dt)] to determine k_A:

$$k_A = \frac{(-\frac{dC_A}{dt})_p}{(C_{Ap})^{\alpha}} ---------- Eq(2.26)$$

2.6.2. Methods for finding $-dC_A/dt$ from concentration time data

To obtain the derivative $-dC_A/dt$ used in this plot in fig(2.8), we must differentiate the concentration-time data either numerically or graphically. We describe two methods to determine the derivative from data giving the concentration as a function of time. These methods are:

2.6.2.1 Numerical method

Numerical differentiation formulas can be used when the data points in the independent variable are equally spaced . Such as $t_1 - t_0 = t_2 - t_1 = \Delta t$:

Time(sec)	**t_o**	**t_1**	**t_2**	**t_3**
Concentration (mol/lit)	**C_{A0}**	**C_{A1}**	**C_{A2}**	**C_{A3}**

The three-point differentiation formulas

Initial point:

$$\left[\frac{dC_A}{dt}\right]_{t=0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t} \quad ------------ Eq(2.27)$$

Interior points:

$$\left[\frac{dC_A}{dt}\right]_{t=i} = \frac{(C_{A(i+1)} - C_{A(i-1)})}{2\Delta t} --------------- Eq(2.28)$$

Last point:

$$\left[\frac{dC_A}{dt}\right]_{t=n} = \frac{-3C_{A(n-2)} + 4C_{A(n-1)} - C_{A(n)}}{2\Delta t} --------- Eq(2.29)$$

Can be used to calculate dC_A/dt . Equations (2.27) and (2.29) are used for the first and last data points, respectively, while Equation (2.28) is used for all intermediate data points.

2.6.2.2 Polynomial fit

Another technique to differentiate the data is to fit the concentration time data to an *n*th-order polynomial:

$$C_A = a_0 + a_1.t + a_2.t^2 + a_3.t^3 + \ldots\ldots \quad ------------ \quad Eq(2.30)$$

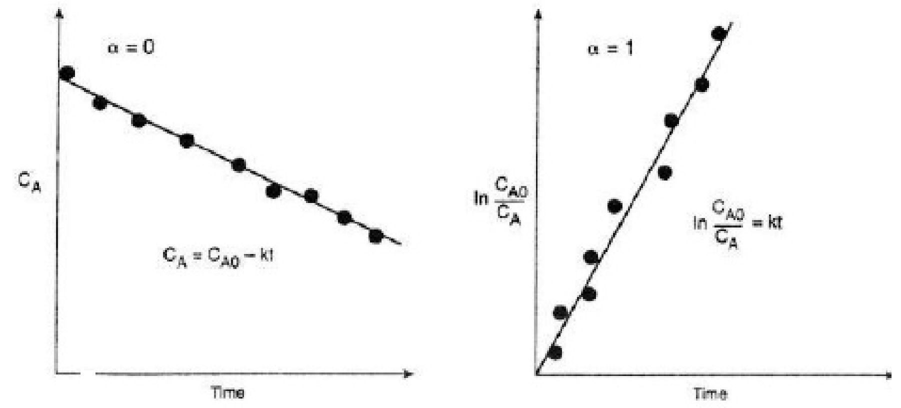
$$\frac{dC_A}{dt} = a_1 + 2a_2.t + 3a_3.t^2 + \ldots\ldots. \quad ------------- \quad Eq(2.31)$$

Many personal computer software packages contain programs that will calculate the best values for the constants a_i. One has only to enter the concentration time data and choose the order of the polynomial. After determining the constants a_i, one has only to differentiate Eq(2.30) to get Eq(2.31) .

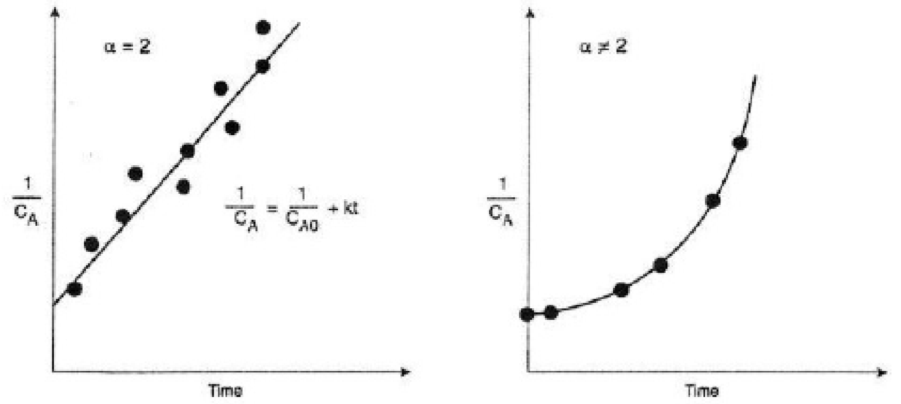
2.6.3 Integral method of analysis

To determine the reaction order by the integral method, we guess the reaction order and integrate the differential equation used to model the batch system. If the order we assume is correct, the appropriate plot (determined from this integration) of the concentration-time data should be linear. The integral method is used most often when the reaction order is known and it is desired to evaluate specific reaction rate constants at different temperatures to determine order and the activation energy.

In the integral method of analysis of rate data, we are looking for the appropriate function of concentration corresponding to a particular rate law that is linear with time. You should be thoroughly familiar with the methods of obtaining these linear plots for reactions of zero. first, and second order. For the reaction:



Zero-order reaction. First-order reaction.



Second-order reaction. Plot of reciprocal concentration as a function of time.

Figure 2.12: Integral method (the necessary graph for order guessed)

2.6.4 Comparison between differential and integral methods

By comparing the methods of analysis of the rate data (Table 2.2) .we note that the differential method tends to accentuate the uncertainties in the data, while the integral method tends to smooth the data ,there by disguising the uncertainties in it. In most analyses, it is imperative that the engineer know the limits and uncertainties in the data. This prior knowledge is necessary to provide for a safety factor when scaling up a process from laboratory experiments to design either a pilot plant or full-scale industrial plant. [1]

Table 2.4: Comparison between differential and integral methods. [2]

Integral Method	Differential Method
• Easy to use and is recommended for testing specific mechanism • Require small amount of data • Involves trial and error • Cannot be used for fractional orders • Very accurate	• Useful in complicated cases • Require large and more accurate data • No trial and error • Can be used for fractional orders • Less accurate

2.7. Saponification: A Case Study.

Rate of reaction was found to be first order with respect to each reactants rate of reaction second order overall with rate 0.112 L/mole-sec at 25°C and the activation energy was 11.56 kcal/mol (48390.16 J/mol). Rate constant versus Temperatures in literature Appendix C.[3]

CHAPTER THREE

EQUIPMENT, MATERIALS & METHODS

3.1. Introduction

To run saponification reaction we need to equipment, materials like chemical, methods to collect and analyze data.

3.2. Equipment

1. Repaired batch reactor at unit operations lab

The batch reactor was repaired to the model shown in (Figure 3.1). Firstly, it was contained on parts (electrical heater, Motor, reactor vessel, Impeller). Impeller was repaired by taking apart it and lubricate it, thereafter, the maintenance of the reactor includes change of bearing and pushes the modification was made on the motion transmission from the electric motor to the agitator and on the temperature control system where digital thermometer was used , medical injection was withdraw the samples from reactor.

Two methods were tried for the temperature control, the first method used an electric heater plus a cooling jacket around the reactor but it failed to precisely control the temperature according to procedure below:

One of reactants was placed in reactor vessel , the electrical heater was opened to heat reactant temperature till reached to above required temperature about + 0.5^0C the electrical heater was closed the valve of cold water was opened to decrease its temperature till reached below required temperature about -0.5^0C the valve was closed and opened the electrical heater again . We Observed in this method the temperature of reactant was not constant because the reactor put on heater and the heater it gave heat after we closed it (the temperature of resource was not constant).The second method used consists of water bath of controlled temperature where the reactants are heated to the required temperature before they were fed to the reactor which was also heated to the same temperature using the water jacket , this method was successful to control the temperature according to procedure below:

One of reactants was placed in reactor vessel ,the switch of thermostat water bath was set at constant temperature let us say (30^0C) the valve of hot water was opened to heat the reactant its temperature was increased slowly after 20 min the temperature of reactant was reached to above required temperature (30^0C) of thermostat bath about 1.2^0C at last the temperature of reactant was constant at the ($31.2\ ^0$C), we observed in this method the temperature of reactor if the switch was set at an another values in the thermostat bath (35^0C, 45^0C) the constant temperature of reactor according to this the values (37.7^0C, 45.5^0C) respectively in this case get good results at constant temperatures for reactor(31.2^0C, 37.7^0C and 45.5^0C).

Figure 3.1: water bath of controlled temperature for the batch reactor

2. Other equipments used include
    1. Stopwatch.
    2. Volumetric flasks.
    3. Graduated cylinders.
    4. Pipits.
    5. 50 mL Buret.
    6. 250 mL E-flasks.
    7. scale

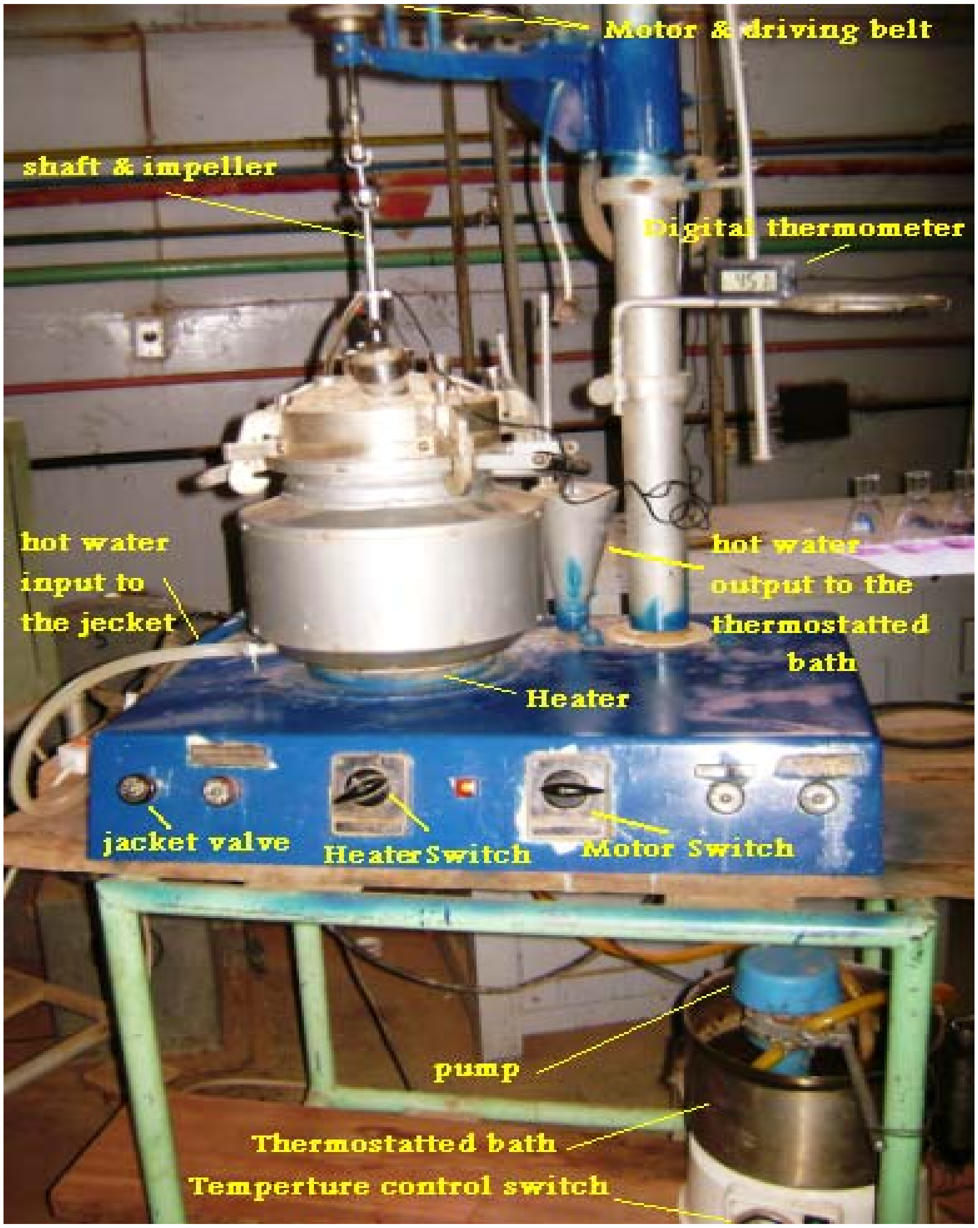


Figure 3.1: Batch reactor with water around it from thermostat bath

3.3. Materials

3.3.1. Chemicals

1. Phenolphthalein

Use as indicator is added to the acid in the E-flask . Causes the solutions to change color when the acid is neutralized.

2. Hydrochloric Acid (HCl)

Properties: Liquid, Concentration 32 %, M.W 36.46,Wt.per ml at $20\ ^0C$ equal 1.189 g/ml

3. Sodium Hydroxide (NaOH)

Properties: Solid Pellets, M.W 40.00

4. Ethyl Acetate($CH_3COOC_2H_5$)

Properties: liquid, Concentration 99 %, M.W 88.11, Wt.per ml at 20 ^{0}C equal 0.902 g/ml

5. Distillated Water

Distillated water was Prepared in unit operation lab.

3.3.2. Prepare solution of the reactants

The reactants were prepared through the following procedure:

1. If the solution of reactants was prepared from solid material like Sodium Hydroxide .

   For example when preparing solution of 0.1 M NaOH /litter

$$\text{The weight taken from the bottle} = \text{Morality} \times \text{M.W} = 0.1 \times 40 = 4\,g \ ------Eq(3.1)$$

4 g is discharged to 1000 ml volumetric flask and complete the flask by distillate water to its volume.

2. If the solution of reactants was prepared from liquid material like Hydrochloric Acid , Ethyl Acetate.

For example when preparing solution of 0.1 M HCl/litter

$$\text{The morality of the bottle} = \frac{\text{concentration \%} \times \text{specific gravity} \times 1000}{\text{Molecular weight} \times 100}$$

$$= \frac{32 \times 1.189 \times 1000}{36.46 \times 100} = 10.44 \ mol/\text{ml} - - - - - - - - - \text{Eq(3.2)}$$

$$10.44 \text{mol/ml} \times \text{volume from bottle} = 0.1 \times 1000 \rightarrow \text{volume from bottle} = 9.58 \text{ml}$$

Withdraw 9.58 ml and discharged in to 1000 ml volumetric flask and complete it by distillate water to its volume.

3.4. Methods

The batch reactor had been modified to the model shown in Fig(3.1),As result, it was operated at constant temperatures (31.2 ^{0}C , 37.7 ^{0}C and 45.5 ^{0}C). It was used to get kinetic data for the liquid phase saponification reaction of caustic soda with ethyl acetate.

3.4.1 The Algorithm for kinetic evaluation of Saponification Reaction.

1. Stoichiomettic equation

$$NaOH + CH3COOC2H5 \rightarrow CH3COONa + C2H5OH$$

$$aA + bB \rightarrow rR + sS$$

2. Postulate rate law

Power law models for Homogeneous reaction $-r_A = kC_A^a C_B^b - - - Eq(3.3)$

3. Select reactor type and corresponding mole balance

Batch reactor $-\frac{dC_A}{dt} = -r_A \ - - - - - - - - - - - - - - - - - - Eq(3.4)$

4. Process your data in terms of measured variables

In this case C_A $vs\ to\ time$

5. Look for simplification

Consider $-r_A = k_A C_A^a C_B^b - - - Eq(3.3)$

Where a and b and k_A are unknown factors.

6. Run the saponification experiments as follows:

1. Isothermal operation

Run the experiment at constant temperature to fix k_A as described in groups of Experiments (A & B) and thus determine the coefficient a and b respectively .

2. Non isothermal operation

Run the experiment at different temperatures (Experiment C) to see the affect of temperature on reaction constant k_A thus calculate activation energy of reaction , frequency factor Eq(2.15) .

3.4.2 General consideration for saponification Experiments

The experiments should include the following investigations.

1. For all batch experiments use equal volumes of each reactant to give a 1000mL (1 litter) total reaction mixture volume at the start of the experiment (time = 0.0).
2. The reactants should be as close to the same temperature as possible before starting the experiment. This can be done by placing one reactant in the reaction vessel (Batch reactor) and the other reactant in the constant temperature bath and letting them reach the same temperature before mixing them together .[4]

3.4.3 Analysis procedure for saponification experiments

In order to monitor the rate of the reaction in these experiments, it is necessary to determine the amount of un-reacted NaOH at appropriate time intervals. The reaction mixture can be monitored by using a titration method.[5]

3.4.4 Titration Method

A small sample is collected from the reaction vessel and quenched (reaction terminated) in a known volume and concentration of HCl. The excess HCl is titrated with NaOH. From this titration the amount of un-reacted NaOH can be determined and used in the determination of kinetic data. 10 mL burette is use to titrate the samples.

The steps needed to accomplish this are listed below:

1. Prepare HCl use in the experiments , 0.05M HCl was prepared .
2. 10 mL of the 0.05 M HCl is draw back to each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiments begins and add the indicator.
3. Concentration of NaOH in titration (in burette) is determined using the 0.05 M HCl was prepare above (a minimum of three titrations) , firstly prepare 0.05M NaOH , secondly titrate with 0.05 M HCl above to correct concentration of NaOH prepared may be less or more than its prepared value 0.05 M NaOH .
4. Samples should be collected from the reactor vessel using a 10 mL transfer pipette or medical injection at appropriate time intervals to monitor the rate of reaction. At the start of the reaction samples should be collected at short time intervals. No more than 6 or 7 samples should be collected during the run because 6 or 7 points construct the necessary graph .The 10 mL sample should be discharged into the 250 mL E-flask containing 10 mL of HCl and indicator. The time of collection shall be taken when one-half of the sample has been discharged from the pipette or the medical injection in to the E-flask .
5. The sample is titrated with the calculated base in (3) and the volume recorded. [5]

Figure 3.2: Withdrew the sample by medical injection, acid with an indicator in E-flask and the titration unit

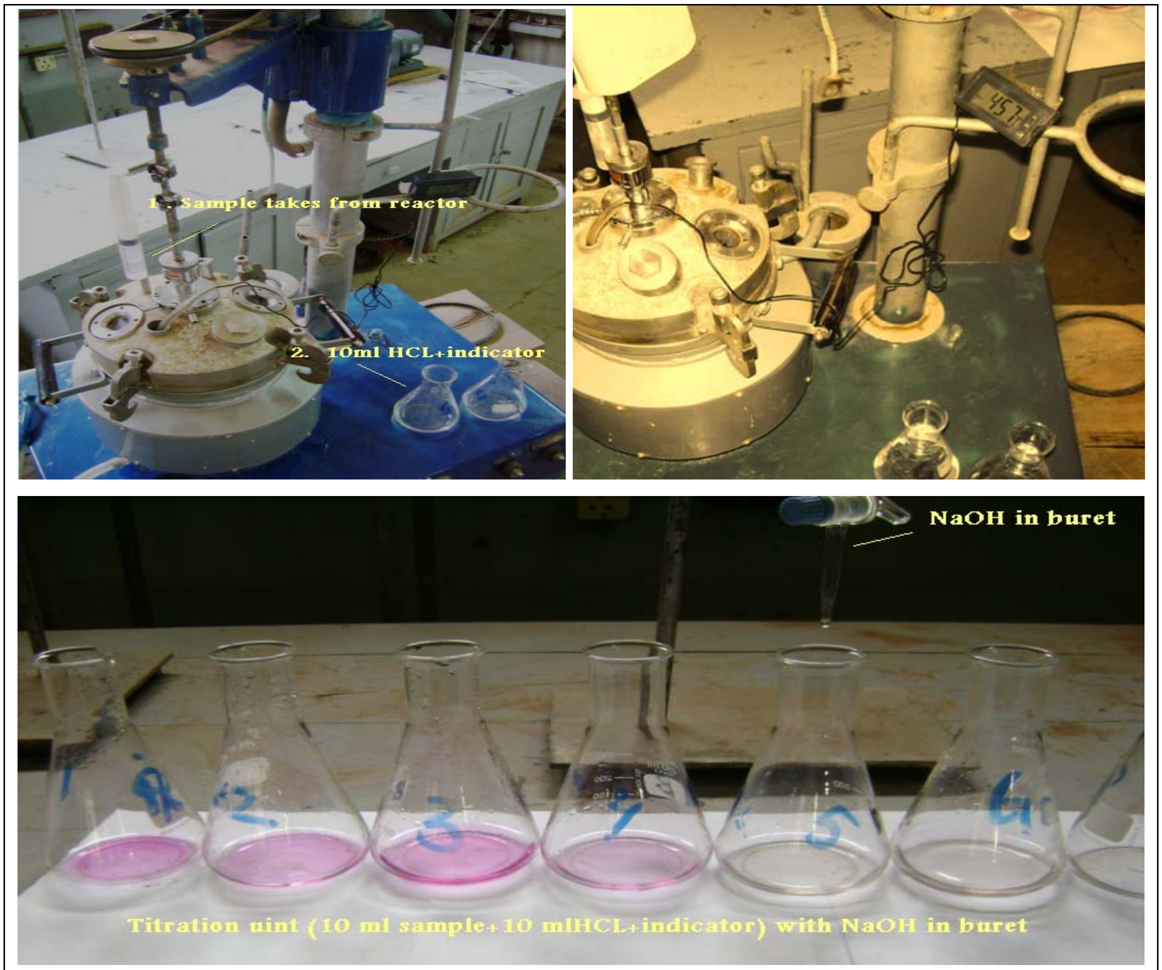


Figure 3.2: Withdraw the sample by medical injection, acid with an indicator in E-flask and the titration unit

3.4.5 Experiment A: Determination of concentration dependency factor for caustic soda

Consider $-r_A = k_A C_A^a C_B^b = k_A C_{NaOH}^a C_{Ethyl\ Acetate}^b --- Eq(3.3)$

Experiment A Concept

1. Using the Method of Excess to determine the order with respect to one of the reactants. (Three times the concentration) is sufficient in this experiment. A reaction of this type may be called a pseudo-first order reaction.
2. Perform the experiment with $C_{B0} >> C_{A0}$ so that C_B remain essentially unchanged during the reaction and measure C_A as a function of time.
3. From the experiment get the volume of NaOH used in the titration.
4. Calculate the concentration (in mol/lit) of unreacted NaOH in each sample withdrawn from the reactor, the following equation may be used

$$C_A = C_{NaOH} = \frac{V_{acid} \times M_{acid} - V_{tit} \times M_{base}}{V_{sample}} (mol/litter) --------- Eq(3.5)$$

Where:

$C_A = C_{NaOH}$ = concentration (in mol/lit) of unreacted NaOH in each sample withdrawn from the reactor.

V_{acid}, M_{acid} = volume and molarity of the HCl is pipettd into each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiment begins (Standard solution) .

M_{basic} = concentration of NaOH in titration is determined using the HCl Standard solution (a minimum of three titrations).

V_{sample} = Volume of sample.

Table 3.1: Experiment A Concept Concentration of unreacted NaOH

Time , second	t_0	t_1	t_2	t_3	t_4	t_n
Concentration of C_{NaOH} (mol/lit)	C_{A0}	C_{A1}	C_{A2}	C_{A3}	C_{A4}	C_{An}

5. Using differential method to evaluate $k'\ and\ a$ because one might get

   a fractional order.

$$-r_A = k_A C_A^a C_B^b = k_A C_B^b C_A^a = k' C_A^a ------------ Eq(3.6)$$
$$k' = k_A C_B^b \approx k_A C_{B0}^b --------------------- Eq(3.7)$$
$$\ln(-r_A) = \ln(k') + a\ln(C_A) ----------------- Eq(3.8)$$

6. Used method of finite difference to calculate $(-r_A)$ or $(\frac{-dC_A}{dt})$

   (2.6.2 , Eqs(2.27 to 2.29))

7. Use Excel program to Plot log-log graph for $(-r_A)$ vs C_A

   and Trend (Line, power) to get $k'\ and\ a$

Experiment A Procedure (Three Batches) :

Isothermal operation at $37.7\ ^0C$

Procedure:

1. 0.05 M HCl was prepared and used in the experiment (Standard acid solution) ,10 mL of it is pipetted into each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiment began .
2. Concentration of NaOH in titration (in burette) is determined using the 0.05 M HCl was prepared above (a minimum of three titrations) , firstly prepare 0.05M NaOH , secondly titrate it with 0.05 M HCl above to correct concentration of NaOH prepared may be less or more than its prepared value 0.05 M NaOH in Table(3.2) .

$$V_{acid} \times M_{acid} = V_{base} \times M_{basic} --------------------- Eq(3.9)$$

Table 3.2: Experiment A acid base titration

NO(titrations)	**Standard acid solution**		**Measured base solution**		
	V_{acid} **(ml)**	M_{acid} **(mol/lit)**	V_{base} **(ml)**	M_{base} **(mol/lit)**	**Average** M_{base} **(mol/lit)**
1	10	0.05	10.35	0.048309	0.048544
2	10	0.05	10.30	0.048544	
3	10	0.05	10.25	0.048780	

3. In the reactor, mix 0.5 liter of the 0.1M caustic soda solution with 0.5 liter of the 0.3M ethyl acetate solution at an arbitrary time (t = 0) at $37.7\ ^{0}C$ switch on the stirrer immediately and set it to an intermediate speed to avoid splashing.
4. Start the timer as soon as you start mixing the reactants.
5. After a certain time interval, use a medical injection to withdraw 10ml sample from the reactor, and immediately quench it with 10ml of excess 0.05M hydrochloric acid (You should have the quenching acid sample ready before taking the sample from the reactor) .
6. Add 2 - 3 drops of phenolphthalein to the quenched sample and back titrate with 0.048544 M NaOH solution until the end point is detected (in this case a stable pink color) .
7. Record the amount of NaOH used in the titration (V titration.).
8. Repeat steps (5) - (7) every 1 minute for the samples. Take a total of 6-7samples making sure that you record the time for each new sample.
9. Calculate experiment A batch (I) volume of NaOH used in the titration, the results are shown in (Table 3.3).

Table 3.3: Experiment A batch (I) volume of NaOH used in the titration

Sample	Time (s)	Initial Burette reading (ml)	Final Burette Reading(ml)	Volume NaOH used in Titration[Final-Initial](ml)
0	0	0	0	0
1	60	10.3	19.25	8.95
2	120	19.25	29.1	9.85
3	180	29.1	39.15	10.05
4	240	39.15	49.30	10.15
5	300	0	10.2	10.2
6	360	10.2	20.45	10.25

10. Calculate the concentration (in mol/lit) of un reacted NaOH in each sample withdrawn from the reactor in (Table 3.3) by use Eq (3.5) , The results are shown in (Table 3.4)

$$C_{NaOH} = \frac{V_{acid} \times M_{acid} - V_{tit} \times M_{base}}{V_{sample}} = \frac{10 \times 0.05 - V_{tit} \times 0.048544}{10}$$

$$[C_{NaOH}]_{t=0} = \frac{10 \times 0.05 - 0 \times 0.048544}{10} = 0.1$$

$$[C_{NaOH}]_{t=60} = \frac{10 \times 0.05 - 8.95 \times 0.048544}{10} = 0.0065531$$

$$[C_{NaOH}]_{t=120} = \frac{10 \times 0.05 - 9.85 \times 0.048544}{10} = 0.0021842$$

$$[C_{NaOH}]_{t=180} = \frac{10 \times 0.05 - 10.05 \times 0.048544}{10} = 0.0012133$$

$$[C_{NaOH}]_{t=240} = \frac{10 \times 0.05 - 10.15 \times 0.048544}{10} = 0.0007278$$

$$[C_{NaOH}]_{t=300} = \frac{10 \times 0.05 - 10.2 \times 0.048544}{10} = 0.0004851$$

$$[C_{NaOH}]_{t=360} = \frac{10 \times 0.05 - 10.25 \times 0.048544}{10} = 0.0002424$$

Add column un reacted NaOH to the (Table 3.3) :

Table 3.4: Experiment A batch (I) Concentration of unreacted NaOH

Sample #	Time (s)	Volume NaOH used in titration (ml)	Un reacted NaOH(mol/lit)
0	0	0	0.1
1	60	7.95	0.00655312
2	120	9.85	0.00218416
3	180	10.05	0.00121328
4	240	10.15	0.00072784
5	300	10.2	0.00048512
6	360	10.25	0.00024240

11. Use the Numerical Methods (finite difference) to calculate $(-r_A)$ or $(\frac{-dC_A}{dt})$.(2.6.2 , Eqs 2.27 to 2.29) ,The results are shown in(Table 3.5)

Initial point:

$$-\left[\frac{dC_A}{dt}\right]_{t=0} = -\frac{-3C_{A0} + 4C_{A60} - C_{A120}}{2\Delta t} = -\frac{-3 \times 0.1 + 4 \times 0.00655312 - 0.00218416}{2 \times 60}$$

$$= 0.0022998$$

Interior points:

$$-\left[\frac{dC_A}{dt}\right]_{t=60} = -\frac{C_{A120} - C_{A0}}{2\Delta t} = -\frac{(0.0021842 - 0.1000000)}{2 \times 60} = 0.0008151$$

$$-\left[\frac{dC_A}{dt}\right]_{t=120} = -\frac{C_{A180} - C_{A60}}{2\Delta t} = -\frac{(0.0012133 - 0.0065531)}{2 \times 60} = 0.0000445$$

$$-\left[\frac{dC_A}{dt}\right]_{t=180} = -\frac{C_{A240} - C_{A120}}{2\Delta t} = -\frac{(0.0007278 - 0.0021842)}{2 \times 60} = 0.0000121$$

$$-\left[\frac{dC_A}{dt}\right]_{t=240} = -\frac{C_{A300} - C_{A180}}{2\Delta t} = -\frac{(0.0004851 - 0.0012133)}{2 \times 60} = 0.0000061$$

$$-\left[\frac{dC_A}{dt}\right]_{t=300} = -\frac{C_{A360} - C_{A240}}{2\Delta t} = -\frac{(0.0002424 - 0.0007278)}{2 \times 60} = 0.0000040$$

Last point:

$$-\left[\frac{dC_A}{dt}\right]_{t=360} = -\frac{-3C_{A240}+4C_{A300}-C_{A360}}{2\Delta t} = -\frac{-3\times 0.0007278+4\times 0.0004851-0.0002424}{2\times 60}$$

$$= 0.0000040$$

Add column of the rate of reaction NaOH to the (Table 3.4) .

Table 3.5: Experiment A batch (I) rate of reaction of NaOH

time (s)	**V titration**	C_A	$-r_A\ or -dC_A/dt$
0	0	0.1000000	0.0022998
60	8.95	0.0065531	0.0008151
120	9.85	0.0021842	0.0000445
180	10.05	0.0012133	0.0000121
240	10.15	0.0007278	0.0000061
300	10.2	0.0004851	0.0000040
360	10.25	0.0002424	0.0000040

12. Experiment A the three batches had been calculated, the results are showing in (Table 3.6).

Table 3.6: Experiment A the three batches (t,vtit,Con,rate) of NaOH

Time (sec)	**Batch I**			**Batch II**			**Batch III**		
	V(tit)	C_A	$-r_A$	**V(tit)**	C_A	$-r_A$	**V(tit)**	C_A	$-r_A$
0	0	0.1000000	0.0022998	0	0.1	0.002278	0	0.10000000	0.002275
60	8.95	0.0065531	0.0008151	8.8	0.00728128	0.000813	8.75	0.00752400	0.000807
120	9.85	0.0021842	0.0000445	9.8	0.00242688	0.000097	9.65	0.00315504	0.000109
180	10.05	0.0012133	0.0000121	10	0.00145600	0.000028	10.1	0.00097056	0.000040
240	10.15	0.0007278	0.0000061	10.15	0.00072784	0.000016	10.15	0.00072784	0.000008
300	10.2	0.0004851	0.0000040	10.2	0.00048512	0.000008	10.2	0.00048512	0.000008
360	10.25	0.0002424	0.0000040	10.25	0.0002424	0.000004045	10.25	0.00024	0.000004005

13. Use Excel program to Plot log-log graph between $(-r_A)$ vs C_A and Trend (power) to get $k'\ and\ a$: The results are shown in Figures (4.1 to 4.6)

3.4.6 Experiment B: Determination of concentration dependency factor for Ethyl Acetate.

Consider $-r_A = k_A C_A^a C_B^b = k_A C_{NaOH}^a C_{Ethyl\ Acetate}^b --- Eq(3.3)$

Experiment B Concept

1. To determine the reaction order overall. This can be done by running the experiment as a batch reactor with equal initial concentrations of both reactants. A minimum of three batch experiments should be run with equal concentrations of reactants, one at the same temperature of Experiment A.
2. Perform the experiment with $C_{A0} = C_{B0}$ and measure C_A as a function of time.
3. From the experiment get the volume of NaOH used in the titration .
4. Calculate the concentration (in mol/lit) of unreacted NaOH in each sample withdrawn from the reactor, the following equation may be used

$$C_A = C_{NaOH} = \frac{V_{acid} \times M_{acid} - V_{tit} \times M_{base}}{V_{sample}} (mol / litter) --------- Eq(3.5)$$

Where:

$C_A = C_{NaOH}$ = concentration (in mol/lit) of unreacted NaOH in each sample withdrawn from the reactor.

V_{acid}, M_{acid} = volume and molarity of the HCl is pipettd into each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiment begins (Standard solution) .

M_{basic} = concentration of NaOH in titration is determined using the HCl Standard solution (a minimum of three titrations).

V_{sample} = Volume of sample.

Table 3.7: Experiment B Concept Concentration of unreacted NaOH

Time , second	t_0	t_1	t_2	t_3	t_4	t_n
Concentration of C_{NaOH} (mol/lit)	C_{A0}	C_{A1}	C_{A2}	C_{A3}	C_{A4}	C_{An}

5. Using differential method to evaluate $k'' \; and \; \alpha$ because one might get a fractional order.

$$-r_A = kC_A^a C_B^b = k''C_A^{(a+b)} = k''C_A^{\alpha} ------------------------ Eq(3.10)$$

$$\ln(-r_A) = \ln(k'') + \alpha \ln(C_A) ---------------------------Eq(3.11)$$

6. Use the Numerical Methods (finite difference) to calculate $(-r_A)$ or $(\frac{-dC_A}{dt})$ at points . (2.6.2 , Eqs 2.27 to 2.29)
7. Use Excel program to plot log-log graph for $(-r_A)$ vs C_A and Trend (Line, power) to get $k'' \; and \; \alpha$.
8. Evaluate $b = \alpha - a$ the order with respect to Ethyl acetate.

Experiment B Procedure (Three Batches):

Isothermal operation at $37.7\ ^0C$

Procedure:

1. 0.05 M HCl prepared and used in the experiment (Standard acid solution) ,10 mL of it is pipetted into each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiment began .
2. Concentration of NaOH in titration (in burette) is determined using the 0.05 M HCl was prepared above (a minimum of three titrations) , firstly prepare 0.05M NaOH , secondly titrate it with 0.05 M HCl above to correct concentration of NaOH prepared may be less or more than its prepared value 0.05 M NaOH in (Table3.8) .

$$V_{acid} \times M_{acid} = V_{base} \times M_{basic} ---------------------- Eq(3.9)$$

Table 3.8: Experiment B acid base titration

NO(titrations)	Standard acid solution		Measured base solution		
	V_{acid} (ml)	M_{acid} (mol/lit)	V_{base} (ml)	M_{base} (mol/lit)	Average M_{base} (mol/lit)
1	10	0.05	10.30	0.048544	0.048544
2	10	0.05	10.35	0.048309	
3	10	0.05	10.25	0.048780	

3. In the reactor, mix 0.5 liter of the 0.1M caustic soda solution with 0.5 liter of the 0.1M ethyl acetate solution at an arbitrary time (t = 0) at $37.7\ ^0C$. Switch on the stirrer immediately and set it to an intermediate speed to avoid splashing.
4. Start the timer as soon as you start mixing the reactants.
5. After a certain time interval, use a pipette or medical injection to withdraw 10ml sample from the reactor, and immediately quench it with 10ml of excess 0.05M hydrochloric acid (You should have the quenching acid sample ready before taking the sample from the reactor) .
6. Add 2 - 3 drops of phenolphthalein to the quenched sample and back titrate with 0.048544 M NaOH solution until the end point is detected (in this case a stable pink color) .
7. Record the amount of NaOH used in the titration (V titration.).
8. Repeat steps (5) - (7) every 2 minute for the samples. Take a total of 6-7samples making sure that you record the time for each new sample
9. Calculate experiment B batch (I) volume of NaOH used in the titration ,The results are shown in (Table 3.9)

Table 3.9: Experiment B batch (I) volume of NaOH used in the titration

Sample	Time (s)	Initial Burette reading (ml)	Final Burette Reading(ml)	Volume NaOH used in Titration [Final-Initial](ml)
0	0	0	0	0
1	120	0	5.9	5.9
2	240	5.7	13.7	7.8
3	360	13.7	21.7	8
4	480	21.7	30	8.3
5	600	30	38.5	8.5

10. Calculate the concentration (in mol/lit) of unreacted NaOH in each sample withdrawn from the reactor in Table (3.9) . by using Eq (3.5) , The results are shown in (Table 3.10).

$$C_{NaOH} = \frac{V_{acid} \times M_{acid} - V_{tit} \times M_{base}}{V_{sample}} = \frac{10 \times 0.05 - V_{tit} \times 0.048544}{10}$$

$$\left[C_{NaOH}\right]_{t=0} = \frac{10 \times 0.05 - 0 \times 0.048544}{10} = 0.1$$

$$\left[C_{NaOH}\right]_{t=120} = \frac{10 \times 0.05 - 5.9 \times 0.048544}{10} = 0.02135904$$

$$\left[C_{NaOH}\right]_{t=240} = \frac{10 \times 0.05 - 7.8 \times 0.048544}{10} = 0.01213568$$

$$\left[C_{NaOH}\right]_{t=360} = \frac{10 \times 0.05 - 8 \times 0.048544}{10} = 0.0111648$$

$$\left[C_{NaOH}\right]_{t=480} = \frac{10 \times 0.05 - 8.3 \times 0.048544}{10} = 0.00970848$$

$$\left[C_{NaOH}\right]_{t=600} = \frac{10 \times 0.05 - 8.5 \times 0.048544}{10} = 0.0087376$$

$$\left[C_{NaOH}\right]_{t=720} = \frac{10 \times 0.05 - 8.7 \times 0.048544}{10} = 0.00776672$$

Add column un reacted NaOH to the (Table 3.9):

Table 3.10: Experiment B batch (I) Concentration of unreacted NaOH

Sample #	**Time (s)**	**Volume NaOH used in titration (ml)**	**Un reacted NaOH(mol/lit)**
0	0	0	0.1
1	120	5.9	0.02135904
2	240	7.8	0.01213568
3	360	8	0.01116480
4	480	8.3	0.00970848
5	600	8.5	0.00873760
6	720	8.7	0.00776672

11. Use the Numerical Methods (finite difference) to calculate $(-r_A)$ or $(\frac{-dC_A}{dt})$. (2.6.2 , Eqs 2.27 to 2.29) , The results are shown in (Table 3.11)

Initial point:

$$-\left[\frac{dC_A}{dt}\right]_{t=0} = -\frac{-3C_{A0} + 4C_{A120} - C_{A240}}{2\Delta t} = -\frac{-3\times 0.1 + 4\times 0.02135904 - 0.01213568}{2\times 120}$$

$$= 0.0009446$$

Interior points:

$$-\left[\frac{dC_A}{dt}\right]_{t=120} = -\frac{C_{A240} - C_{A0}}{2\Delta t} = -\frac{(0.01213568 - 0.1000000)}{2\times 120} = 0.0003661$$

$$-\left[\frac{dC_A}{dt}\right]_{t=240} = -\frac{C_{A360} - C_{A120}}{2\Delta t} = -\frac{(0.0111648 - 0.02135904)}{2\times 120} = 0.0000425$$

$$-\left[\frac{dC_A}{dt}\right]_{t=360} = -\frac{C_{A480} - C_{A240}}{2\Delta t} = -\frac{(0.00970848 - 0.01213568)}{2\times 120} = 0.0000101$$

$$-\left[\frac{dC_A}{dt}\right]_{t=480} = -\frac{C_{A600} - C_{A360}}{2\Delta t} = -\frac{(0.0087376 - 0.0111648)}{2\times 120} = 0.0000101$$

$$-\left[\frac{dC_A}{dt}\right]_{t=600} = -\frac{C_{A720} - C_{A480}}{2\Delta t} = -\frac{(0.00776672 - 0.00970848)}{2\times 120} = 0.0000081$$

Last point:

$$-\left[\frac{dC_A}{dt}\right]_{t=720} = -\frac{-3C_{A480}+4C_{A600}-C_{A720}}{2\Delta t} = -\frac{-3\times 0.00970848+4\times 0.0087376-0.00776672}{2\times 60}$$

$$=0.0000081$$

Add column rate of NaOH to the (Table 3.10) .

Table 3.11: Experiment B batch (I) rate of reaction of NaOH

time (s)	**V titration**	C_A	$-r_A\ or - dC_A/dt$
0	0	0.10000000	0.0009446
120	5.9	0.02135904	0.0003661
240	7.8	0.01213568	0.0000425
360	8	0.01116480	0.0000101
480	8.3	0.00970848	0.0000101
600	8.5	0.00873760	0.0000081
720	8.7	0.00776672	0.0000081

12. Experiment B the three batches had been calculated ,the results are showing in (Table3.12):

Table 3.12: Experiment B the three batches (t,v_{tit},Con,rate) of NaOH

Time (sec)	**Batch I**			**Batch II**			**Batch III**		
	V(tit)	C_A	$-r_A$	**V(tit)**	C_A	$-r_A$	**V(tit)**	C_A	$-r_A$
0	0	0.1	0.0009446	0	0.1	0.00100728	0	0.1	0.000967
120	5.9	0.02135904	0.0003661	6.6	0.01796096	0.00036003	6.1	0.02038816	0.000360
240	7.8	0.01213568	0.0000425	7.5	0.01359200	0.00002427	7.5	0.01359200	0.000040
360	8	0.0111648	0.0000101	7.8	0.01213568	0.00001011	8.1	0.01067936	0.000016
480	8.3	0.00970848	0.0000101	8	0.01116480	0.00001011	8.3	0.00970848	0.000006
600	8.5	0.0087376	0.0000081	8.3	0.00970848	0.00001214	8.4	0.00922304	0.000007

13. Use Excel program to Plot log-log graph for $(-r_A)$ vs C_A and Trend (power) to get $k'\ and\ \alpha$: The results are shown in Figures (4.7 to 4.12)
14. Evaluate $b=\alpha-a$ the order with respect to Ethyl acetate.
15. Once a,b are determined k_A calculate See Experiment C

3.4.7 Experiment C: Determination of dependency factor for temperatures.

Experiment C Concept

1. After determined the overall reaction order in the Experiment B at run with equal initial concentrations of both reactants at constant temperature ,the value of $\alpha \cong 2$ this result the reaction is overall second order with respect to NaOH .

$$-r_A = \frac{-dC_A}{dt} = kC_A^a C_B^b = k''C_A^{(a+b)} = k''C_A^2 ----------------- Eq(3.12)$$

2. Integrate equation (3.12)

$$\frac{1}{C_A} = k''.t + \frac{1}{C_{A0}} ---------------------------------- Eq(3.13)$$

Eq (3.13) is linear and k'' the reaction constant .

3. Use Excel program to plot $\frac{1}{C_A}$ vs t and set the Trend Line to get k''

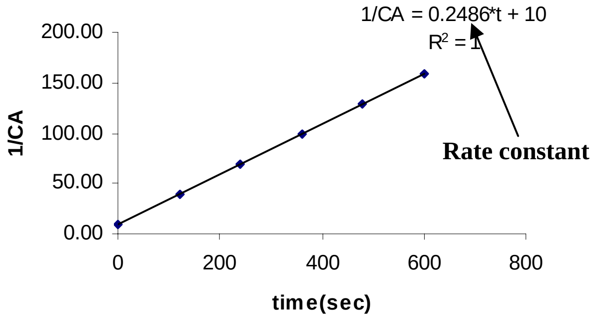


Figure 3.3: Experiment C Concept Excel program to Plot graph for $\frac{1}{C_A}$ vs t and Trend (Line) to get k''

4. The experiment was run at equal concentration at three different temperatures ($31.2\ ^0C$, $37.7\ ^0C$, $45.5\ ^0C$)

Experiment C: Procedure (Three Batches):

I. Isothermal Operation at $31.2\ ^0C$

Procedure:

1. 0.05 M HCl was prepared used in the experiment (Standard acid solution) ,10 mL of it is pipetted into each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiment began .
2. Concentration of NaOH in titration (in burette) is determined using the 0.05 M HCl was prepared above (a minimum of three titrations) , firstly prepare 0.05M NaOH , secondly titrate it with 0.05 M HCl above to correct concentration of NaOH prepared may be less or more than its prepared value 0.05 M NaOH in (Table3.13) .

$$V_{acid} \times M_{acid} = V_{base} \times M_{basic} ---------------------- Eq(3.9)$$

Table 3.13: Experiment C batch (I) acid base titration

NO(titrations)	**Standard acid solution**		**Measured base solution**		
	V_{acid} **(ml)**	M_{acid} **(mol/lit)**	V_{base} **(ml)**	M_{base} **(mol/lit)**	**Average** M_{base} **(mol/lit)**
1	10	0.05	10.30	0.048544	0.048544
2	10	0.05	10.35	0.048309	
3	10	0.05	10.25	0.048780	

3. In the reactor, mix 0.5 liter of the 0.1M caustic soda solution with 0.5 liter of the 0.1M ethyl acetate solution at an arbitrary time (t = 0) at $31.2\ ^0C$. Switch on the stirrer immediately and set it to an intermediate speed to avoid splashing.
4. Start the timer as soon as you start mixing the reactants.
5. After a certain time interval, use a pipette or medical injection to withdraw 10ml sample from the reactor, and immediately quench it with 10ml of excess 0.05M hydrochloric acid (You should have the quenching acid sample ready before taking the sample from the reactor) .

6. Add 2 - 3 drops of phenolphthalein to the quenched sample and back titrate with 0.048544 M NaOH solution until the end point is detected (in this case a stable pink color) .
7. Record the amount of NaOH used in the titration (V titration.).
8. Repeat steps (5) - (7) every 2 minute for the samples. Take a total of 6-7samples making sure that you record the time for each new sample.
9. Calculation Experiment C batch (I) at $31.2\ ^0C$. The results are shown in (Table 3.14)

Table 3.14: Experiment C batch (I) volume of NaOH used in the titration

Sample	**Time (s)**	**Initial Burette reading (ml)**	**Final Burette Reading(ml)**	**Volume NaOH used in Titration [Final-Initial](ml)**
0	0	0	0	0
1	120	0	5.1	5.1
2	240	5.1	12	6.9
3	360	12	19.5	7.5
4	480	19.5	27.6	8.1
5	600	27.6	36.3	8.7

10. Calculate the concentration (in mol/lit) of unreacted NaOH in each sample withdrawn from the reactor (Table 3.14) by using Eq (3.5) . The results are shown in (Table 3.15)

$$C_{NaOH} = \frac{V_{acid} \times M_{acid} - V_{tit} \times M_{base}}{V_{sample}} = \frac{10 \times 0.05 - V_{tit} \times 0.048544}{10}$$

$$[C_{NaOH}]_{t=0} = \frac{10 \times 0.05 - 0 \times 0.048544}{10} = 0.1$$

$$[C_{NaOH}]_{t=120} = \frac{10 \times 0.05 - 5.1 \times 0.048544}{10} = 0.02524256$$

$$[C_{NaOH}]_{t=240} = \frac{10 \times 0.05 - 6.9 \times 0.048544}{10} = 0.01650464$$

$$[C_{NaOH}]_{t=360} = \frac{10 \times 0.05 - 7.5 \times 0.048544}{10} = 0.013592$$

$$[C_{NaOH}]_{t=480} = \frac{10 \times 0.05 - 8.1 \times 0.048544}{10} = 0.01067936$$

$$[C_{NaOH}]_{t=600} = \frac{10 \times 0.05 - 8.7 \times 0.048544}{10} = 0.00776672$$

Add column un reacted NaOH to the (Table 3.14) :

Table 3.15: Experiment C batch (I) Concentration of unreacted NaOH

Sample #	Time (s)	Volume NaOH used in titration (ml)	Un reacted NaOH(mol/lit)
0	0	0	0.1
1	120	5.1	0.02524256
2	240	6.9	0.01650464
3	360	7.5	0.01359200
4	480	8.1	0.01067936
5	600	8.7	0.00776672

11. Add experimental concentration of NaOH and its inverse from (Table 3.15) and Actual concentration and its inverse from literature at the same time from Appendix B Eq(B.1), The results are shown in (Table 3.16)

Table 3.16: Experiment C batch (I) Concentration of NaOH and its inverse (Experimental, Actual)

time (s)	V titration	Exp(CA)	Exp(1/CA)	AC(CA)	AC(1/CA)
0	0	0.1	10.00	0.1000	10.00
120	5.1	0.02524256	39.62	0.0333	30.00
240	6.9	0.01650464	60.59	0.0200	50.01
360	7.5	0.013592	73.57	0.0143	70.01
480	8.1	0.01067936	93.64	0.0111	90.02
600	8.7	0.00776672	128.75	0.0091	110.02

12. Use Excel program to plot $\frac{1}{C_A}$ vs t and Trend(Line) to get rate constant. The results are shown in Figures (4.13 to 4.14)

II. Isothermal Operation at $37.7\ ^{0}C$

Procedure:

1. 0.05 M HCl was prepared used in the experiment (Standard acid solution) ,10 mL of it is pipetted into each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiment began .
2. Concentration of NaOH in titration (in burette) is determined using the 0.05 M HCl was prepared above (a minimum of three titrations) , firstly prepare 0.05M NaOH , secondly titrate it with 0.05 M HCl above to correct concentration of NaOH prepared may be less or more than its prepared value 0.05 M NaOH in (Table 3.17) .

$$V_{acid} \times M_{acid} = V_{base} \times M_{basic} ---------------------- Eq(3.9)$$

Table 3.17: Experiment C batch (II) acid base titration

NO(titrations)	**Standard acid solution**		**Measured base solution**		
	V_{acid} **(ml)**	M_{acid} **(mol/lit)**	V_{base} **(ml)**	M_{base} **(mol/lit)**	**Average** M_{base} **(mol/lit)**
1	10	0.05	10.30	0.048544	0.048544
2	10	0.05	10.35	0.048309	
3	10	0.05	10.25	0.048780	

3. In the reactor, mix 0.5 liter of the 0.1M caustic soda solution with 0.5 liter of the 0.1M ethyl acetate solution at an arbitrary time (t = 0) at $37.7\ ^{0}C$. Switch on the stirrer immediately and set it to an intermediate speed to avoid splashing.
4. Start the timer as soon as you start mixing the reactants.
5. After a certain time interval, use a pipette or medical injection to withdraw 10ml sample from the reactor, and immediately quench it with 10ml of excess 0.05M hydrochloric acid (You should have the quenching acid sample ready before taking the sample from the reactor) .

6. Add 2 - 3 drops of phenolphthalein to the quenched sample and back titrate with 0.048544 M NaOH solution until the end point is detected (in this case a stable pink color) .
7. Record the amount of NaOH used in the titration (V titration.).
8. Repeat steps (5) - (7) every 2 minute for the samples. Take a total of 6-7samples making sure that you record the time for each new sample.
9. Calculation Experiment Three batch (II) at $37.7\ {}^{0}C$. The results are shown in (Table 3.18).

Table 3.18: Experiment C batch (II) volume of NaOH used in titration

Sample	**Time (s)**	**Initial Burette reading (ml)**	**Final Burette Reading(ml)**	**Volume NaOH used in Titration [Final-Initial](ml)**
0	0	0	0	0
1	120	0	6	6
2	240	6	13.5	7.5
3	360	13.5	21.3	7.8
4	480	21.3	29.6	8.3
5	600	29.6	38	8.4

10. Calculate the concentration (in mol/lit) of un reacted NaOH in each sample withdrawn from the reactor (Table 3.18) by using Eq (3.5) . The results are shown in (Table 3.19)

$$C_{NaOH} = \frac{V_{acid} \times M_{acid} - V_{tit} \times M_{base}}{V_{sample}} = \frac{10 \times 0.05 - V_{tit} \times 0.048544}{10}$$

$$[C_{NaOH}]_{t=0} = \frac{10 \times 0.05 - 0 \times 0.048544}{10} = 0.1$$

$$[C_{NaOH}]_{t=120} = \frac{10 \times 0.05 - 6 \times 0.048544}{10} = 0.0208736$$

$$[C_{NaOH}]_{t=240} = \frac{10 \times 0.05 - 7.5 \times 0.048544}{10} = 0.013592$$

$$[C_{NaOH}]_{t=360} = \frac{10 \times 0.05 - 7.8 \times 0.048544}{10} = 0.01213568$$

$$[C_{NaOH}]_{t=480} = \frac{10\times 0.05 - 8.3\times 0.048544}{10} = 0.00970848$$

$$[C_{NaOH}]_{t=600} = \frac{10\times 0.05 - 8.4\times 0.048544}{10} = 0.00922304$$

Add column un reacted NaOH to the (Table 3.18) .

Table 3.19: Experiment C batch (II) Concentration of unreacted NaOH

Sample #	Time (s)	Volume NaOH used in titration (ml)	Un reacted NaOH(mol/lit)
0	0	0	0.1
1	120	6	0.0208736
2	240	7.5	0.0135920
3	360	7.8	0.01213568
4	480	8.3	0.00970848
5	600	8.4	0.00922304

11. Add experimental concentration of NaOH and its inverse from (Table 3.19) and Actual concentration and its inverse from literature at the same time from Appendix B Eq(B.1), The results are shown in (Table 3.20) .

Table 3.20: Experiment C batch (II) Concentration of NaOH and its inverse (Experimental, Actual)

time (s)	V titration	Exp(CA)	Exp(1/CA)	AC(CA)	AC(1/CA)
0	0	0.1	10.00	0.1000	10.00
120	6	0.02087360	47.91	0.0251	39.83
240	7.5	0.01359200	73.57	0.0144	69.66
360	7.8	0.01213568	82.40	0.0101	99.50
480	8.3	0.00970848	103.00	0.0077	129.33
600	8.4	0.00922304	108.42	0.0063	159.16

12. Use Excel program to plot between $\frac{1}{C_A}$ vs t and Trend(Line) to get rate constant , The results are shown in Figures (4.15 to 4.16)

III. Isothermal Operation at $45.5\ ^{0}C$

Procedure:

1. 0.05 M HCl was prepared used in the experiment (Standard acid solution) ,10 mL of it is pipettd into each of several 250 mL Erlenmeyer flasks (E-flasks) before the experiment began .
2. Concentration of NaOH in titration (in burette) is determined using the 0.05 M HCl was prepared above (a minimum of three titrations) , firstly prepare 0.05M NaOH , secondly titrate it with 0.05 M HCl above to correct concentration of NaOH prepared may be less or more than its prepared value 0.05 M NaOH in (Table3.21) .

$$V_{acid} \times M_{acid} = V_{base} \times M_{basic} ---------------------- Eq(3.9)$$

Table 3.21: Experiment C batch (III) acid base titration

NO(titrations)	**Standard acid solution**		**Measured base solution**		
	V_{acid} **(ml)**	M_{acid} **(mol/lit)**	V_{base} **(ml)**	M_{base} **(mol/lit)**	**Average** M_{base} **(mol/lit)**
1	10	0.05	10.30	0.048544	0.048544
2	10	0.05	10.35	0.048309	
3	10	0.05	10.25	0.048780	

3. In the reactor, mix 0.5 liter of the 0.1M caustic soda solution with 0.5 liter of the 0.1M ethyl acetate solution at an arbitrary time (t = 0) at $45.5\ ^{0}C$. Switch on the stirrer immediately and set it to an intermediate speed to avoid splashing.
4. Start the timer as soon as you start mixing the reactants.
5. After a certain time interval, use a pipette or medical injection to withdraw 10ml sample from the reactor, and immediately quench it with 10ml of excess 0.05M hydrochloric acid (You should have the quenching acid sample ready before taking the sample from the reactor) .

6. Add 2 - 3 drops of phenolphthalein to the quenched sample and back titrate with 0.048544 M NaOH solution until the end point is detected (in this case a stable pink color) .
7. Record the amount of NaOH used in the titration (V titration.).
8. Repeat steps (5) - (7) every 2 minute for the samples. Take a total of 6-7samples making sure that you record the time for each new sample.
9. Calculation Experiment Three batch (III) at $45.5\ ^{0}C$. The results are shown in (Table 3.22)

Table 3.22: Experiment C batch (III) volume of NaOH used in titration

Sample	**Time (s)**	**Initial Burette reading (ml)**	**Final Burette Reading(ml)**	**Volume NaOH used in Titration [Final-Initial](ml)**
0	0	0	0	0
1	120	0	6.6	6.6
2	240	6.6	14.4	7.8
3	360	14.4	23	8.6
4	480	23	31.8	8.8
5	600	31.8	41	9.2

10. Calculate the concentration (in mol/lit) of unreacted NaOH in each sample withdrawn from the reactor (Table 3.22) by using Eq (3.5) . The results are shown in (Table 3.23).

$$C_{NaOH} = \frac{V_{acid} \times M_{acid} - V_{tit} \times M_{base}}{V_{sample}} = \frac{10 \times 0.05 - V_{tit} \times 0.048544}{10}$$

$$[C_{NaOH}]_{t=0} = \frac{10 \times 0.05 - 0 \times 0.048544}{10} = 0.1$$

$$[C_{NaOH}]_{t=120} = \frac{10 \times 0.05 - 6.6 \times 0.048544}{10} = 0.01796096$$

$$[C_{NaOH}]_{t=240} = \frac{10 \times 0.05 - 7.8 \times 0.048544}{10} = 0.01213568$$

$$[C_{NaOH}]_{t=360} = \frac{10 \times 0.05 - 8.6 \times 0.048544}{10} = 0.00825216$$

$$[C_{NaOH}]_{t=480} = \frac{10 \times 0.05 - 8.8 \times 0.048544}{10} = 0.00728128$$

$$[C_{NaOH}]_{t=600} = \frac{10 \times 0.05 - 9.2 \times 0.048544}{10} = 0.00533952$$

Add column un reacted NaOH to the (Table 3.22) .

Table 3.23: Experiment C batch (III) Concentration of unreacted NaOH

Sample #	Time (s)	Volume NaOH used in titration (ml)	Un reacted NaOH(mol/lit)
0	0	0	0.1
1	120	6.6	0.01796096
2	240	7.8	0.01213568
3	360	8.6	0.00825216
4	480	8.8	0.00728128
5	600	9.2	0.00533952

11. Add experimental concentration of NaOH and its inverse from (Table 3.23) and Actual concentration and its inverse from literature at the same time from Appendix B Eq(B.1), The results are shown in (Table 3.24)

Table 3.24: Experiment C batch (III) Concentration of NaOH and its inverse (Experimental, Actual)

time (s)	V titration	Exp(CA)	Exp(1/CA)	AC(CA)	AC(1/CA)
0	0	0.1	10.00	0.1000	10.00
120	6.6	0.01796096	55.68	0.0175	57.18
240	7.8	0.01213568	82.40	0.0096	104.37
360	8.6	0.00825216	121.18	0.0066	151.55
480	8.8	0.00728128	137.34	0.0050	198.74
600	9.2	0.00533952	187.28	0.0041	245.92

12. Use Excel program to plot between $\frac{1}{C_A}$ vs t and Trend (Line) to get rate constant. The results are shown in Figures (4.17 to 4.18)

CHAPTER FOUR

RESULTS & DISCUSSION

4.1. Results

Results for experiments (A,B,C) are showing in figures (4.1 to 4.18)

4.1.1. Experiment A (isothermal at 37.7^0C)

Figure 4.1 Shows Experiment A (isothermal at 37.7^0C) batch (I) the change of concentration of caustic soda versus time for the simulated literature values from Appendix B versus the experimental values from (Table 3.6) .

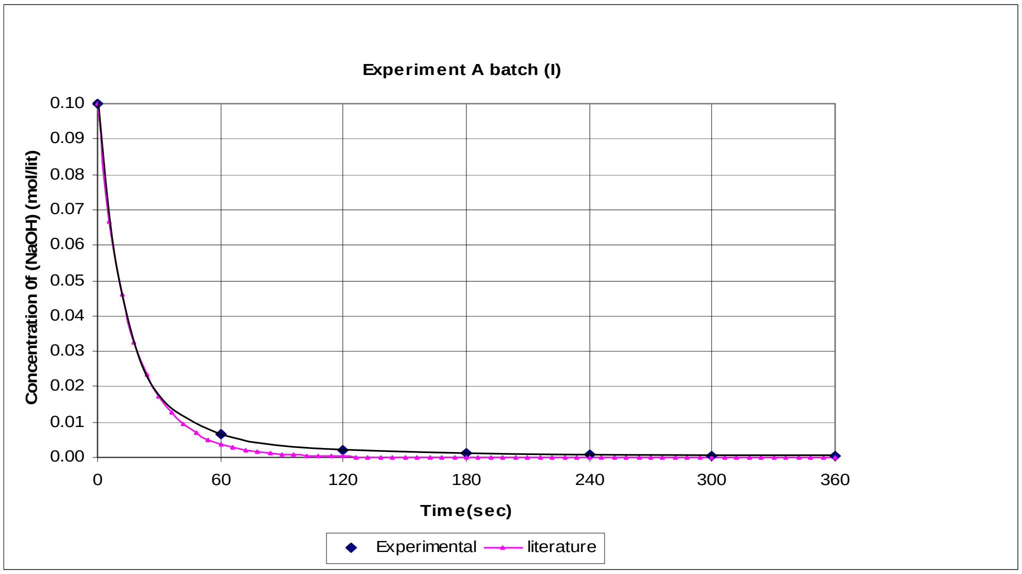


Figure 4.1: Experiment A (isothermal at 37.7^0C) batch (I) Concentration time data from Experimental in (Table 3.6) and literature values from Appendix B .

Figure 4.2 Shows Experiment A (isothermal at 37.7^0C) batch (I) Excel log - log plot for experimental rate of reaction of caustic soda versus its concentration from (Table 3.6) .

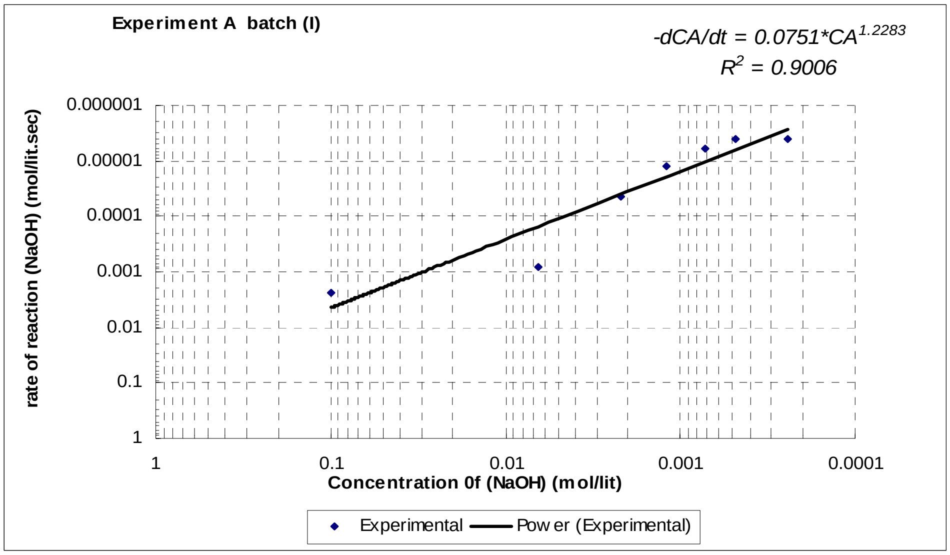


Figure 4.2: Experiment A (isothermal at 37.7^0C) batch (I) Experimental rate of reaction (NaOH) versus its concentration in (Table 3.6) .

Figure 4.3 Shows Experiment A (isothermal at 37.7^0C) batch (II) the change of concentration of caustic soda versus time for the simulated literature values from Appendix B versus the experimental values from (Table 3.6) .

Figure 4.3: Experiment A(isothermal at 37.7^0C) batch (II) Concentration time data from Experimental in (Table 3.6) and literature values from Appendix B.

Figure 4.4 Shows Experiment A (isothermal at 37.70C) batch (II) Excel log - log plot for experimental rate of reaction of caustic soda versus its concentration from (Table 3.6) .

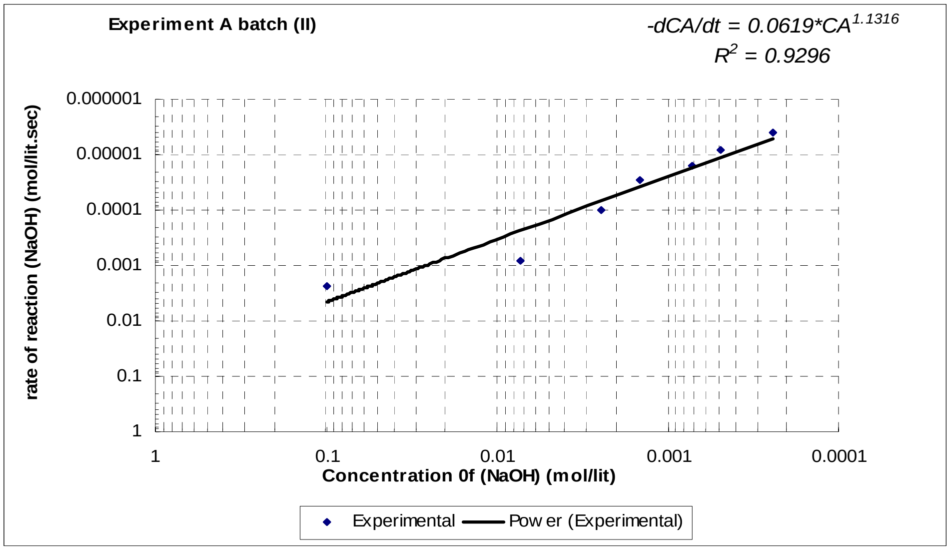


Figure 4.4: Experiment A (isothermal at 37.7^{0}C) batch (II) experimental rate of reaction (NaOH) versus its concentration in (Table 3.6).

Figure 4.5 Shows Experiment A (isothermal at 37.7^{0}C) batch (III) the change of concentration of caustic soda versus time for the simulated literature values from Appendix B versus the experimental values from (Table 3.6).

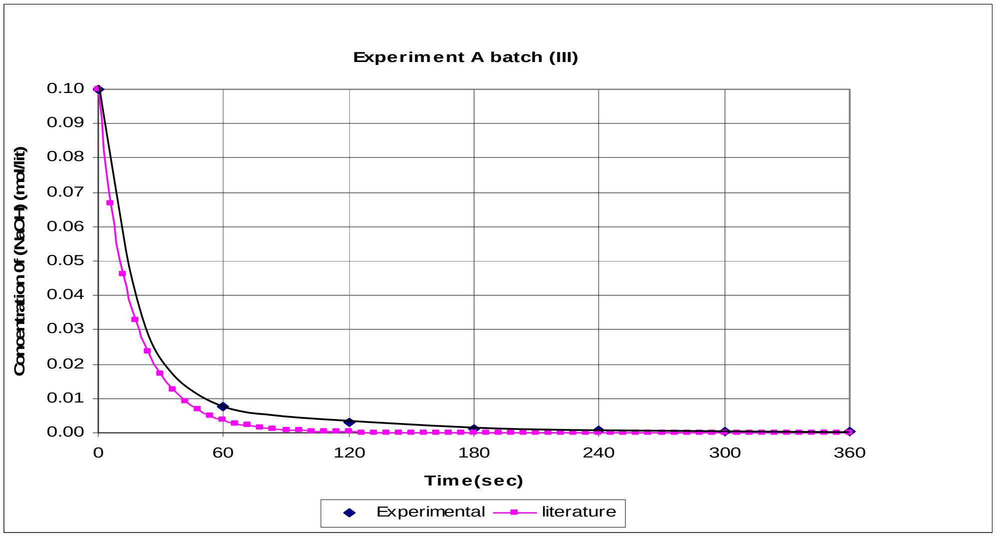


Figure 4.5: Experiment A(isothermal at 37.7^{0}C) batch (III) Concentration time data from Experimental in (Table 3.6) and literature values from Appendix B.

Figure 4.6 Shows Experiment A (isothermal at 37.7^{0}C) batch (III) Excel log - log plot for experimental rate of reaction of caustic soda versus its concentration from (Table 3.6) .

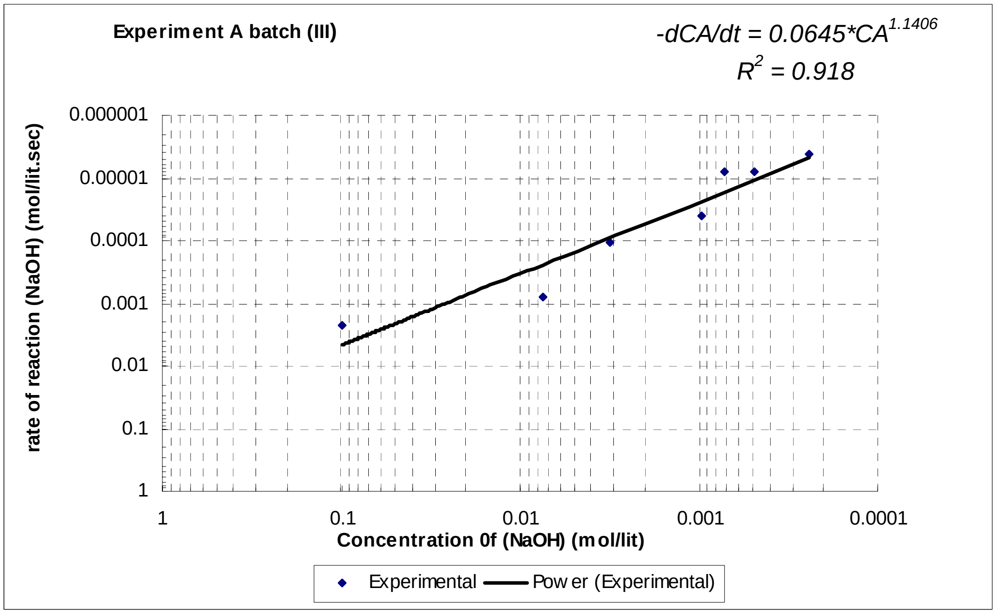


Figure 4.6: Experiment A (isothermal at 37.7^{0}C) batch (III) Experimental rate of reaction (NaOH) versus its concentration in (Table 3.6)

4.1.2. Experiment B (isothermal at 37.7^{0}C)

Figure 4.7 Shows Experiment B (isothermal at 37.7^{0}C) batch (I) the change of concentration of caustic soda versus time for the simulated literature values from Appendix B versus the experimental values from (Table 3.12).

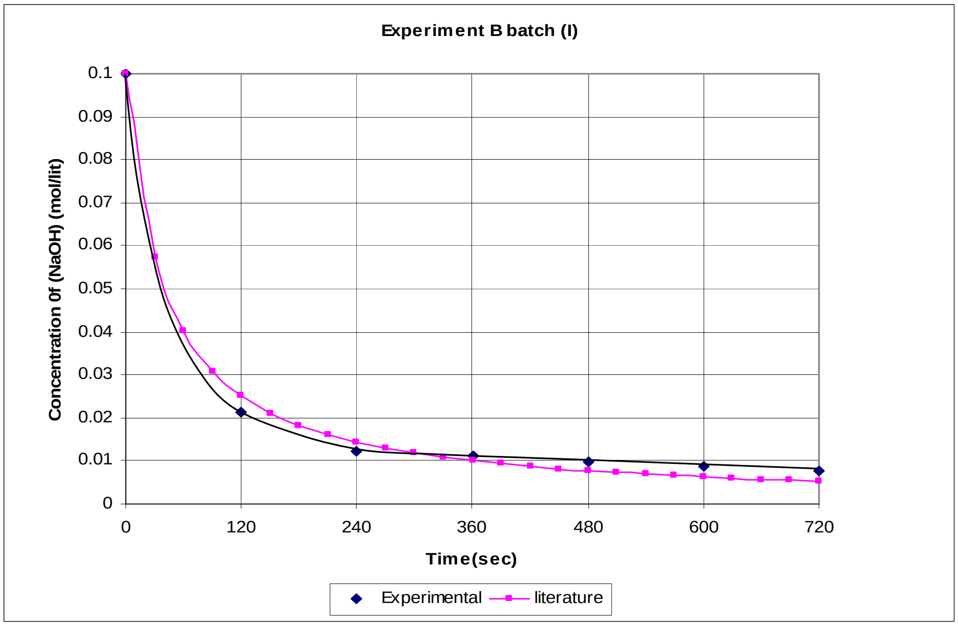


Figure 4.7: Experiment B (isothermal at 37.7^{0}C) batch (I) Concentration time data from Experimental in (Table 3.12) and literature values from Appendix B.

Figure 4.8 Shows Experiment B (isothermal at 37.7^{0}C) batch (I) Excel log - log plot for experimental rate of reaction of caustic soda versus its concentration from (Table 3.12).

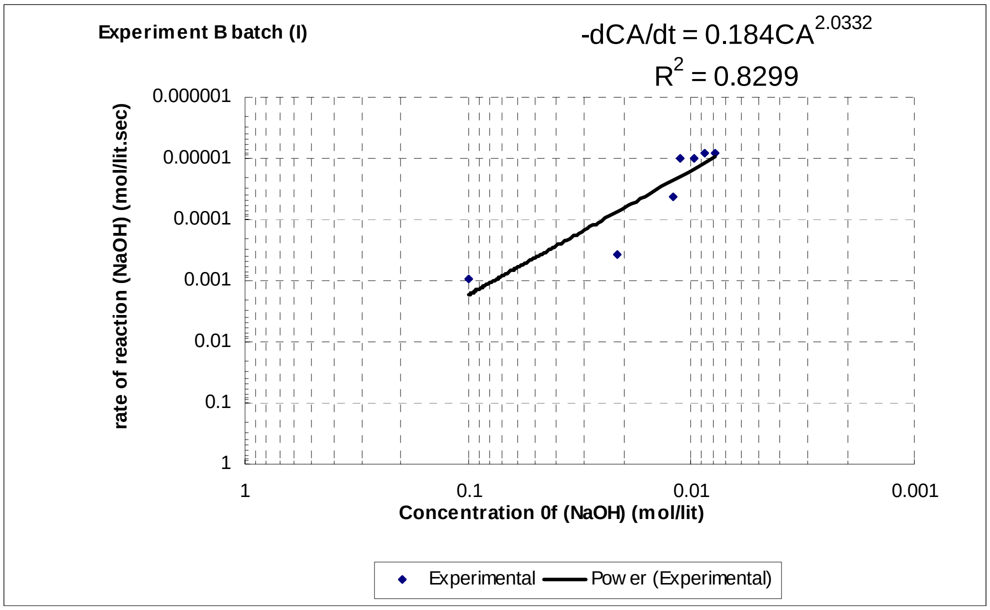


Figure 4.8: Experiment B (isothermal at 37.7^{0}C) batch (I) Experimental rate of reaction (NaOH) versus its concentration in (Table 3.12).

Figure 4.9 Shows Experiment B (isothermal at 37.7^{0}C) batch (II) the change of concentration of caustic soda versus time for the simulated literature values from Appendix B versus the experimental values from (Table 3.12) .

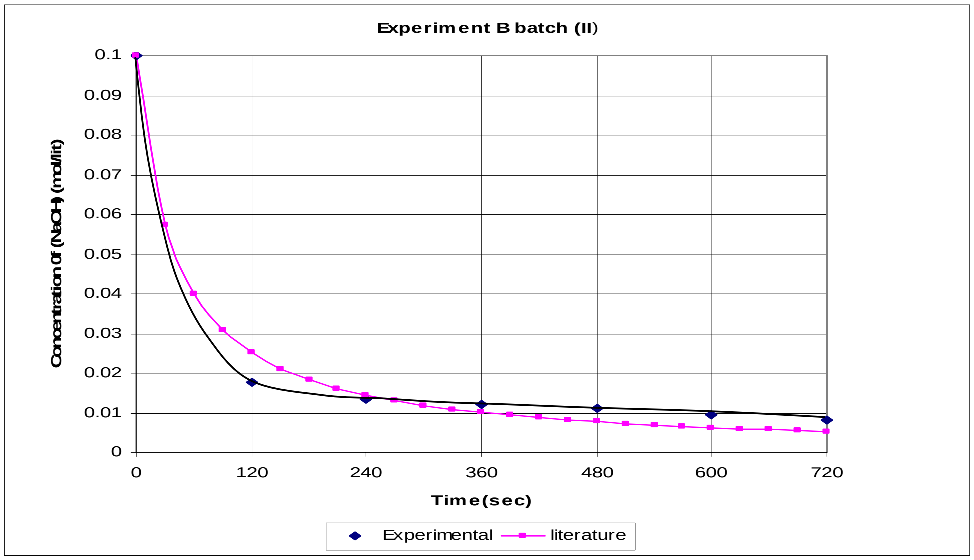


Figure 4.9: Experiment B (isothermal at 37.7^{0}C) batch (II) Concentration time data from Experimental in (Table 3.12) and literature values from Appendix B.

Figure 4.10 Shows Experiment B (isothermal at 37.7^0C) batch (II) Excel log - log plot for experimental rate of reaction of caustic soda versus its concentration from (Table 3.12) .

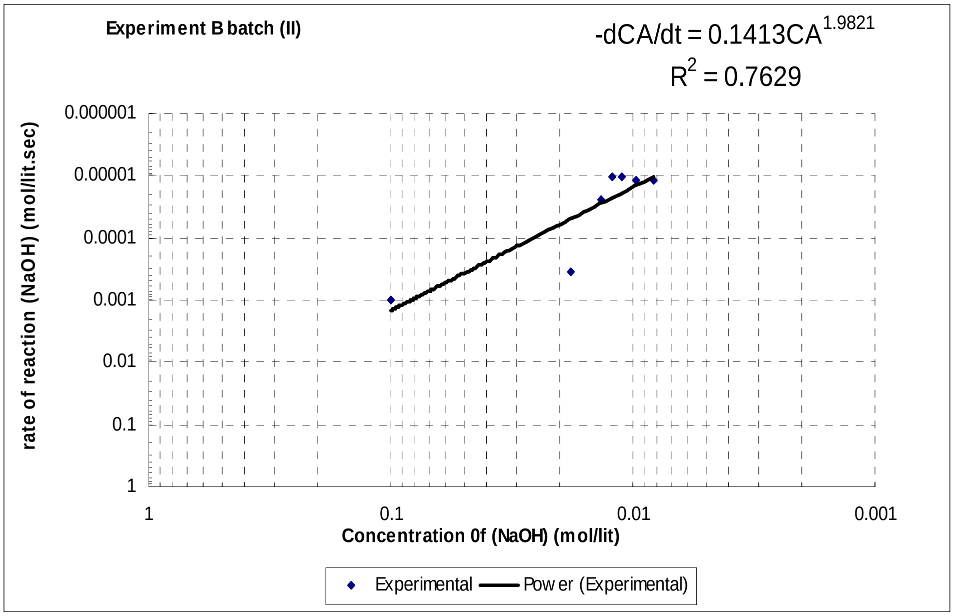


Figure 4.10: Experiment B (isothermal at 37.7^0C) batch (II) Experimental rate of reaction (NaOH) versus its concentration in Table (3.12) .

Figure 4.11 Shows Experiment B (isothermal at 37.7^0C) batch (III) the change of concentration of caustic soda versus time for the simulated literature values from Appendix B versus the experimental values from (Table 3.12)

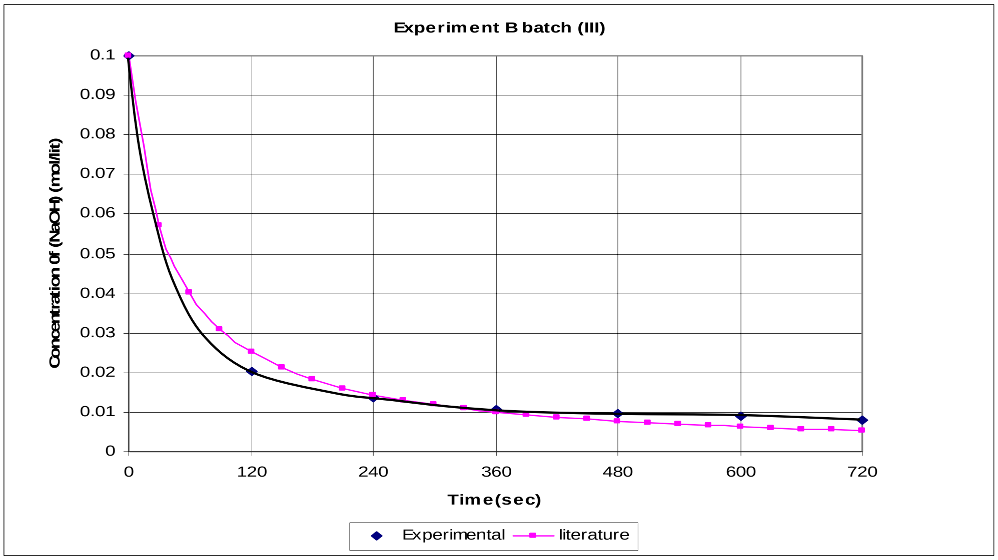


Figure 4.11: Experiment B (isothermal at 37.7^0C) batch (III)Concentration time data from Experimental in (Table 3.12) and literature values from Appendix B.

Figure 4.12 Shows Experiment B (isothermal at 37.7^0C) batch (III) Excel log - log plot for experimental rate of reaction of caustic soda versus its concentration from (Table 3.12).

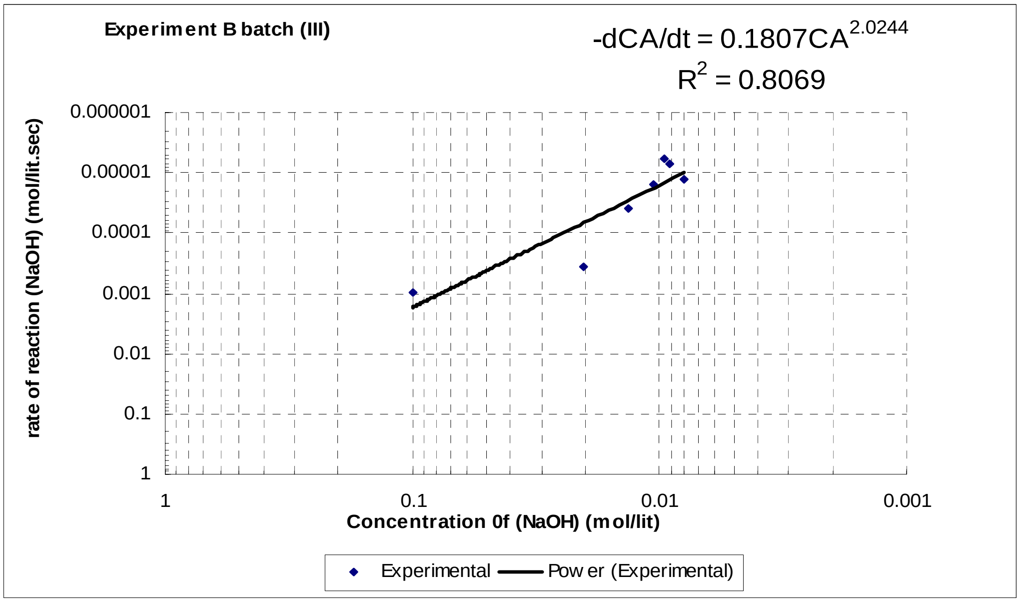


Figure 4.12: Experiment B (isothermal at 37.7^0C) batch (III) Experimental rate of reaction (NaOH) versus its concentration in (Table 3.12) .

4.1.3. Experiment C (non isothermal)

Figure 4.13 Shows Experiment C (at 31.2^0C) batch (I) the change of concentration of caustic soda versus time for the simulated literature values versus the experimental values from (Table 3.16) .

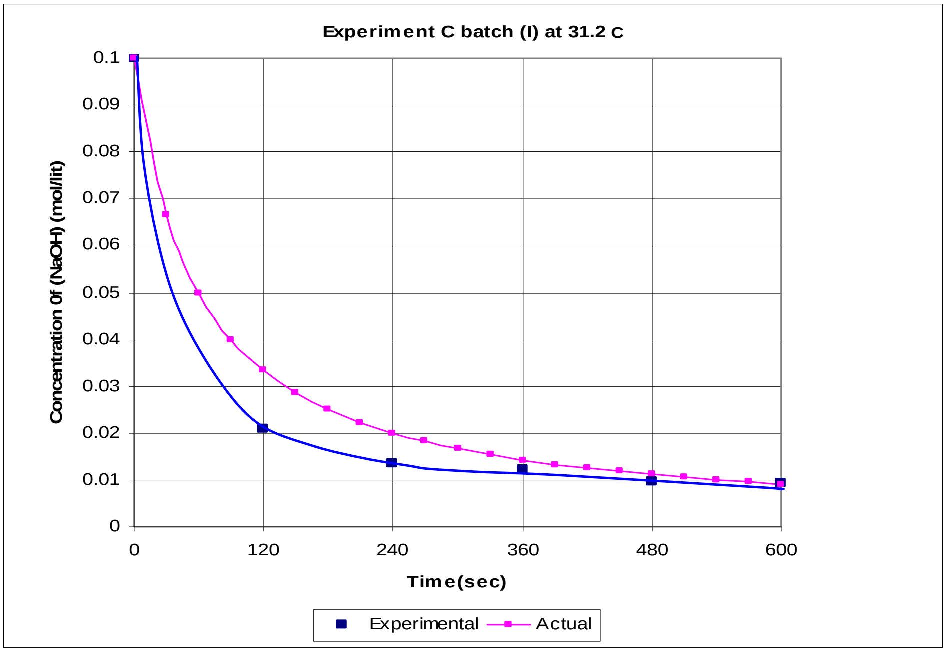


Figure 4.13: Experiment C (at 31.2^0C) batch (I) Concentration time data from Experimental and literature values from (Table 3.16) .

Figure 4.14 Shows Experiment C (at 31.2^0C) batch (I) Excel plot for inverse experimental and actual concentration on literature of caustic soda versus time from (Table 3.16).

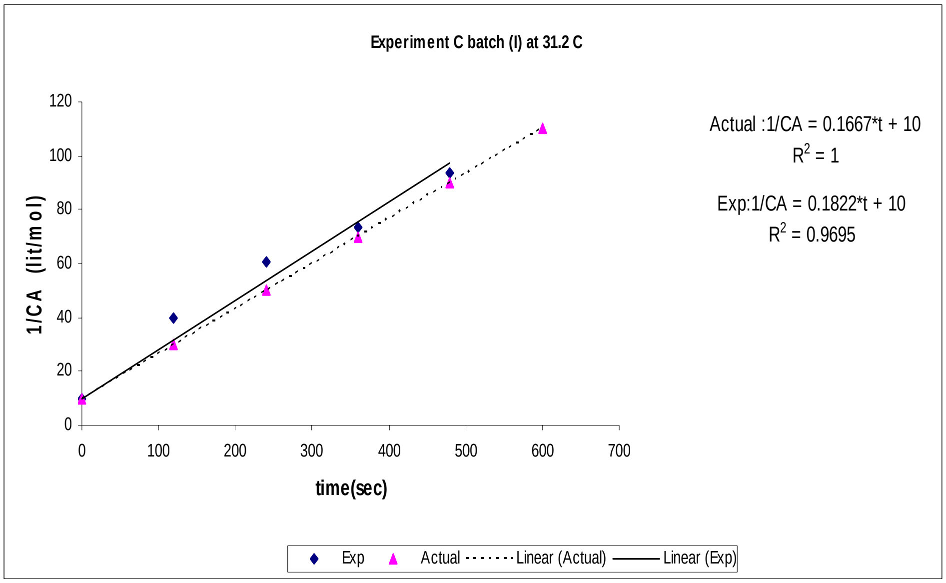


Figure 4.14: Experiment C (at 31.2 ^{0}C) batch (I) Excel program to plot $1/C_A$ vs t , from (Table 3.16) .

Figure 4.15 Shows Experiment C (at 37.7^{0}C) batch (II) the change of concentration of caustic soda versus time for the simulated literature values versus the experimental values from (Table 3.20).

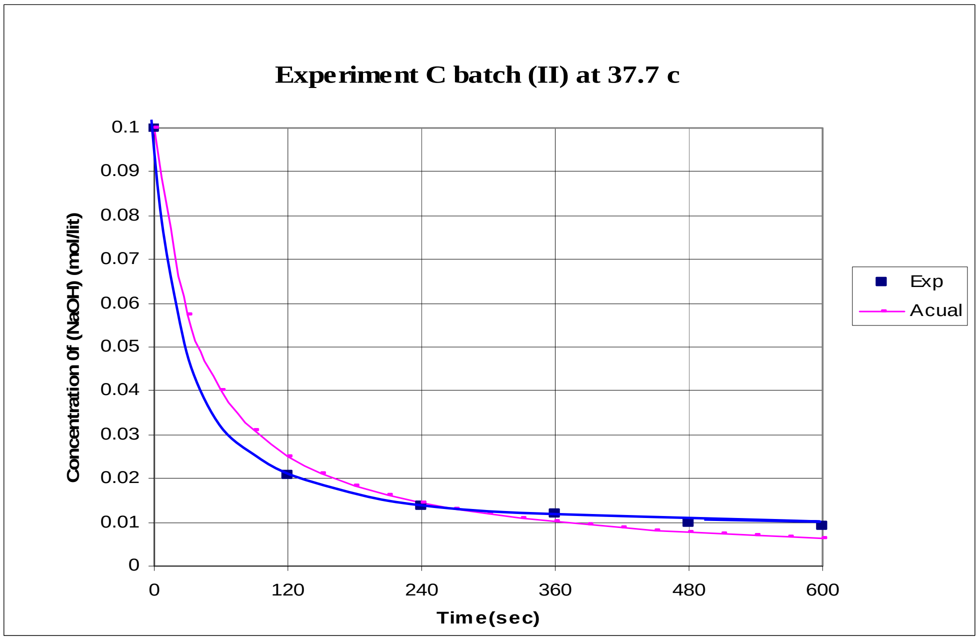


Figure 4.15: Experiment C (at 37.7^{0}C) batch (II) Concentration time data from Experimental and Actual from (Table 3.20).

Figure 4.16 Shows Experiment C (at 37.7^0C) batch (II) Excel plot for inverse experimental and actual concentration on literature of caustic soda versus time from (Table 3.20).

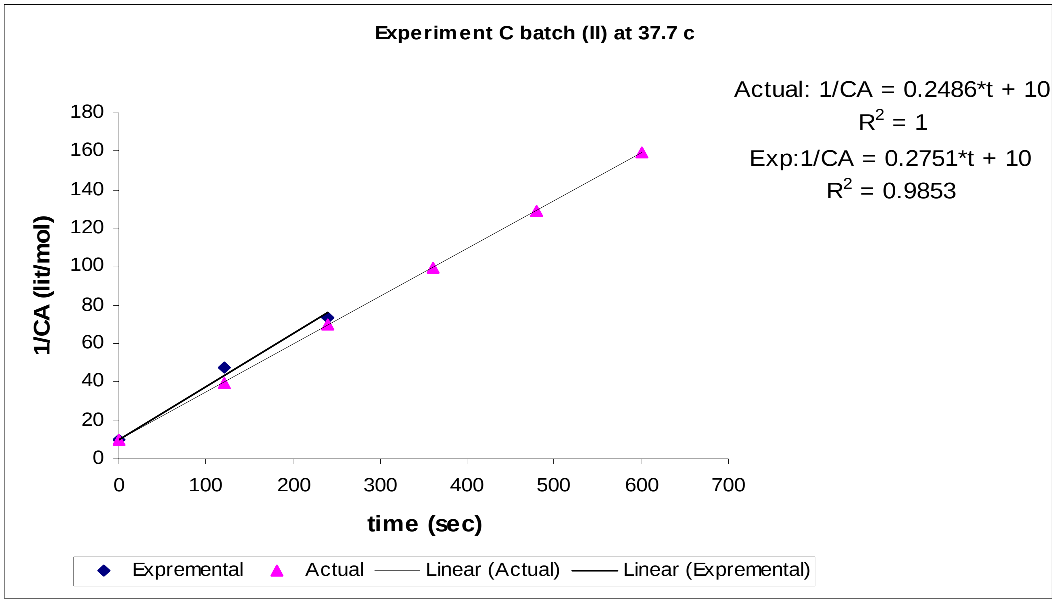


Figure 4.16: Experiment C (at 37.7^0C) batch (II) Excel program to plot $1/C_A$ vs t from (Table 3.20) .

Figure 4.17 Shows Experiment C (at 45.5^0C) batch (III) the change of concentration of caustic soda versus time for the simulated literature values versus the experimental values from (Table 3.24) .

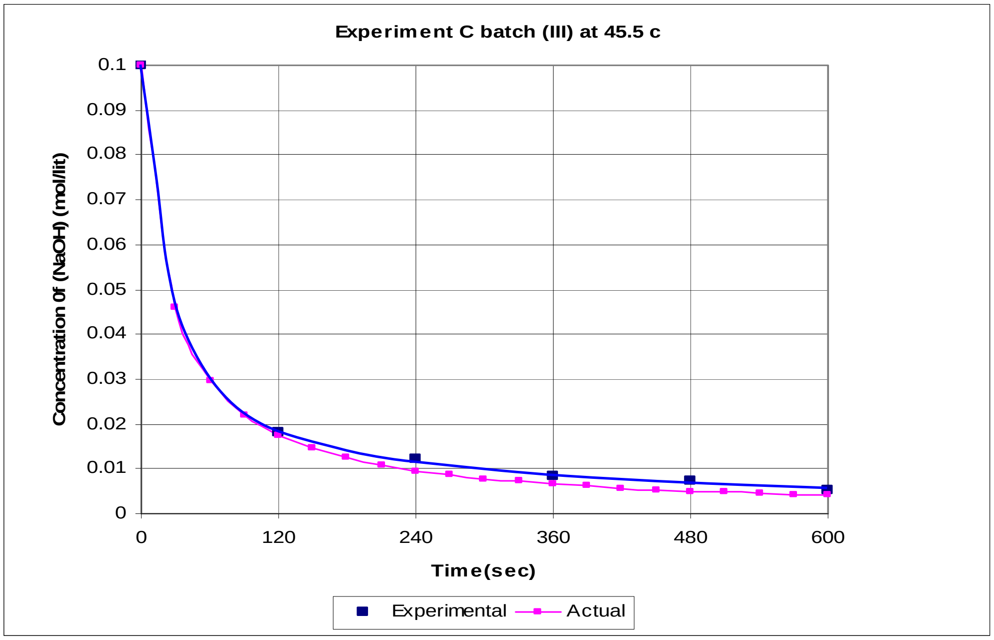


Figure 4.17: Experiment C (at 45.5^{0}C) batch (III) Concentration time data from Experimental and Actual (Table 3.24) .

Figure 4.18 Shows Experiment C (at 45.5^{0}C) batch (III) Excel plot for inverse experimental and actual concentration on literature of caustic soda versus time from (Table 3.24) .

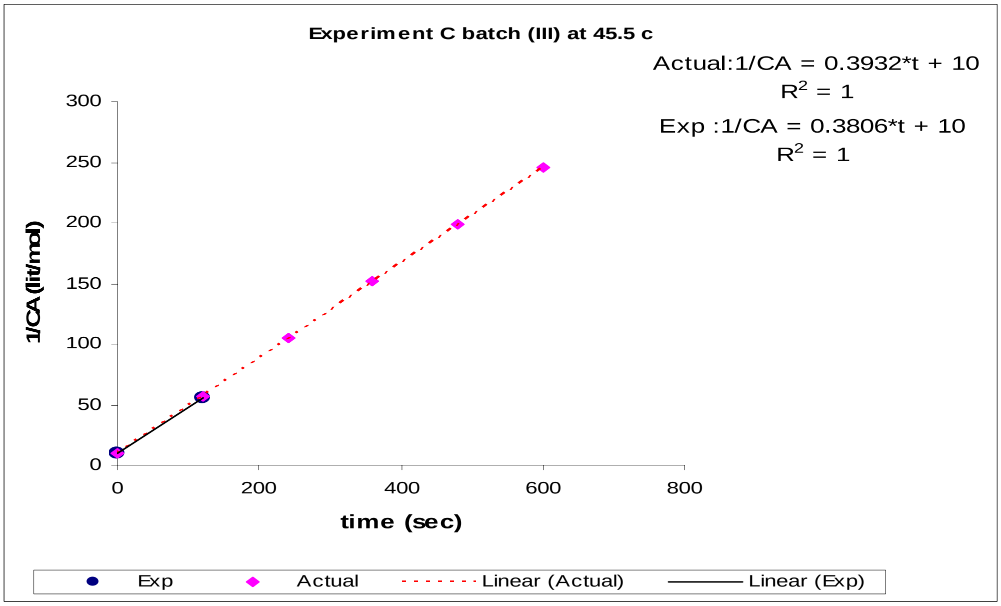


Figure 4.18: Experiment C (at 45.5^{0}C) batch (III) Excel program to plot $1/C_A$ vs t from (Table 3.24).

4.2. Discussion

4.2.1. Discussion Experiment A (isothermal at 37.7^0C)

The results of order with respect to caustic soda (*a*) is showing in Figures (4.2 ,4.4 and 4.6) and (Table 4.1).

Table 4.1: Experiment A average order with respect to (NaOH)

NO Of Batches	reaction order with respect to (NaOH)	Average reaction order with respect to (NaOH)
1	1.2283	1.16683
2	1.1316	
3	1.1406	

Average reaction order with respect to (NaOH) was obtained in Experiment A equal 1.16683 on average, which is a 16.683 % high than literature value.

Reasons of this difference:

1. Possible difference in Numerical Methods (finite difference) , another method was used (Polynomial equation) is called Polynomial fit, section (2.6.2)

Polynomial Fit

Another technique to differentiate the data is to fit the concentration time data to an *n*th-order polynomial:

$$C_A = a_0 + a_1.t + a_2.t^2 + a_3.t^3 + ... \quad ------------ \quad Eq\,(2.30)$$

$$\frac{dC_A}{dt} = a_1 + 2a_2.t + 3a_3.t^2 + ... \quad ------------- Eq\,(2.31)$$

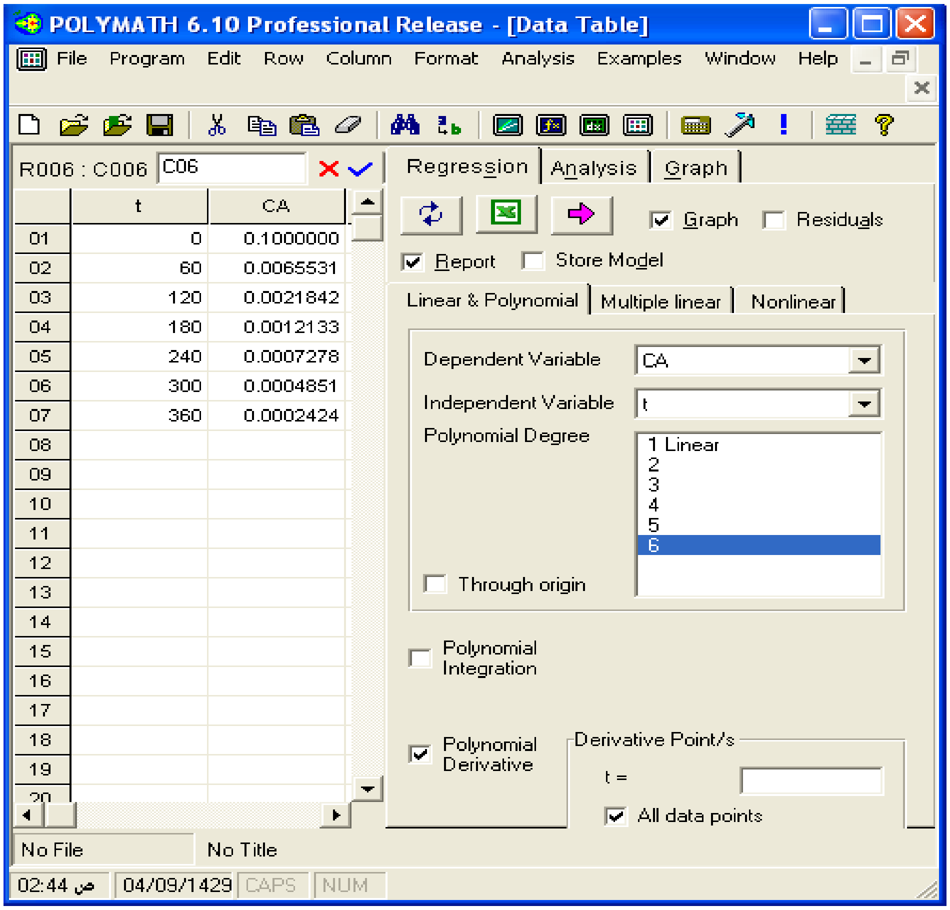
Many personal computer software packages contain programs that will calculate the best values for the constants a_i. One has only to enter the concentration time data and choose the order of the polynomial. After determining the constants a_i, one has only to differentiate Eq(2.30) to get Eq(2.31) .

The program was used poly math 6.1 the experiment A the three batches are shown below:

Experiment A batch (I)

1. Enter the concentration time data from (Table 3.6) and choose the order of the polynomial 6 is show in (Figure4.19) .

Where t = time (sec) , CA= concentration of NaOH



	t	CA
01	0	0.1000000
02	60	0.0065531
03	120	0.0021842
04	180	0.0012133
05	240	0.0007278
06	300	0.0004851
07	360	0.0002424

Dependent Variable: CA

Independent Variable: t

Polynomial Degree: 6

☐ Through origin

☐ Polynomial Integration

☑ Polynomial Derivative

Derivative Point/s

t =

☑ All data points

Figure 4.19: Experiment A batch (I) data input to poly math program

2. Poly math report **:**

POLYMATH Report

Polynomial Regression

Model: CA = a0 + a1*t + a2*t^2 + a3*t^3 + a4*t^4 + a5*t^5 + a6*t^6

Variable	Value	95% confidence
a0	0.1	0
a1	-0.0036027	0
a2	5.226E-05	0
a3	-3.821E-07	0
a4	1.486E-09	0
a5	-2.933E-12	0
a6	2.305E-15	0

Analytical polynomial derivative

CA = 0.1 -0.0036027*t + 5.226E-05*t^2 -3.821E-07*t^3 + 1.486E-09*t^4 -2.933E-12*t^5 + 2.305E-15*t^6

d(CA)/d(t) = -0.0036027 + 0.0001045*t -1.146E-06*t^2 + 5.946E-09*t^3 -1.466E-11*t^4 + 1.383E-14*t^5

t	d(CA)/d(t)
0	-0.0036027
60	-0.0003524
120	1.254E-05
180	-3.075E-05
240	1.463E-05
300	-4.416E-05
360	0.0002008

General

Degree of polynomial = 6

Regression including a free parameter

Number of observations = 7

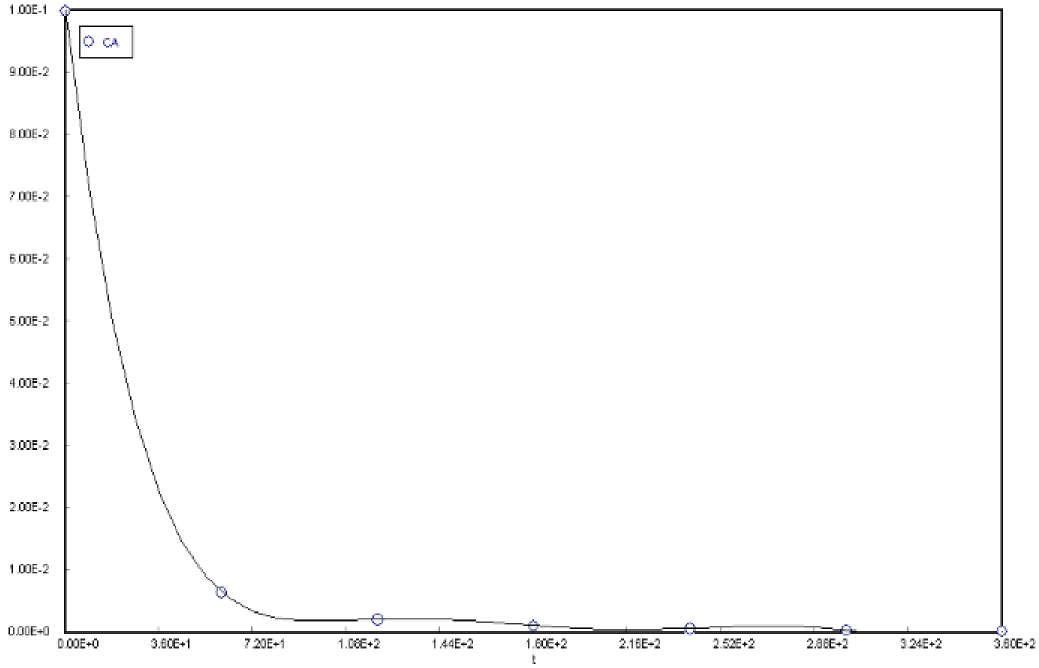
Statistics

R^2	1.
R^2adj	0
Rmsd	3.412E-12
Variance	1.0E+99

Source data points and calculated data points

	t	CA	CA calc	Delta CA
1	0	0.1	0.1	9.43E-13
2	60	0.0065531	0.0065531	-5.299E-12
3	120	0.0021842	0.0021842	1.257E-11
4	180	0.0012133	0.0012133	-1.548E-11
5	240	0.0007278	0.0007278	1.12E-11
6	300	0.0004851	0.0004851	-4.284E-12
7	360	0.0002424	0.0002424	-4.187E-13

Graph



3. From report the polynomial equation is accurate for negative derivatives points and choose the first negative derivatives points at the (Table 4.2) and excel plot ($-dC_A/dt$) of (NaOH) versus its concentration in (Table 4.2) showing in (Figure4.20) **.**

Table 4.2: Poly math batch (I) first negative derivative points

Time (s)	**C_A**	**polynomial equation [dC_A/dt]**	**Rate of reaction [$- dC_A/dt$]**
0	0.1000000	-0.0036027	0.0036027
60	0.0065531	-0.0003524	0.0003524
180	0.0012133	-3.075E-05	3.075E-05

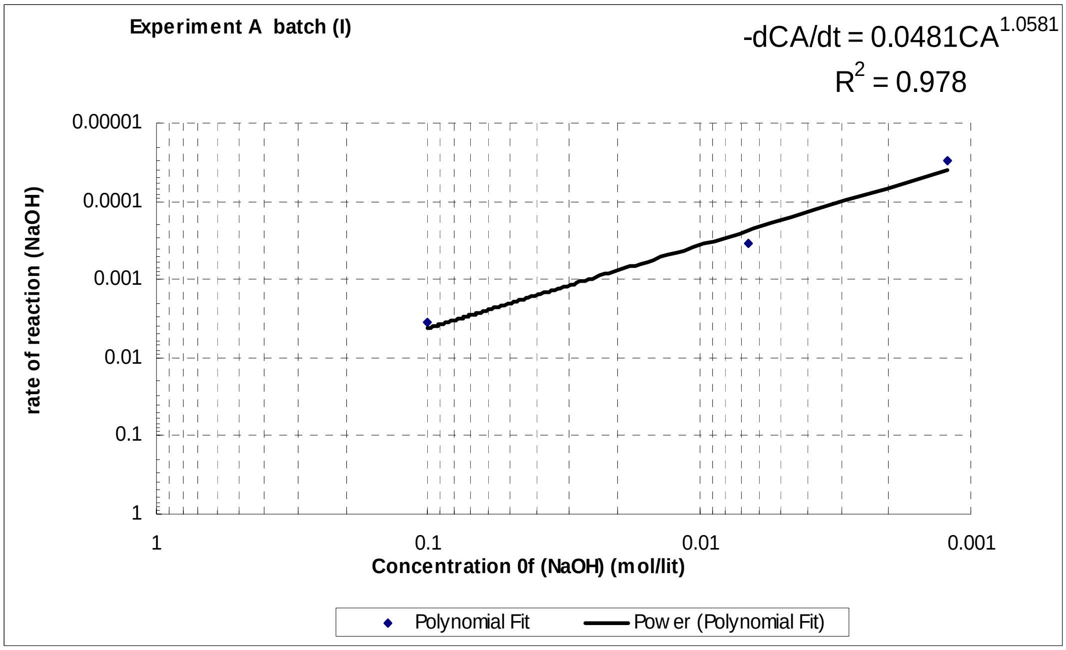
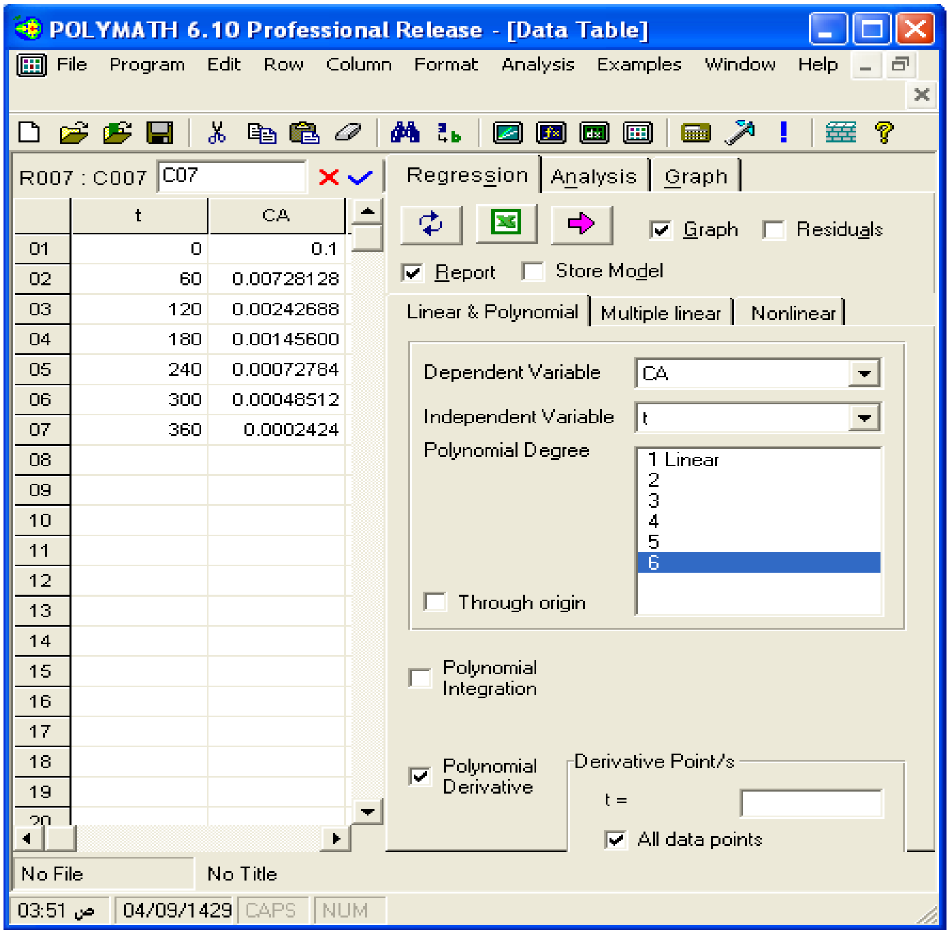


Figure 4.20: Experiment A batch (I) Excel program to plot rate of reaction (NaOH) versus its concentration in (Table 4.2).

Experiment A batch (II)

1. Enter the concentration time data from (Table 3.6) and choose the order of the polynomial 6 is show in (Figure 4.21).

Where t = time(sec) , C_A= concentration of NaOH



R007 : C007 C07

	t	CA
01	0	0.1
02	60	0.00728128
03	120	0.00242688
04	180	0.00145600
05	240	0.00072784
06	300	0.00048512
07	360	0.0002424
08		
09		
10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		

☑ Graph ☐ Residuals
☑ Report ☐ Store Model

Dependent Variable: CA
Independent Variable: t
Polynomial Degree: 1 Linear, 2, 3, 4, 5, 6 (6 selected)
☐ Through origin
☐ Polynomial Integration
☑ Polynomial Derivative
Derivative Point/s
t =
☑ All data points

Figure 4.21: Experiment A batch (II) data input to poly math program

2. Poly math report **:**

POLYMATH Report

Polynomial Regression

Model: CA = a0 + a1*t + a2*t^2 + a3*t^3 + a4*t^4 + a5*t^5 + a6*t^6

Variable	**Value**	**95% confidence**
a0	0.1	0
a1	-0.0035332	0
a2	5.054E-05	0
a3	-3.65E-07	0
a4	1.404E-09	0
a5	-2.744E-12	0
a6	2.139E-15	0

Analytical polynomial derivative

CA = 0.1 -0.0035332*t + 5.054E-05*t^2 -3.65E-07 *t^3 + 1.404E-09*t^4 -2.744E-12*t^5 + 2.139E-15*t^6

d(CA)/d(t) = -0.0035332 + 0.0001011*t -1.095E-06*t^2 + 5.617E-09*t^3 -1.372E-11*t^4 + 1.283E-14*t^5

t	**d(CA)/d(t)**
0	-0.0035332
60	-0.0003646
120	1.072E-05
180	-3.196E-05
240	9.641E-06
300	-3.776E-05
360	0.0001744

General

Degree of polynomial = 6

Regression including a free parameter

Number of observations = 7

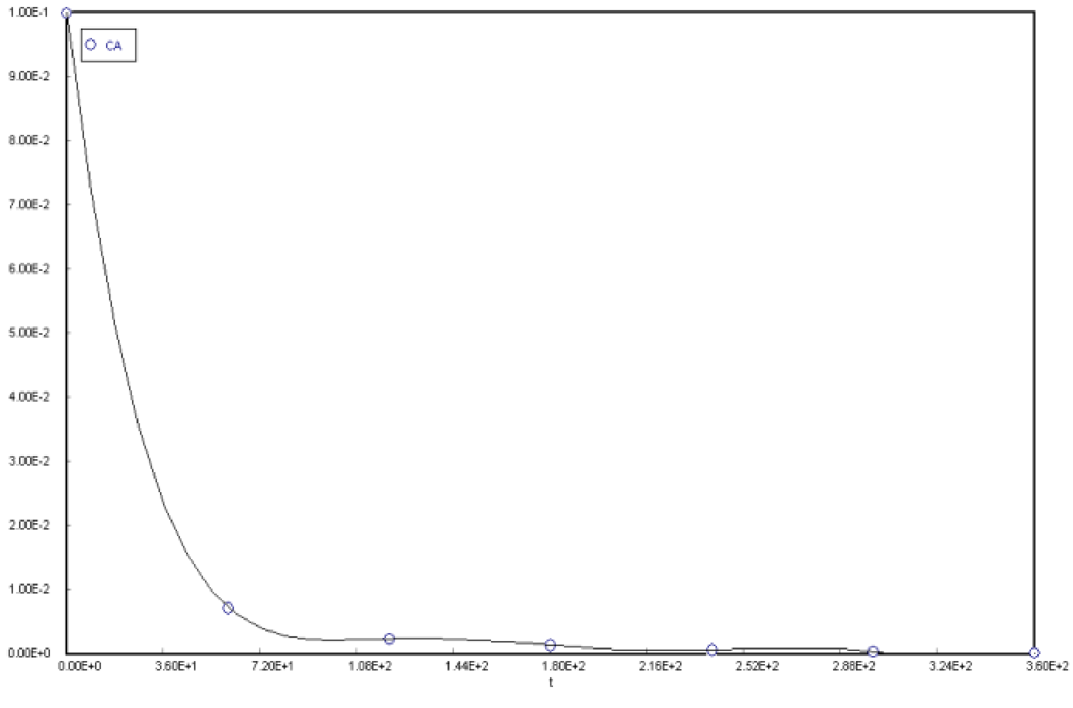
Statistics

R^2	1.
R^2adj	0
Rmsd	3.2E-12
Variance	1.0E+99

Source data points and calculated data points

	t	**CA**	**CA calc**	**Delta CA**
1	0	0.1	0.1	8.833E-13
2	60	0.00728128	0.0072813	-4.964E-12
3	120	0.00242688	0.0024269	1.179E-11
4	180	0.001456	0.001456	-1.45E-11
5	240	0.00072784	0.0007278	1.052E-11
6	300	0.00048512	0.0004851	-4.043E-12
7	360	0.0002424	0.0002424	-5.218E-13

Graph



3. From report the polynomial equation is accurate for negative derivatives points and choose the first negative derivatives points at the Table 4.3 and excel plot ($-dC_A/dt$) of (NaOH) versus its concentration in Table 4.3 showing in Figure 4.22.

Table 4.3: Poly math batch (II) first negative derivative points

Time (s)	CA	polynomial equation [dC_A/dt]	Rate of reaction [$- dC_A/dt$]
0	0.1	-0.0035332	0.0035332
60	0.00728128	-0.0003646	0.0003646
180	0.001456	-3.196E-05	3.196E-05

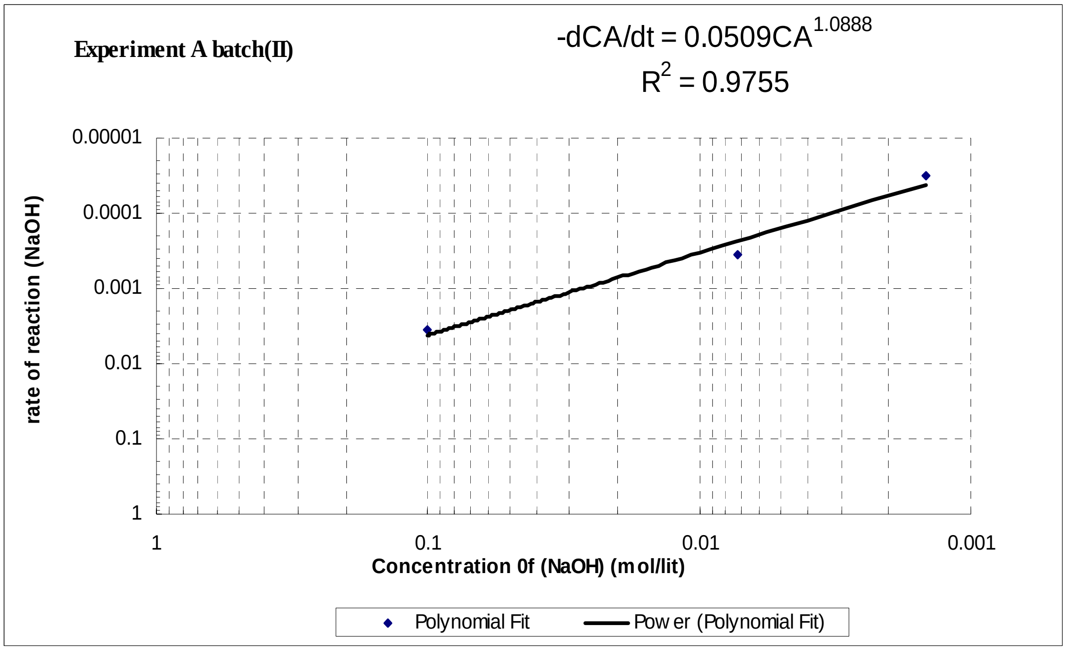
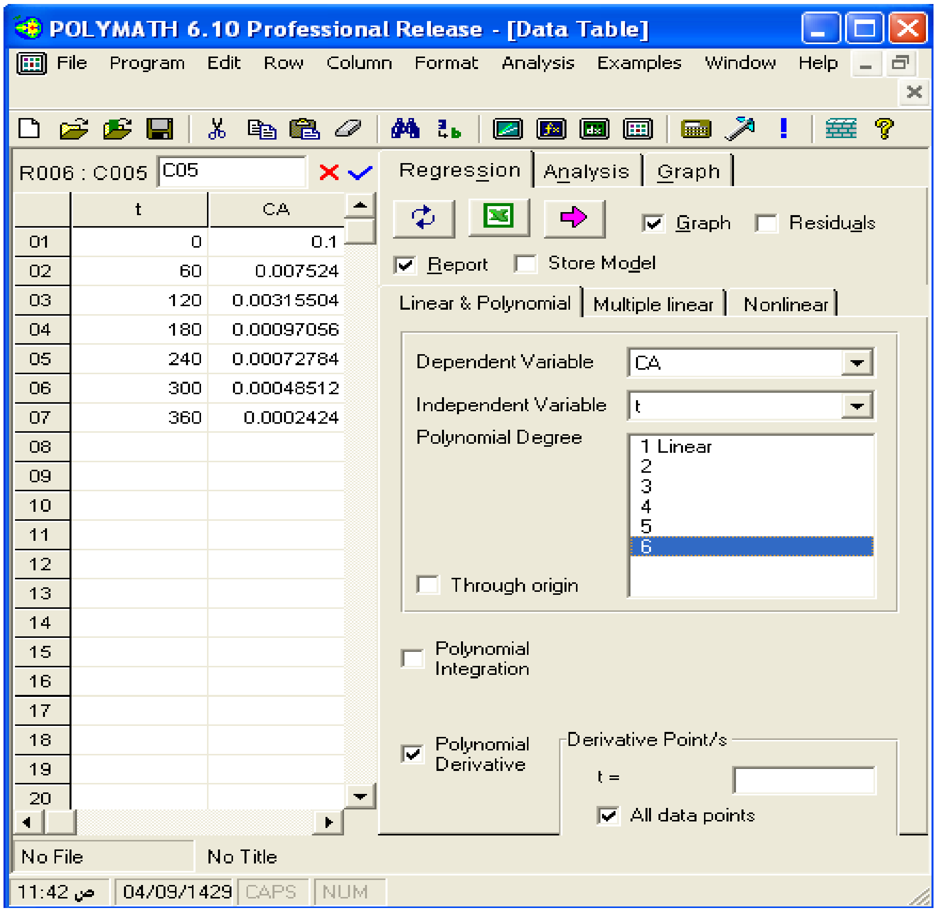


Figure 4.22: Experiment A batch (II) Excel program to plot rate of reaction (NaOH) versus its concentration in (Table 4.3).

Experiment A batch (III)

1. Enter the concentration time data from (Table 3.6) and choose the order of the polynomial 6 is show in (Figure 4.23).

Where t = time(sec) , CA= concentration of NaOH



R006 : C005 C05

	t	CA
01	0	0.1
02	60	0.007524
03	120	0.00315504
04	180	0.00097056
05	240	0.00072784
06	300	0.00048512
07	360	0.0002424
08		
09		
10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		

☑ Graph ☐ Residuals

☑ Report ☐ Store Model

Dependent Variable: CA

Independent Variable: t

Polynomial Degree: 1 Linear, 2, 3, 4, 5, **6** (selected)

☐ Through origin

☐ Polynomial Integration

☑ Polynomial Derivative

Derivative Point/s

t =

☑ All data points

Figure 4.23: Experiment A batch (III) data input to poly math program

2. Poly math report **:**

POLYMATH Report

Polynomial Regression

Model: CA = a0 + a1*t + a2*t^2 + a3*t^3 + a4*t^4 + a5*t^5 + a6*t^6

Variable	**Value**	**95% confidence**
a0	0.1	0
a1	-0.0036539	0
a2	5.481E-05	0
a3	-4.151E-07	0
a4	1.666E-09	0
a5	-3.375E-12	0
a6	2.71E-15	0

Analytical polynomial derivative

CA = 0.1 -0.0036539*t + 5.481E-05*t^2 -4.151E-07*t^3 + 1.666E-09*t^4 -3.375E-12*t^5 + 2.71E-15 *t^6

d(CA)/d(t) = -0.0036539 + 0.0001096*t -1.245E-06*t^2 + 6.666E-09*t^3 -1.688E-11*t^4 + 1.626E-14*t^5

t	**d(CA)/d(t)**
0	-0.0036539
60	-0.000326
120	8.765E-06
180	-4.045E-05
240	2.596E-05
300	-6.034E-05
360	0.000269

General

Degree of polynomial = 6

Regression including a free parameter

Number of observations = 7

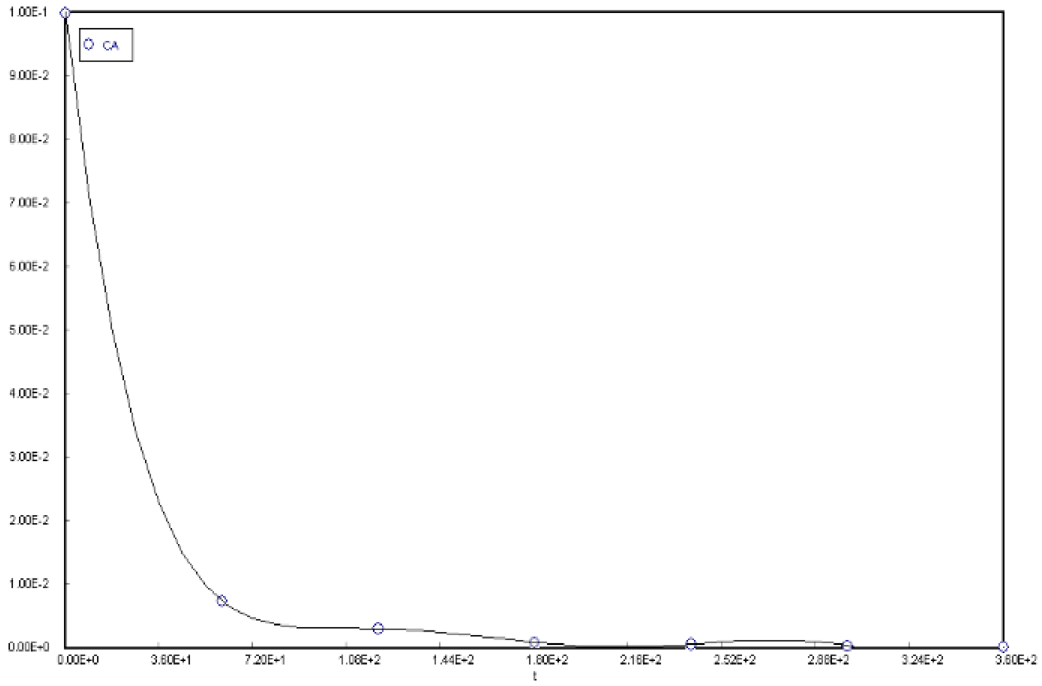
Statistics

R^2	1.
R^2adj	0
Rmsd	3.902E-12
Variance	1.0E+99

Source data points and calculated data points

	t	CA	CA calc	Delta CA
1	0	0.1	0.1	1.082E-12
2	60	0.007524	0.007524	-6.075E-12
3	120	0.00315504	0.003155	1.438E-11
4	180	0.00097056	0.0009706	-1.773E-11
5	240	0.00072784	0.0007278	1.278E-11
6	300	0.00048512	0.0004851	-4.861E-12
7	360	0.0002424	0.0002424	-3.196E-13

Graph



3. From report the polynomial equation is accurate for negative derivatives points and choose the first negative derivatives points at the (Table 4.4) and excel plot ($-dC_A/dt$) of (NaOH) versus its concentration in (Table 4.4) showing in (Figure 4.24).

Table 4.4**:** poly math batch (III) first negative derivative points

Time (s)	**CA**	**polynomial equation [dC_A/dt]**	**Rate of reaction [$- dC_A/dt$]**
0	0.1	-0.0036539	0.0036539
60	0.007449505	-0.000326	0.000326
180	0.00096095	-4.045E-05	4.045E-05

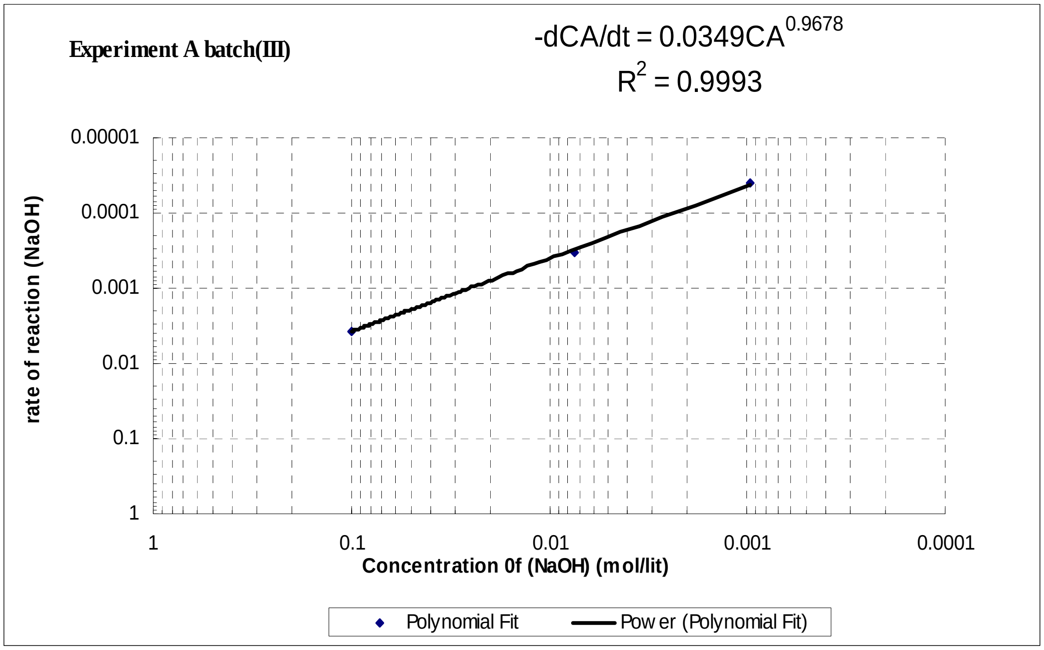


Figure 4.24: Experiment A batch (III) Excel program to plot rate of reaction (NaOH) versus its concentration in (Table 4.4).

4. Summary of discussion of experiment A

Table 4.5: Summary of discussion of experiment A

NO of Batches	Numerical Method	average	CHEMCAD Appendix B Actual values	average	Poly math	average
1	1.2283	1.16683	1.007	1.007	1.0581	1.0382
2	1.1316		1.007		1.0888	
3	1.1406		1.007		0.9678	

4.2.2. Discussion Experiment B

The results of overall order with respect to caustic soda are shown in Figures (4.7 to 4.12) and (Table 4.6) .

Table 4.6: Experiment B Average overall reaction order with respect to (NaOH)

NO Of Batches	overall reaction order with respect to (NaOH)	Average over all reaction order with respect to (NaOH)
1	2.0332	2.0144
2	1.9821	
3	2.0279	

Average overall reaction order with respect to (NaOH) was obtained in Experiment B equal 2.0144 on average, which is a 0.72 % high than literature value .

Therefore, the difference is simple and acceptable.

1. Evaluate $b = \alpha - a$ the order with respect to Ethyl acetate

b= 2.0144-1.16683 = 0.8476

2. Summary of discussion of experiment B

Table 4.7: Summary of discussion of experiment B

NO of Batches	Numerical Method	average	CHEMCAD Appendix B Actual values	average
1	2.0332	2.0144	2.0011	2.0011
2	1.9821		2.0011	
3	2.0279		2.0011	

4.2.3. Discussion Experiment C

The results of rate constant for second order with respect to caustic soda are shown in Figures(4.13 to 4.18) and (Table 4.8).

Table 4.8: Experiment C rate constant for second order reaction with respect to (NaOH)

NO Of Batches	**Temperatures (^0C)**	**rate constant for second order reaction with respect to (NaOH)**	**Literature value**	**Error %**
Batch (I)	31.2	0.1822	0.1667	9.298
Batch (II)	37.7	0.2751	0.2486	10.6596
Batch (III)	45.5	0.3806	0.3932	-3.204

We obtained a reaction rate in Experiment C batch (I) 0.1822 lit/mol*s which is a 9.298 % high than literature value.

We obtained a reaction rate in Experiment C batch (II) 0.2751 lit/mol*s which is a 10.6596 % high than literature value.

We obtained a reaction rate in Experiment C batch (III) 0.3806 L/mol*s which is a 3.204 % less than literature value.

Reasons of this difference:

1. Temperature reading, at the time of samples withdrawn

Before mixing the reactants the temperature of reactor was constant then after reactants mixed the reaction increased temperatures of reactants according to heat of reaction, temperatures of every sample was withdrawn from reactor was measured ,The results are shown that in (Table 4.9)

Table 4.9: Measuring the temperatures of every sample was withdraw from reactor

Samples	**Temp batch(I)**	**Average**	**Temp batch (II)**	**Average**	**Temp batch (III)**	**Average**
1	31.2	31.3	37.7	38.12	45.1	45.22
2	31.3		38.3		45.2	
3	31.5		38.6		45.5	
4	31.3		38.3		45.2	
5	31.2		37.7		45.1	

From (Table 4.9) a new value of reactor temperature and value of rate constant from literature (Appendix C , Table C.1) ,the result shown in (Table 4.10).

Table 4.10: Experiment C reason (1) rate constant for second order reaction with respect to (NaOH)

NO of batches	**Temperatures (^{0}C)**	**rate constant for second order reaction with respect to (NaOH)**	**New Literature value according to reason(1)**	**Error %**
Batch (I)	31.3	0.1822	0.1677	8.65
Batch (II)	38.12	0.2751	0.2547	8.01
Batch (III)	45.22	0.3806	0.3865	-1.527

We obtained a reaction rate in Experiment C batch (I) 0.1822 lit/mol*s which is a 8.65 % high than literature value.

We obtained a reaction rate in Experiment C batch (II) 0.2751 lit/mol*s which is a 8.01 % high than literature value.

We obtained a reaction rate in Experiment C batch (III) 0.3806 lit/mol*s which is a 1.527 % less than literature value.

4.2.4. Discussion Activation Energy

The Activation Energy was determined experimentally calculation of the by carrying out the reaction at several different temperatures experiment C showing that.

The activation energy can be found from a plot of $\ln k_A$ as a function of (1/T) for equation (2.16), the results shown in (Table 4.11) and (Figure 4.25),(Figure 4.26) .

$$\ln k_A = \ln A - \frac{E}{R}(\frac{1}{T}) ----------------------- Eq(2.16)$$

1) Calculation Activation Energy from Experiment C (Table 4.8) and literature from Appendix C .

Table 4.11: Activation Energy Experiment C and Actual or literature value from Appendix C

Measurement	**Temperature [C]**	**Exp(k)**	**Ac (k)**	**T(^{0}K)**	**1/T (1/^{0}K)**	**Exp ln(k)**	**Ac ln(k)**
Batch (I)	31.2	0.1822	0.1667	304.35	0.003286	-1.70265	-1.7915595
Batch (II)	37.7	0.2751	0.2486	310.85	0.003217	-1.29062	-1.3919101
Batch (III)	45.5	0.3806	0.3932	318.65	0.003138	-0.96601	-0.9334369

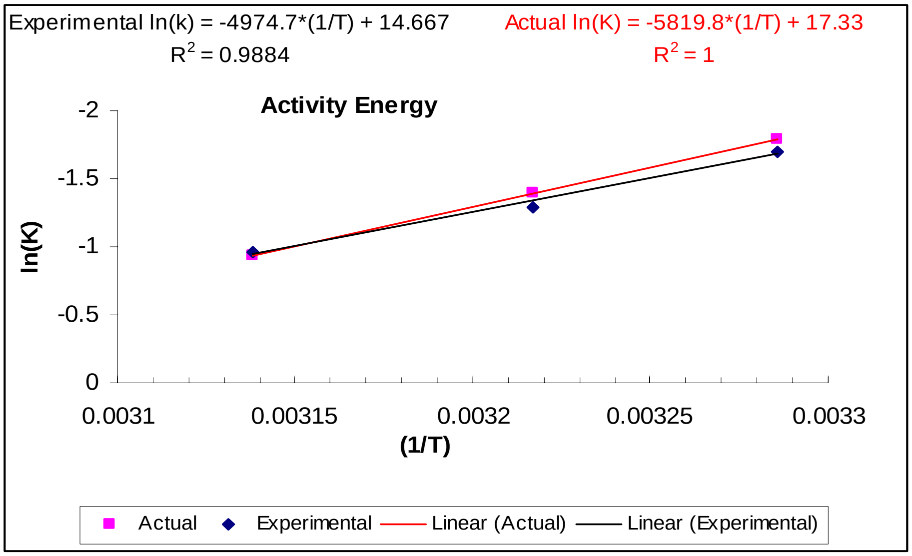


Figure 4.25: Excel plot Activation Energy form (Table 4.11).

$$\frac{E_{Exp}}{R} = -4974.7^0k \Rightarrow E_{Exp} = -4974.7^0k \times 8.314\frac{Jole}{mol.^0k} = -41359.6558 \quad Jole/mol$$

We obtained activation energy 41359.6558 J/mol, which is a 14.529 % less than literature value .

2) Activation Energy from Experiment C batch (I) and batch (II)

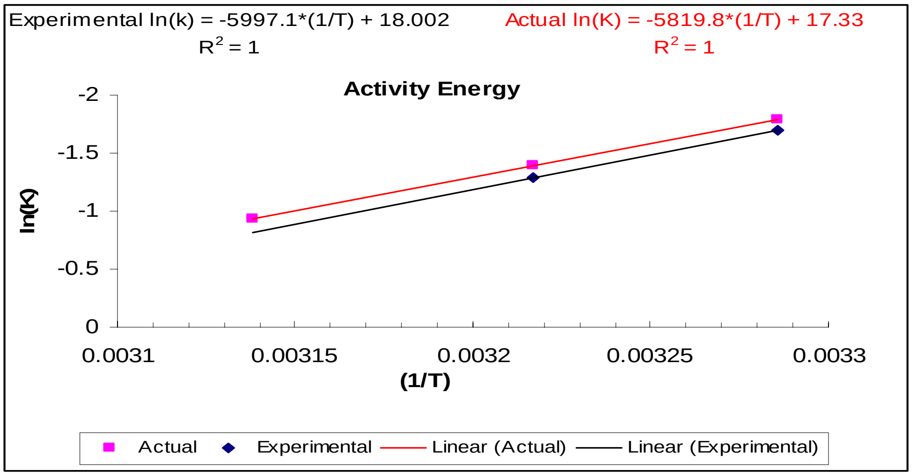


Figure 4.26: Excel plot Activation Energy for Experiment C batch(I) and batch(II) from (Table 4.11).

$$\frac{E_{Exp}}{R} = -5997.1\ {}^{0}k \Rightarrow E_{Exp} = -5997.1^{0}k \times 8.314 \frac{Jole}{mol.^{0}k} = -49859.8894\ \frac{Jole}{mol}$$

We obtained activation energy 49859.8894 J/mol, which is a 3.1 % high than literature value.

3) Summary discussion of saponification experiments.

Table 4.12: Summary discussion of saponification experiments

Experiments	Temperatures	Equation	Average experimental value	Appendix B Actual values	Order
A (Excess material)	**Iso thermal operation at 37.7 °C**	$-r_A = k'C_A^{a}$	$-r_A = 0.0672\,C_A^{1.16683}$	$-r_A = 0.0545\,C_A^{1.0078}$	a = 1.16683
B (Equal molar)	**Iso thermal operation at 37.7 °C**	$-r_A = k''C_A^{\alpha}$	$-r_A = 0.169\,C_A^{2.0144}$	$-r_A = 0.2463\,C_A^{2.0011}$	b =0.8476
C (Equal molar)	**31.2 °C**	$-r_A = k''C_A^{2}$	$-r_A = 0.1822\,C_A^{2}$	$-r_A = 0.1667C_A^{2.0011}$	
	37.7 °C		$-r_A = 0.2751C_A^{2}$	$-r_A = 0.2486C_A^{2.0011}$	
	45.5 °C		$-r_A = 0.3806\,C_A^{2}$	$-r_A = 0.3932C_A^{2.0011}$	

4) The comprehensive rate equation

Described by Eq (2.13)

$$-r_A = k_A C_A^a C_B^b ---------------------- Eq(2.13)$$

By use Eq(2.17)

$$k_A[T] = k_A[T_o]\ e^{\frac{E}{R}(\frac{1}{T_o}-\frac{1}{T})} ------------------ Eq(2.17)$$

Table 4.13: The comprehensive rate equation

Temperatures	Reaction constant		Activation Energy		Order			
	Experimental value Experiment C	Appendix B Actual values	Experimental value Experiment C	Actual values section (2.7)	Experimental		Actual values	
					a	b	a	b
$T_o = 31.2^0 C$ $=304.35^{\circ} k$	0.1822	0.1667	(49859.8894 J/mol)	(48390.16 J/mol).	1.1667	0.8476	1.0	1.0

From (Table 4.13) by use equation (2.13 and 2.17)

1. Actual comprehensive rate equation :

$$-r_A = k_A[T_o]\cdot e^{\frac{E}{R}(\frac{1}{T_o}-\frac{1}{T})} \times C_A^a\, C_B^b = 0.1667\cdot e^{5820\cdot(\frac{1}{304.35}-\frac{1}{T})} \times C_A\, C_B ---- Eq(4.1)$$

2. Experimental comprehensive rate equation :

$$-r_A = k_A[T_o]\cdot e^{\frac{E}{R}(\frac{1}{T_o}-\frac{1}{T})} \times C_A^a\, C_B^b = 0.1822\cdot e^{5997.1\cdot(\frac{1}{304.35}-\frac{1}{T})} \times C_A^{1.1667}\, C_B^{0.8476} ---- Eq(4.2)$$

CHAPTER FIVE

CONCLUSION & RECOMMENDATION

5.1 Conclusion

1. The pilot - scale batch reactor has been refurbished with a minimal cost.
2. Use of the unit with the water bath has provided better temperature control compared with using the heater and cold water around the jacket of reactor.
3. A saponification reaction provides a safe option for use as a case study.
4. Reaction kinetics is in line with literature.
5. In experiment A access material (Three times the concentration) is sufficient in this experiment. The use of the Polynomial Fit method (poly math software) provided better than finite difference method.
6. In experiment B (equal molar) the use of finite difference method to calculate the derivative is sufficient.

5.2 Recommendations

1. Automation for batch reactor through adding hardware and software components such as lab view, Matlab.
2. To add experiment to fifth year undergraduate students to reinforce their experimental skills.

REFERENCES

1. Fogler, S. H.; “Elements of Chemical Reaction Engineering,” Prentice Hall, 4rd Edition (2006)
2. A. SARATH BABU,“BATCH REACTOR - Interpretation of rate data”, (http://www.engin.umich.edu/3.Batch_reactor.ppt)
3. Tsujikawa, Hiroo, and Inoue, Hakuai. “The Reaction Rate of Alkaline Hydrolysis of Ethyl Acetate”, Bulletin of the Chemical Society of Japan, 39: 1837-1842
4. www.csupomona.edu/~tknguyen/che435/Notes/files_2Experiments_ Homogenuous_Batch_Reactor.pdf
5. UNIVERSITY OF MINNESOTA DULUTH - DEPARTMENT OF CHEMICAL ENGINEERING- ChE 3211-4211,” BATCH REACTOR “, exbatrea.pdf

APPENDIXES

Appendix A : Materials Safety Data Sheet (MSDS)

1. Chemical Safety Data: Sodium Hydroxide

Common synonyms	Caustic soda, soda lye
Formula	NaOH
Physical properties	Form: White semi-transparent solid, often supplied as pellets weighing about 0.1g Stability: Stable, but hygroscopic. Absorbs carbon dioxide from the air. Melting point: 318 C Water solubility: high (dissolution is very exothermic) Specific gravity: 2.12
Principal hazards	Contact with the eyes can cause serious long-term damage The solid and its solutions are corrosive. Significant heat is released when sodium hydroxide dissolves in water
Safe handling	Always wear safety glasses. Do not allow solid or solution to come into contact with your skin. When preparing solutions swirl the liquid constantly to prevent "hot spots" developing.

Emergency	Eye contact: Immediately flush the eye with plenty of water. Continue for at least ten minutes and call for immediate medical help. Skin contact: Wash off with plenty of water. Remove any contaminated clothing. If the skin reddens or appears damaged, call for medical aid. If swallowed: If the patient is conscious, wash out the mouth well with water. Do not try to induce vomiting. Call for immediate medical help
Disposal	Small amounts of dilute sodium hydroxide can be flushed down a sink with a large quantity of water, unless local rules prohibit this. Larger amounts should be neutralised before disposal.
Protective equipment	ALWAYS wear safety glasses when handling sodium hydroxide or its solutions. If you need gloves, neoprene, nitrile or natural rubber are suitable for handling solutions at concentrations of up to 70%

Table A.1 : Chemical Safety Data for Sodium Hydroxide

2. Chemical Safety Data : Ethyl acetate

Common synonyms	Ethyl ethanoate , acetic acid ethyl ester, ethanoic acid ethyl ester
Formula	$CH_3COOC_2H_5$
Physical properties	Form: Colourless liquid with a sweet, fruity smell Stability: Stable, but highly flammable

	Melting point: -84 C Boiling point: 77 C Water solubility: soluble Specific gravity: 0.9 Flash point: -4 C
Principal hazards	Ethyl acetate is very flammable
Safe handling	Wear safety glasses. Make sure that there is no source of ignition near where you work. The vapour may be ignited by contact with a hot plate or hot water pipe - no naked flame is needed.
Emergency	Eye contact: Immediately flush the eye with plenty of water. If irritation persists call for medical help. Skin contact: Wash off with water. If swallowed: Flush the mouth out with water if the person is conscious. If the amount swallowed is substantial call for medical help.
Disposal	Small amounts of ethyl acetate can be flushed down a sink with a large quantity of water, unless local rules prohibit this. This material is very flammable, so care must be taken to avoid any build-up of vapour in sink or sewers.
Protective equipment	Safety glasses. If gloves are required, use polyvinyl alcohol (PVA).

Table A.2 : Chemical Safety Data for Ethyl acetate

Appendix B : CHEMCAD Software (Saponification Reaction Simulation)

1. Experiment A access material isothermal operation $37.7\ ^{0}C$

Sodium Hydroxide concentration of 0.1M and ethyl acetate concentration of 0.3M are fed to the reactor as an initial charge at $37.7\ ^{0}$C and 101325 Pa. The rate constant is 0.2486 lit/mole*sec. Simulate the dynamic batch reactor for 6 minutes and plot the change in concentration of NaOH as it changes with time.

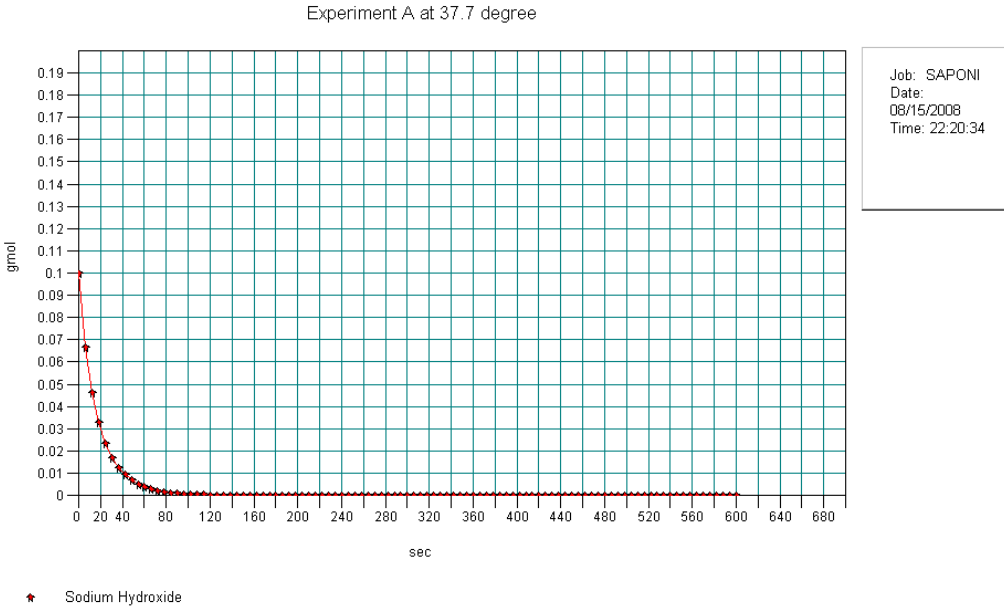


Figure B .1: CHEMCAD Experiment A concentration time data

Table B .1: CHEMCAD, Experiment A concentration time data combine with finite difference and Excel

Plot Title:		**Experiment A at 37.7 degree**			
Set Name:		**Sodium Hydroxide**			
Data Points:		**61**			
sec	gmol	rate	sec	gmol	rate
0	0.1	0.006628	186	8.76E-06	4.27E-07
6	0.066648	0.00449	192	6.57E-06	3.2E-07
12	0.046122	0.00283	198	4.92E-06	2.4E-07
18	0.032689	0.001882	204	3.69E-06	1.8E-07
24	0.023541	0.001296	210	2.77E-06	1.35E-07
30	0.017141	0.000914	216	2.07E-06	1.01E-07
36	0.012578	0.000655	222	1.55E-06	7.57E-08
42	0.009282	0.000475	228	1.16E-06	5.67E-08
48	0.006877	0.000348	234	8.73E-07	4.25E-08
54	0.005111	0.000256	240	6.54E-07	3.19E-08
60	0.003806	0.000189	246	4.90E-07	2.39E-08
66	0.002839	0.00014	252	3.68E-07	1.79E-08
72	0.002121	0.000105	258	2.75E-07	1.34E-08
78	0.001585	7.79E-05	264	2.06E-07	1.01E-08
84	0.001186	5.81E-05	270	1.55E-07	7.54E-09
90	0.000887	4.34E-05	276	1.16E-07	5.65E-09
96	0.000664	3.25E-05	282	8.69E-08	4.24E-09
102	0.000498	2.43E-05	288	6.52E-08	3.17E-09
108	0.000373	1.82E-05	294	4.88E-08	2.38E-09
114	0.000279	1.36E-05	300	3.66E-08	1.78E-09
120	0.000209	1.02E-05	306	2.74E-08	1.34E-09
126	0.000157	7.64E-06	312	2.06E-08	1E-09
132	0.000117	5.73E-06	318	1.54E-08	7.51E-10
138	8.80E-05	4.29E-06	324	1.16E-08	5.63E-10
144	6.60E-05	3.22E-06	330	8.66E-09	4.22E-10
150	4.94E-05	2.41E-06	336	6.49E-09	3.16E-10
156	3.71E-05	1.81E-06	342	4.86E-09	2.37E-10
162	2.78E-05	1.35E-06	348	3.65E-09	1.78E-10
168	2.08E-05	1.01E-06	354	2.73E-09	1.33E-10
174	1.56E-05	7.6E-07	360	2.05E-09	9.50E-11
180	1.17E-05	5.7E-07			

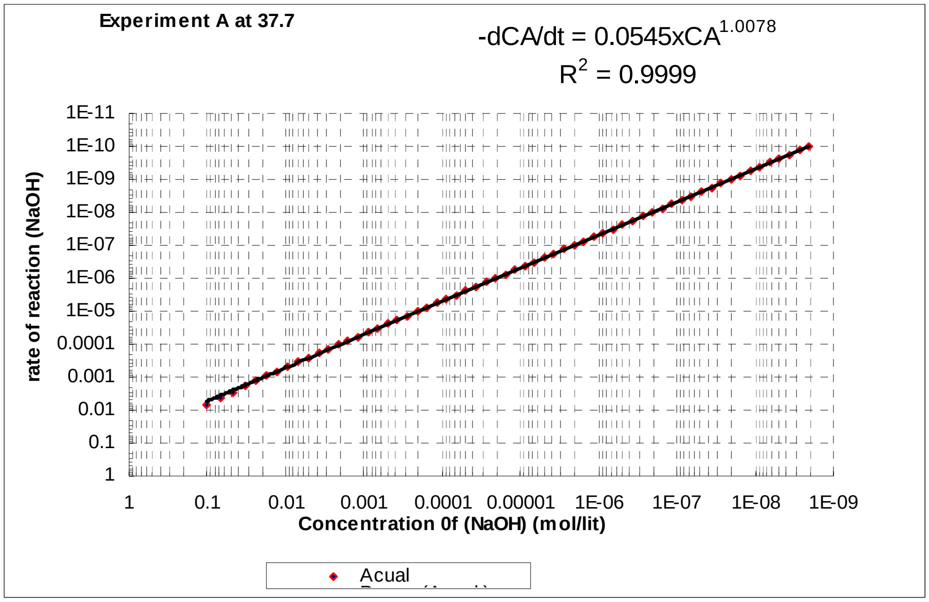


Figure B .2: CHEMCAD, Experiment A Excel plot log-log data in (Table B.1).

2. Experiment B Equal molar isothermal operation $37.7\ ^0C$

Sodium Hydroxide concentration of 0.1M and ethyl acetate concentration of 0.1M are fed to the reactor as an initial charge at 37.7C and 101325 Pa. The rate constant is 0.2486 lit/mole*sec. Simulate the dynamic batch reactor for 6 minutes and plot the change in concentration of NaOH as it changes with time.

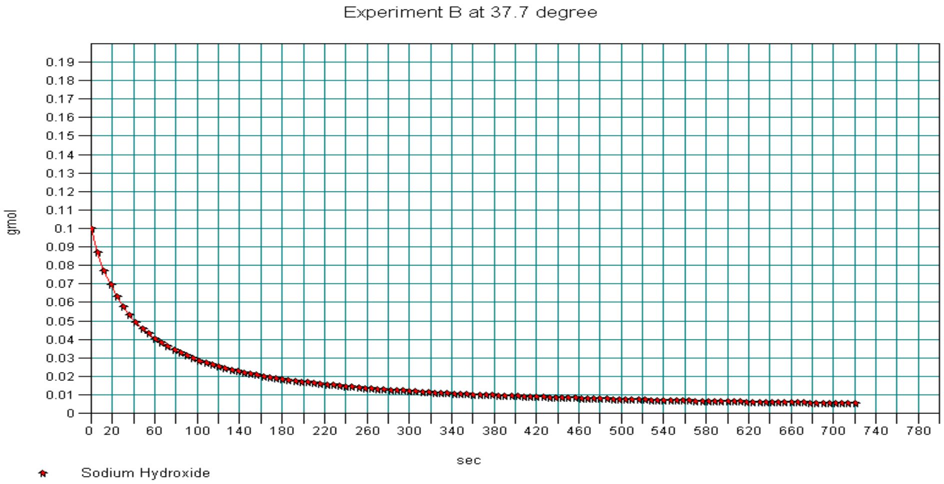


Figure B.3 : CHEMCAD Experiment B concentration time data

Table B .2: CHEMCAD, Experiment B concentration time data combine with finite difference and Excel

Plot Title:		**Experiment B at 37.7 degree**			
Set Name:		**Sodium Hydroxide**			
Data Points:		**121**			
sec	gmol	rate	sec	gmol	rate
0	0.1	0.002374858	186	0.018004	0.00007945
6	0.087202	0.001891142	192	0.01754	7.54083E-05
12	0.077306	0.0014813	198	0.017099	7.16667E-05
18	0.069426	0.0011919	204	0.01668	6.81917E-05
24	0.063004	0.000979875	210	0.016281	6.49667E-05
30	0.057668	0.000819875	216	0.0159	6.19667E-05
36	0.053165	0.000696142	222	0.015537	5.91667E-05
42	0.049314	0.000598475	228	0.01519	0.00005655
48	0.045983	0.000520042	234	0.014858	5.41E-05
54	0.043074	0.000456083	240	0.014541	5.18167E-05
60	0.04051	0.000403242	246	0.014237	4.9675E-05
66	0.038235	0.000359092	252	0.013945	4.76583E-05
72	0.036201	0.000321817	258	0.013665	4.57583E-05
78	0.034373	0.000290058	264	0.013396	4.3975E-05
84	0.032721	0.000262792	270	0.013137	4.22917E-05
90	0.03122	0.000239192	276	0.012888	0.0000407
96	0.02985	0.000218633	282	0.012649	3.92083E-05
102	0.028596	0.000200617	288	0.012418	3.77917E-05
108	0.027443	0.000184742	294	0.012195	3.64417E-05
114	0.026379	0.000170683	300	0.01198	0.000035175
120	0.025395	0.000158167	306	0.011773	3.39667E-05
126	0.024481	0.000146975	312	0.011573	3.28167E-05
132	0.023631	0.000136933	318	0.011379	3.17333E-05
138	0.022838	0.000127892	324	0.011192	3.06917E-05
144	0.022096	0.000119717	330	0.011011	2.97083E-05
150	0.021401	0.000112292	336	0.010835	0.000028775
156	0.020749	0.000105542	342	0.010666	0.000027875
162	0.020135	9.93917E-05	348	0.010501	2.70167E-05
168	0.019556	9.37583E-05	354	0.010341	2.62083E-05
174	0.01901	8.85833E-05	360	0.010186	2.5425E-05
180	0.018493	0.000083825	366	0.010036	2.46783E-05

Table B.2: continuous

Plot Title:		**Experiment B at 37.7 degree**			
Set Name:		**Sodium Hydroxide**			
Data Points:		**121**			
sec	gmol	rate	sec	gmol	rate
372	0.00989	2.39725E-05	558	0.006818	1.13892E-05
378	0.009749	2.32875E-05	564	0.00675	1.11642E-05
384	0.009611	2.26333E-05	570	0.006684	1.09458E-05
390	0.009477	2.20075E-05	576	0.006619	1.07333E-05
396	0.009347	2.14067E-05	582	0.006555	1.05275E-05
402	0.00922	2.083E-05	588	0.006492	1.03283E-05
408	0.009097	2.02775E-05	594	0.006431	1.01333E-05
414	0.008977	1.97458E-05	600	0.006371	9.94417E-06
420	0.00886	1.92342E-05	606	0.006312	9.76083E-06
426	0.008746	1.87425E-05	612	0.006254	9.5825E-06
432	0.008635	1.827E-05	618	0.006197	9.40833E-06
438	0.008527	1.78158E-05	624	0.006141	9.23917E-06
444	0.008421	1.73767E-05	630	0.006086	9.075E-06
450	0.008318	1.69542E-05	636	0.006032	8.91417E-06
456	0.008218	1.65475E-05	642	0.005979	8.75833E-06
462	0.00812	1.61542E-05	648	0.005927	8.60667E-06
468	0.008024	1.57758E-05	654	0.005875	8.45917E-06
474	0.00793	0.00001541	660	0.005825	8.31417E-06
480	0.007839	1.50567E-05	666	0.005776	8.17333E-06
486	0.00775	1.47158E-05	672	0.005727	8.03667E-06
492	0.007662	1.43858E-05	678	0.005679	7.90333E-06
498	0.007577	1.40667E-05	684	0.005632	7.77333E-06
504	0.007494	1.37592E-05	690	0.005586	7.645E-06
510	0.007412	1.34608E-05	696	0.00554	7.52083E-06
516	0.007332	1.31725E-05	702	0.005496	7.40083E-06
522	0.007254	1.28933E-05	708	0.005452	7.2825E-06
528	0.007177	1.26217E-05	714	0.005408	7.16667E-06
534	0.007102	0.00001236	720.001	0.005366	7.05333E-06
540	0.007029	1.21058E-05			
546	0.006957	1.18592E-05			
552	0.006887	1.16208E-05			

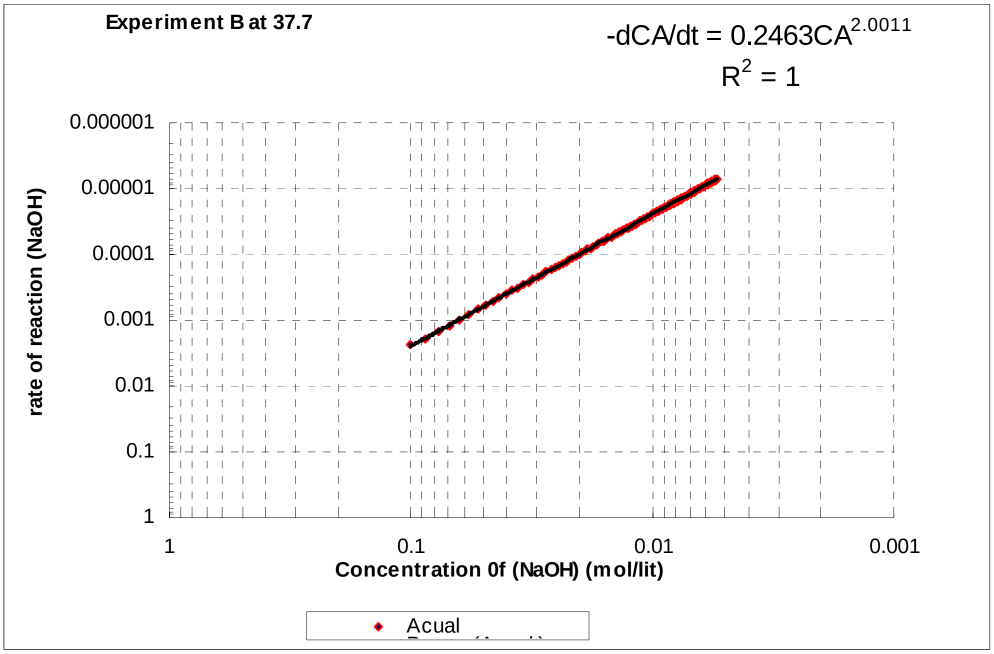


Figure B .4: CHEMCAD Experiment B Excel plot log-log data in (Table B.2).

3. Experiment C from literature the reaction is second order Table (C.1) Substitute in Eq (3.13).

$$\frac{1}{C_A} = k''.t + \frac{1}{C_{A0}} ---------------------------------- Eq(3.13)$$

Batch (I) at 31.2^0C :

$$\frac{1}{C_A} = k''.t + \frac{1}{C_{A0}} = 0.1667.t + \frac{1}{0.1} = 0.1667.t + 10 ------------- Eq(B.1)$$

Batch (II) at 37.7^0C :

$$\frac{1}{C_A} = k''.t + \frac{1}{C_{A0}} = 0.2486.t + \frac{1}{0.1} = 0.2486.t + 10 -------------- Eq(B.2)$$

Batch (III) at 45.5^0C :

$$\frac{1}{C_A} = k''.t + \frac{1}{C_{A0}} = 0.3932.t + \frac{1}{0.1} = 0.3932.t + 10 -------------- Eq(B.3)$$

Appendix C: Rate constant versus Temperatures in Saponification Literature Values

Table C.1: Rate constant vs Temperatures Saponification Literature Values

Temp (c)	k	Temp (c)	k	Temp (c)	k	Temp (c)	k	Temp (c)	k
25.0	0.1120	28.3	0.1387	31.6	0.1709	34.9	0.2097	38.2	0.2562
25.1	0.1127	28.4	0.1396	31.7	0.1720	35.0	0.2110	38.3	0.2578
25.2	0.1135	28.5	0.1405	31.8	0.1731	35.1	0.2123	38.4	0.2593
25.3	0.1142	28.6	0.1414	31.9	0.1742	35.2	0.2136	38.5	0.2609
25.4	0.1150	28.7	0.1423	32.0	0.1753	35.3	0.2149	38.6	0.2625
25.5	0.1157	28.8	0.1432	32.1	0.1764	35.4	0.2163	38.7	0.2640
25.6	0.1165	28.9	0.1441	32.2	0.1775	35.5	0.2176	38.8	0.2656
25.7	0.1172	29.0	0.1450	32.3	0.1786	35.6	0.2189	38.9	0.2672
25.8	0.1180	29.1	0.1460	32.4	0.1797	35.7	0.2203	39.0	0.2688
25.9	0.1188	29.2	0.1469	32.5	0.1808	35.8	0.2216	39.1	0.2704
26.0	0.1196	29.3	0.1478	32.6	0.1819	35.9	0.2230	39.2	0.2720
26.1	0.1203	29.4	0.1488	32.7	0.1831	36.0	0.2243	39.3	0.2737
26.2	0.1211	29.5	0.1497	32.8	0.1842	36.1	0.2257	39.4	0.2753
26.3	0.1219	29.6	0.1507	32.9	0.1854	36.2	0.2271	39.5	0.2769
26.4	0.1227	29.7	0.1516	33.0	0.1865	36.3	0.2284	39.6	0.2786
26.5	0.1235	29.8	0.1526	33.1	0.1877	36.4	0.2298	39.7	0.2803
26.6	0.1243	29.9	0.1536	33.2	0.1889	36.5	0.2312	39.8	0.2819
26.7	0.1251	30.0	0.1545	33.3	0.1900	36.6	0.2326	39.9	0.2836
26.8	0.1259	30.1	0.1555	33.4	0.1912	36.7	0.2341	40.0	0.2853
26.9	0.1267	30.2	0.1565	33.5	0.1924	36.8	0.2355	40.1	0.2870
27.0	0.1276	30.3	0.1575	33.6	0.1936	36.9	0.2369	40.2	0.2887
27.1	0.1284	30.4	0.1585	33.7	0.1948	37.0	0.2384	40.3	0.2904
27.2	0.1292	30.5	0.1595	33.8	0.1960	37.1	0.2398	40.4	0.2921
27.3	0.1301	30.6	0.1605	33.9	0.1972	37.2	0.2413	40.5	0.2939
27.4	0.1309	30.7	0.1615	34.0	0.1984	37.3	0.2427	40.6	0.2956
27.5	0.1317	30.8	0.1626	34.1	0.1997	37.4	0.2442	40.7	0.2974
27.6	0.1326	30.9	0.1636	34.2	0.2009	37.5	0.2457	40.8	0.2991
27.7	0.1334	31.0	0.1646	34.3	0.2021	37.6	0.2471	40.9	0.3009
27.8	0.1343	31.1	0.1656	34.4	0.2034	37.7	0.2486	41.0	0.3027
27.9	0.1352	31.2	0.1667	34.5	0.2046	37.8	0.2501	41.1	0.3045
28.0	0.1360	31.3	0.1677	34.6	0.2059	37.9	0.2517	41.2	0.3063
28.1	0.1369	31.4	0.1688	34.7	0.2072	38.0	0.2532	41.3	0.3081
28.2	0.1378	31.5	0.1699	34.8	0.2085	38.1	0.2547	41.4	0.3099

Table C.1: Continuous

Temp (c)	k	Temp (c)	k	Temp (c)	k	Temp (c)	k	Temp (c)	k
41.5	0.3117	44.8	0.3777	48.1	0.4558	51.4	0.5480	54.7	0.6565
41.6	0.3136	44.9	0.3799	48.2	0.4584	51.5	0.5511	54.8	0.6600
41.7	0.3154	45.0	0.3821	48.3	0.4610	51.6	0.5541	54.9	0.6636
41.8	0.3173	45.1	0.3843	48.4	0.4636	51.7	0.5572	55.0	0.6672
41.9	0.3191	45.2	0.3865	48.5	0.4662	51.8	0.5603	55.1	0.6708
42.0	0.3210	45.3	0.3887	48.6	0.4689	51.9	0.5634	55.2	0.6744
42.1	0.3229	45.4	0.3910	48.7	0.4715	52.0	0.5665	55.3	0.6781
42.2	0.3248	45.5	0.3932	48.8	0.4742	52.1	0.5696	55.4	0.6818
42.3	0.3267	45.6	0.3955	48.9	0.4768	52.2	0.5727	55.5	0.6854
42.4	0.3286	45.7	0.3977	49.0	0.4795	52.3	0.5759	55.6	0.6891
42.5	0.3305	45.8	0.4000	49.1	0.4822	52.4	0.5791	55.7	0.6929
42.6	0.3325	45.9	0.4023	49.2	0.4849	52.5	0.5823	55.8	0.6966
42.7	0.3344	46.0	0.4046	49.3	0.4876	52.6	0.5855	55.9	0.7004
42.8	0.3364	46.1	0.4069	49.4	0.4904	52.7	0.5887	56.0	0.7041
42.9	0.3383	46.2	0.4093	49.5	0.4931	52.8	0.5919	56.1	0.7079
43.0	0.3403	46.3	0.4116	49.6	0.4959	52.9	0.5952	56.2	0.7117
43.1	0.3423	46.4	0.4140	49.7	0.4987	53.0	0.5984	56.3	0.7156
43.2	0.3443	46.5	0.4163	49.8	0.5015	53.1	0.6017	56.4	0.7194
43.3	0.3463	46.6	0.4187	49.9	0.5043	53.2	0.6050	56.5	0.7233
43.4	0.3483	46.7	0.4211	50.0	0.5071	53.3	0.6083	56.6	0.7272
43.5	0.3504	46.8	0.4235	50.1	0.5099	53.4	0.6117	56.7	0.7311
43.6	0.3524	46.9	0.4259	50.2	0.5128	53.5	0.6150	56.8	0.7350
43.7	0.3544	47.0	0.4283	50.3	0.5156	53.6	0.6184	56.9	0.7389
43.8	0.3565	47.1	0.4308	50.4	0.5185	53.7	0.6218	57.0	0.7429
43.9	0.3586	47.2	0.4332	50.5	0.5214	53.8	0.6251	57.1	0.7468
44.0	0.3607	47.3	0.4357	50.6	0.5243	53.9	0.6286	57.2	0.7508
44.1	0.3628	47.4	0.4382	50.7	0.5272	54.0	0.6320	57.3	0.7549
44.2	0.3649	47.5	0.4406	50.8	0.5301	54.1	0.6354	57.4	0.7589
44.3	0.3670	47.6	0.4431	50.9	0.5331	54.2	0.6389	57.5	0.7629
44.4	0.3691	47.7	0.4457	51.0	0.5360	54.3	0.6424	57.6	0.7670
44.5	0.3712	47.8	0.4482	51.1	0.5390	54.4	0.6459	57.7	0.7711
44.6	0.3734	47.9	0.4507	51.2	0.5420	54.5	0.6494	57.8	0.7752
44.7	0.3755	48.0	0.4533	51.3	0.5450	54.6	0.6529	57.9	0.7793