# EFFECT OF TEMPEERATURE ON THE RATE OF PRODUCTION OF OXALIC ACID FROM THE BARK OF EUCALYPTUS CAMALDULENSIS AT REACTION TEMPERATURES OF 60 $^{o}$C AND 70 $^{o}$C

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**MINNA, NIGER -STATE**

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DEPARTMENT OF CHEMICAL ENGINEERING

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NOVEMBER 2004.

# DECLARATION

I Dare Folorunsho Morakinyo hereby declare that this project work was wholly and solely done by me under the supervision of Dr K.R. Onifade, during the 2003/2004 academic session of the federal university of technology, Minna. Niger-state.

Dare Folorunsho Morakinyo
(98/6938EH)

20/11/2004
DATE

# CERTIFICATION

This is to certify that this project work was wholly and solely done by Dare Folorunsho Morakinyo (98/6938EH) of the department chemical engineering, under the supervision of Dr.K.R. Onifade as partial fulfillment for the award of Bachelor of Engineering (B. ENG) by the federal university of technology, Minna. Niger-state.

---------------------------- 20/11/2004

Dr.K.R. Onifade — DATE

(Supervisor)

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Dr.F. Aberuagba — DATE

(H.O.D.)

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EXTERNAL EXAMINER — DATE

# DEDICATION

I dedicate this project work to the memory of my late, wonderful, caring, and loving parent, Mr. Solomon Olalekan Dare and Mrs. Esther Titilayo Dare. Thank you for believing in me and for preparing me for the challenges of life. I also thank God for using you as a tool in shaping my life.

You are forever remembered, forever loved and forever my heroes.

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# ABSTRACT

The great demand for oxalic acid due to it numerous use has in turn place demand on the chemical engineer to design an economic process from a cheap raw material source (Eucalyptus camaldulensis). But to design a process, it important to know the kinetics of the reaction involved. Hence the aim of the research work is to find the effect of temperature on the rate of production of oxalic acid from eucalyptus camaldulensis at reaction temperature of 60°C and 70°C. Back titration was employed to generate data of how the concentration reduces with time while integral and differential method of analysis was use in finding the rate equation from the laboratory data obtained, which was then compared to deduce the effect of temperature. In conclusion, the research shows that more quantity of oxalic acid (within a particular time interval) is produced at higher temperature.

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# NOMENCLATURE

| | |
|---|---|
| $C_A$ | Concentration of acid left |
| $C_{AO}$ | Initial concentration of acid |
| $C_E$ | Concentration of oxalate left |
| $-r_A$ | Rate of conversion of acid ($dC_A/dt$) |
| $V_{td}$ | Volume of titrand (quenched mixture) |
| $V_t$ | Volume of titrant ($H_2SO_4$) |
| K | Rate constant |
| n | Order of reaction |

# CHAPTER ONE

## 1.0 INTRODUCTION

With the rapid progress and development in technology also came more dependency on chemical industries and chemical engineering for production of chemicals and other intermediates, which serve as raw material to many industries.

There are two main sub-division of chemical industry, the heavy chemical industry where output of a single plant may be thousands of tones a year and the fine chemicals industry which produce chemicals in small quantity but in higher state of purity (Breck 1989). In likewise manner, chemicals are also divided into two groups, the heavy chemicals and the fine chemicals (Ababio 1990) and ( Breck1989 ). Typical examples of heavy chemicals are sulphuric acid, ammonia,chlorine, urea,and methanol.

But, of great interest to us is an organic –heavy chemical of the diacarboxylic acid family. Diacarboxylic acids are organic acid with two carboxylic (COOH) functional group. Oxalic acid ( ethanedioc acid) which is the acid of interest , is the first member of this family. Oxalic acid is the only possible compounds in which two carboxylic groups are joined directly. Unlike other carboxylic acids except (formic acid) oxalic acid oxidizes readily, that explains it use in cleaning of metals ( Dr.Nurettin Sahin 2004). The other places it has found use are in dyeing of textiles, manufacturing of ink, and in preparing compounds such as glycolic acid and glyoxolic acid (anonymous 1994) .The very large demand of this acid in tones places demand on large production of it in tones per annum, which is not feasible on the pilot plant scale , there's therefore need to bring to bear the knowledge of chemical engineering economics .

And so, this drive to satisfy economic consideration bring us to making choice amidst the several method of producing oxalic acid that are available of which fermentation is an example (Baily and Ollis). Invariably, the discovery of relatively large content of calcium oxalate in the bark of eucalyptus camaldulensis opened up another feasible economic method of using(forest product) bark of eucalyptus as the basic raw material, which are most readily available and cheap.

However to make this feasibility a reality it is important to economically design a process and /or plant to produce oxalic acid from bark of camaldulensis. This design in turn depends on some preliminary studies of which kinetic studies is an important factor. It would be said to be impossible to have an economic design and a satisfactory control system, without carrying out kinetic of oxalic acid production from bark of eucalyptus camaldulensis. A minimum cost and optimum product yield is hence achieved from the design. This therefore bring us home to our objective, the kinetic studies of production of oxalic acid from the bark of eucalyptus camaldulensis and also justify the same.

## 1.1 AIM AND OBJECTIVES

The aim of this research work is to find the effect temperature has on the rate of production of oxalic acid from the bark of eucalyptus camaldulensis. And the objectives are; to generate laboratory data from laboratory scale reaction, using back titration method of quantitative analysis. Use integral and differential method of mathematical analysis to develop satisfactory rate equations to represent the process at $60^0$C and $70^0$C. And then comparing the rate equations obtained at both temperatures to deduce what effect temperature has on the production of oxalic acid from the bark of eucalyptus camaldulensis.

# CHAPTER TWO

## 2.1 ORIGIN AND DISTRIBUTION OF EUCALYPTUS CAMALDULENSIS

Eucalyptus camaldulensis, which is commonly, refer to, as river gum is specie of the eucalyptus, which are 20meter to 45 meter tall. Bark smooth throughout, white, gray brown or red. The leaves are leathery and hang vertically or obliquely. The adult leaves are moderately thick, 8cm to 30 cm long and 0.7cm to 2 cm wide, green and gray green in color, with a lateral vein at 40° to 50°. The inter-maginal vein is up to 2 mm from margin. Buds are globular-rostrate or ovoid conical and fruit are hemispherical ovoid, 5mm to 8mm long and wide with yellow seed. The trees are good producer of pollen and nectar for honey and their honey are of the first grade type (Chippendale G.M. 1988). The native of eucalyptus has been trace to Australia where their range extends from sub-alpines area to wet coastal forest temperate woodland and the arid inland. There is about 12 species of which occurs naturally outside of Australia but 700 are Australian endemics(Hill and Johnson 1995).

The eucalyptus species occurs (mostly) in the Australian mainland. Grows along and near watercourses, sometimes extending to hill, usually in open forest and woodland (Brooker and Kleinig 1996). Large distribution of eucalyptus camaldulensis (of Australian origin) has naturalized throughout riparian habitant in Californian has replace native trees in some area (Brooker and Kleinig1996).
Eucalyptus is also distributed over New Zealand, Tasmani and nearby islands.

In Nigeria, about 4000 hectares of eucalyptus has been planted by early 1974 with more of the plantation in the northern part of the country such as Kano, Kastina, Niger, Kaduna, and Plateau states. This large plantation in the northern part of the country cannot be unconnected to the fact that is first planted in this part of the country when the species of eucalyptus first came to Nigeria in 1916(Jackson and Ojo 1973). With increase in cultivation over 50 species of eucalyptus has been grown in Nigeria

## 2.2 EUCALYPTUS CAMALDULENSIS PRODUCTS AND USES

There are over 700 species and variety of the eucalyptus of which only 20 have been exploited commercially and less than a dozen are presently of economic importance.

One important product obtainable from eucalyptus is eucalyptus oil (essential oil) which is use in medicine, disinfectants, household and industrial liquid soaps and perfumes making.

The hard durable nature of the eucalyptus wood has made it important forestry. It is use for making canoe due to it smooth water resisting bark (Brooker and Kleinig 1996). It can also be use as electric pole due to it height and it non-smoking nature makes it useful as fuel in addition to the fact that it burns well when well dried (Hill 1979).

Aside from oxalic acid that is obtained from eucalyptus camaldulensis, tannin and alkanoids are also obtainable from eucalyptus camaldulensis. Tannin are contain as soluble material in the bark of eucalyptus species, use in tanning skins of animals to remove the hair and improve the quality hence converting hides to leather (Irwin 1981). Alkanoids are compounds, which find great use in medicine, emphasizing the importance of eucalyptus in medicine. In addition to the use of eucalyptus camaldulensis in pulp and paper production which is in the neighborhood of million of tones per year, it is also us as ornamental plant due to their attractive form, foliage, colorful flowers (as exemplified in California where they are use for landscaping).

## 2.3 OXALIC ACID

An acid is a substance which when dissolved in water produces hydrogen ion or hydroxonium ion as the only positive ion in solution. Acids could either be organic or inorganic. Oxalic acid is therefore an organic acid which falls under the carboxylic family of it kinds. Carboxylic acids are widespread in nature, often combined with other functional groups. The fatty acids are important components of the biomolecules known as lipids, especially fat and oil. This functional group is characterized by COOH. Hence it chemical formula is given as HOOC-COOH.

Oxalic acid is the only possible compound in which two carboxyl groups are joined directly; for this reason oxalic acid is one of the strongest organic acids. Oxalic acid are produced by the fusion of many oxygen-holding compounds with caustic alkalis, in this process cellulose (in the form of sawdust) is made into a stiff paste with a mixture of strong caustic potash and soda solution and heated in flat iron pans to 200°C-250°C. The somewhat dark-colored mass is lixiviated with a small amount of warm water in order to remove excess of alkali, the residual alkaline oxalates converted into insoluble calcium oxalate by boiling with milk of lime; the lime salt is separated, and decomposed by means of sulphuric acid. It is found that the sawdust obtained from soft woods is the best material for use in this process. Oxalic acid may be obtained synthetically by heating sodium in a current of carbon dioxide to 360°C.; by the oxidation of ethylene glycol; by heating sodium formate to 40°C. (V. Merz and W. Weith, Ber., 1882).

### 2.3.1 PHYSICAL AND CHEMICAL PROPERTIES OF OXALIC ACID

Oxalic acid are transparent, colorless crystals; odorless; whose anhydrous crystals are hygroscopic (absorbs moisture from the air). It commercially available as anhydrous or dehydrated crystals {$(COOH)_2.2H_2O$} or powder, when heated it loses its water of crystallization at 100.5°C., and begins to sublime at about 150 to 160° C, whilst on heating to a still higher temperature it partially decomposes into carbon dioxide and formic acid, or into carbon dioxide then to carbon monoxide and water; the latter decomposition being also brought about by heating oxalic acid with concentrated sulphuric acid. The acid melt at 101°C while it anhydrous acid melts at 189.5° C. Oxalic acid is very poisonous, but has its antidotes in milk of lime, chalk, or whiting followed by evacuation brought about by an enema or castor oil. Solubility of oxalic acid is about 100gram per liter of water, it is however more soluble in alcohol (1gram/2.5ml), glycerol (1gram/100ml), but totally insoluble in benzene, chloroform, petroleum and ether.

One very important chemical property of oxalic acid is it ability to act as reduction agent which is due to the ease with which it oxidizes. For example, potassium permanganate in acid solution oxidizes it to carbon dioxide and water; the manganese sulphate formed has a catalytic accelerating effect on the decomposition.

$$2MnO_4^-(aq) + 5\,H_2C_2O_4\,(aq) + 6\,H^+(aq) \longrightarrow 10\,CO_2(g) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$

Oxalic acid is oxidized to carbon dioxide in this reaction and the permanganate ion is reduced to the $Mn^{2+}$ ion.

$$\begin{array}{lcc} \text{Oxidation:} & H_2C_2O_4 \longrightarrow & CO_2 \\ & +3 & +4 \\ \text{Reduction:} & MnO_4^- \longrightarrow & Mn^{2+} \\ & +7 & +2 \end{array}$$

The permanganate ion removes electrons from oxalic acid molecules and thereby oxidizes the oxalic acid. Thus, the $MnO_4^-$ ion acts as an oxidizing agent in this reaction. Oxalic acid, on the other hand, is a reducing agent in this reaction. By giving up electrons, it reduces the $MnO_4^-$ ion to $Mn^{2+}$. Hence oxalic acid shows typical chemical properties of the carboxylic family. In addition to reduction reaction is esterification reaction which anhydrous oxalic acid refluxes with excess methanol or ethanol to yield ester without need of strong acid as catalyst.

$$(CO_2H)_2 + 2C_2H_5OH \longrightarrow (CO_2C_2H_5)_2 + 2H_2O$$

Acid chloride is also obtain when oxylchloride is reacted with phosphorus pentachloride

$$(CO_2H)_2 + 2PCl_5 \longrightarrow (COCl)_2 + 2POCl_3 + 2HCl$$

Alkali metal oxalate treated with soda lime yields hydrogen and carbonate, it does not form an anhydrate on heating with concentrated

$H_2SO_4$. Oxalic acid and oxalate are dehydrated to an equimolar mixture of carbon monoxide and dioxide. This behavior is the familiar elementary test for oxalic acid (Dazaley 1979).

## 2.3.2 USES OF OXALIC ACID

Unlike other carboxylic acids (except formic acid), Oxalic acid is readily oxidized; this makes it useful as a reducing agent for photography, bleaching, and ink removal. Biological production of high amounts of oxalic acid is of interest for biohydro metallurgical application, as oxalic acid is use to solubilise heavy metals from ores and minerals. The other major uses of oxalic acid are in textile cleaning, flame proofing, rust removal, and fabric dyeing; metal and equipment cleaning; anti-corrosion coating; chemical intermediate and catalyst; in the ceramics, and rubber industries.

## 2.4 CHEMICAL KINETICS

Chemical kinetics is the study of the mechanism and rate at which one chemical specie is converted to another. Hence chemical kinetics deals mainly with the mechanism and the rate of the reaction. The mechanism is the sequence of individual chemical event whose overall result produces the observed reaction. Mechanism could also be explain as the individual Collisional or elementary processes involving molecules ( atom ,ion, and radical inclusive ) that take place simultaneously or consecutively in producing the observe overall rate. Mechanisms of a reaction also give a activated complex of transition state, in term of the constitution molecules and geometry such as inter-atomic distances and angles. In development of mechanism, So much effort over a very long period of time is involved and are subject to changes over the years as new data are uncovered and new concept concerning chemical interaction are develop.

In order for a reaction to occur, a collision must occur; the collision must be of sufficient energy to break the necessary bonds and be of proper orientation. This is the basis of reaction rates. Factors effecting reaction rates are concentration of the reacting species found in the rate equation, temperature and the presence or absence of a catalyst. A rate equation of a reaction is a mathematical expression relating the rate of a reaction to the concentration of either reactants or products. One may not look at stoichiometry equation of the reaction, and determine the rate law. The term *rate* is often used to describe the change in a quantity that occurs per unit of time. The rate of inflation, for example, is the change in the average cost of a collection of standard items per year. The rate at which an object travels through space is the distance traveled per unit of time, such as miles per hour or kilometers per second. In chemical kinetics, the distance traveled is the change in the concentration of one of the components of the reaction. The rate of a reaction is therefore the change in the concentration of one of the reactants (x) that occurs during a given period of time t.

$$-r = x/t$$

In rate equation, the rate (-r) is written in term of concentration of the reactant rate constant (k) and order of reaction (n). As given in the example below

$$\mathbf{-r = k\, C_A{}^n}$$

Molecularity of an elementary reaction is the number of molecules involved in reaction, which has been found to have value of one, two or occasionally three. This however only is applicable to elementary reactions only. And the order of reaction is the power to which the concentration term(s) in the rate equation is raised.

$$-r = k\, C_A{}^a C_B{}^b\, C_C{}^c \,\ldots\ldots\ldots\, C_D{}^d$$

$$a + b + c + d = n$$

Where a, b, c, d are not necessarily related to the stoichiometric coefficients. And since the order refer to empirically found rate expression, it can have a fractional value and do not need be an integer. But it is important that the Molecularity be an integer, because it refers to the mechanism of the reaction.

### 2.4.1 TEMPERATURE AND CONCENTRATION DEPENDANCE OF RATE EQUATION

In order for a reaction to occur, a collision must take place. During this collision, existing bonds break and new bonds form. It takes energy to break bonds and energy is released when new bonds form. The collision must be of sufficient energy to break the necessary bonds. The energy source comes from the kinetic energy of the compound due to the velocity at which it is moving around. But then, the kinetic energy is temperature dependent. The higher the temperature, the faster the molecules are moving around, the greater the kinetic energy. This energy, as a function of kinetic energy and temperature is called the energy of activation. The collision must also be of proper orientation. This is related by the collision factor. The combination of these aspects the reaction are related to the rate of the reaction. These factors are related by a mathematical expression called the Arrhenius equation:

$$K = k_o e^{-E/RT}$$

Where;

$k_o$ = frequency or pre-exponential factor

$k$ = rate constant at a given temperature

$E$ = activation energy

8.314 J/mol K gives R (gas constant) and the choice of R will dictate the units for temperature. Finding $k_o$ and E and other molecular properties would have been an easy way out of chemical kinetics of elementary reaction to which it is applicable but chemical kinetics has not yet develop to this extent. (Smith 1980). At same concentration, but two different temperatures, the Arrhenius law indicates that

$$\ln r_2/r_1 = \ln k_2/k_1 = E/R\,(1/T_1 - 1/T_2)$$

Provided E is constant (Smith 1980).

Also considering the Brownian motions and the collision theory of molecules there most be collision between molecules involved in a reaction for the reaction to occur and the higher the rate of collision the higher would be the rate at which the reaction will proceed. Hence with few molecules of the reactants present, there would be slower reaction and the more the molecules of the reactants the faster the reaction would be. The rate of reaction therefore depends on the concentration of the reactants taking place in the reaction (Ababio 1990).

### 2.4.2 INTERPRETATION OF BATCH REACTOR DATA

The chemical engineer depends on the data obtained by the chemist in his laboratory to design a process line, design a reactor or optimize a process. Kinetics of a system or reaction is always determined in term of concentration at fixed temperature and in term of temperature at fixed concentration.

The experiment use in generating the data is done either in a batch reactor or in a flow reactor, but the batch reactor is preferred because of it high conversion. It also important to know that batch reactor may not be economical on a large-scale production. However an experimental batch reactor is operated at a constant temperature and constant volume. A batch reactor is bowl like reactor that handles a unit volume of reactant per time, in which is helds the reactants as they react.

Integral and differential methods of analysis are the two procedures use in analysing kinetic data obtained from the laboratory. The integral method of analysis involves guessing a form of rate equation, the equation is then use to plot a graph of $1/C_A - 1/C_{Ao}$. against time (t). The rate equation is accepted to satisfactorily fit the data if the plot is a straight line graph passing through the origin, hence it also confirms that reaction is second order reaction.

For differential method of analysis, the suggested rate equation is use (if it fits the data) to plot a graph of $C_A$ against time (t). From the $C_A$ against t plot, few points are picked to represent $dC_A/dt$ (r). Log r is then plotted against log $C_A$, then point at which it intercept the y-axis is log k and the slope of the graphs represent the reaction order.

The differential method is use in complicated situation that requires accurate and large data. The differential method is use to develop a rate equation to fit a data, while the integral method is use only in testing a rate equation or mechanism. Though integral method is easy to use but it is recommended when data are scattered such that derivative cannot be reliably found.

# CHAPTER THREE

## 3.1 APPARATUS AND REAGENT USED

Aside from the pestle and mortar that were used in reducing the bark to small particulate sizes, other apparatus used in the course of this experiment are mainly titration apparatus, which is the experimental analysis that forms the basis of this research work. The apparatus include; measuring cylinder, conical flasks, filter papers, pipette, burette, test tubes, funnels, timer and beakers. Vibratory shake sieve machine with different sieve meshes (Most importantly) consisting of 500µm, and 200µm and collection pan were used in obtaining a very fine particle size.

The hot water bath was used in heating the reacting mixture and the thermometer serve in monitoring the temperature of the mixture. The electronic balance also came handy in measuring little weights, in the course of the experiment.

Reagents that were used include potassium hydroxide (KOH), sulphuric acid ($H_2SO_4$) of 2% concentration. Phenolphthalein indicator was used for getting the end point, and only distilled water was used through out the experiment.

## 3.2 EXPRIMENTAL PROCEDURES

The fresh bark eucalyptus camaldulensis that was obtained from the national forestry department of the federal ministry of agriculture (Minna) and was dried. The drying was carried out such that a bark of constant humidity would be obtained, which was done by monitoring the weight of the bark after each drying day. This was continued until a constant mass was obtained for repeated measurements.

After the drying, the bark was granddad into fine particles using a pestle and mortar. And then using a vibratory shake with sieve screen of different sizes, sample was sieved into mesh size of 500µm, 250µm and through.

The sieved sample obtained, which is more like a powdery brownish substance was poured into a container with a good seal to avoid being blown away and the probability of absorbing atmospheric moisture.

Percentage concentration of potassium hydroxide and sulphuric acid were first converted to molar concentration as shown in the appendix to enable an accurate preparation of standard solutions of potassium hydroxide and sulphuric acid to 4% and 2% concentration respectively.

50g of 250μm sieved bark of eucalyptus camaldulensis was measured into a baker and 500cm$^3$ of 2% sulphuric acid ($H_2SO_4$) was added and stirred to form a homogeneous mixture. The homogeneous mixture was then placed in the water-bath that has been pre-heated to the desired temperature (60°c and 70°c). And 20minutes after the mixture was placed in the water-bath of stable temperature, about 15cm$^3$ of the reacting mixture was drawn for analysis. The 15cm$^3$ of the reacting mixture was filtered to obtain a clear filtrate. Of the clear filtrate, 10cm$^3$ was measured out in a conical flask and 10cm$^3$ of 4% potassium hydroxide (KOH) was also measured to quench, that is stop the reaction between calcium oxide in the bark and sulphuric acid ($H_2SO_4$) producing the oxalic acid. The mixture that results was then titrated with part of 2% $H_2SO_4$ in the burette, using phenolphthalein indicator. The volume of the acid from the burette was read and recorded. This was then repeated for other runs.

### 3.3 EXPERIMENTAL ANALYSIS

The data obtained on the experiment which was carried out at two different temperatures of 60°c and 70°c were separated heated and the conversion calculated using the expression derived below.

At time (t) equal zero (t=0)

Concentration of the reactant will be $C_{Ao}$.

The amount of the reactant consumed after a given time is given as $C_{Ao}X_A$ where $X_A$ is the conversion.

Therefore amount of reactant remaining will be given as

$C_{Ao} - C_{Ao}X_A$

$\therefore C_A = C_{Ao} - C_{Ao}X_A$ (3.0)

And $C_{Ao}X_A = C_{Ao} - C_A$

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}} \qquad (3.1)$$

The above equation 3.1 is therefore the expression used in calculating conversion using 0.375mol/dm3 as reference point for $C_{Ao}$.

### 3.3.1 INTEGRATION METHOD OF ANALYSIS

Having obtained a table from the experiment and the conversion at each stage, the next thing that was done was to suggest a rate equation.

Since an elementary reaction is a reaction whose stoichiometric equation corresponds to the rate equation, let assume that the reaction between calcium oxalate and sulphuric acid is an elementary reaction, which is given as below;

$$H_2SO_4 + CaO_4 \rightarrow (CO_2H)_2 + CaSO_4 \qquad (3.2)$$

From the stoichiometry equation

$$\frac{-dC_A}{dt} = kC_A C_e \qquad (3.3)$$

but since the reactant react at ratio 1:1

$\Rightarrow$ $C_{Ao} = C_e$, and hence $C_A = C_e$

Substituting $C_A$ for $C_e$ in equation 3.3

$$-\frac{dC_A}{dt} = kC_AC_A = kC_A^2 \qquad (3.4)$$

On integration of equation 3.4

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

$$\frac{1}{C_A} - \frac{1}{C_{Ao}} = kt \qquad (3.5)$$

Substituting equation 3.1 into 3.5

$$\frac{1}{C_{Ao}(1-X)} - \frac{1}{C_{Ao}} = kt$$

$$K = \frac{1}{tC_{Ao}}(1/(1-x) - 1) \qquad (3.6)$$

The integral method of analysis was therefore applied to test if the data obtained from the laboratory experiment fits the second order rate equation that was suggested. This involved;

1. Plotting a concentration ($1/C_A - 1/C_{Ao}$) against time (t) as from equation 3.5
2. Calculating the slope of the straight-line graph obtained to evaluate the value of the rate constant k.

Detail calculations and graph (figure 1) obtained is shown in the appendix.

### 3.3.2 DIFFERENTIAL METHOD OF ANALYSIS

Still considering the suggested rate equation as stated by equation 3.4, the logarithm of both sides are taken to have

$$\log (dC_A/dt) = \log k + \log C_A^2 = \log k + 2\log CA \qquad (3.7)$$

log $C_A$ was calculated from available data and log $(dC_A/dt)$ obtained by plotting a graph of $C_A$ against time (t).

Few points where picked on the $C_A$ against time curve and slopes at this these points where evaluated. The value obtained gives the $dC_A/dt$ value for such points.

Another graph of $dC_A/dt$ against $C_A$ was plotted and it intercept on y-axis gives the value of k and the slope of the graph gives value of the order of reaction n as given by equation 3.7 above.

The detail calculations of this analysis method and the graph obtained (figure 2 and figure 3) are shown in the appendix.

# CHAPTER FOUR

## 4.1 RESULTS

Considering the experiment that was carried out at 60°C, the integral method of analysis shows that the reaction would have it rate constant k to be 0.0131mol/sec cm$^3$, with the experimental data fitting into the second order rate equation as tested by the (integral) method and hence the rate equation is given as thus;

$$-r_A = 0.0131C_A^2 \qquad (4.1)$$

However for this same set of data the differential method of analysis was use to develop the rate equation and show that the rate constant (k) at this temperature would be 0.025mol/sec cm$^3$ and the order of reaction to be 1.93 giving rise to the rate equation below.

$$-r_A = 0.025C_A^{1.93} \qquad (4.2)$$

The extent of reaction for the experiment at 60°C was also calculated to be 22.75% after 20 minutes of the reaction and 40.80% after 140minutes of the reaction.

Now considering the set of data obtain from the experiment conducted at 70°C, the integral method of analysis also shows that at temperature the data obtained still conforms with the second order reaction rate. The integral method gave the value of the rate constant (k) to be 0.0152mol/sec cm$^3$, while the differential method of analysis also gave the value to be 0.071mol/sec cm$^3$ while the order of reaction was given to be equal to 2.04 which is approximately equal to 2. The equation below are the reactions rate equation as obtained from the integral and differential methods respectively.

$$-r_A = 0.0152C_A^2 \qquad (4.3)$$

$$-r_A = 0.071C_A^2 \qquad (4.4)$$

The extent of conversion for experiment at 70°C after 20 minutes of reaction is 29.76%and 43.76%after 140 minutes.

All these result are as obtained from the tables of results shown below.

TABLE 4.1: RAW DATA OBTAINED FROM LABORATORY EXPERIMENT

| Time(min) | Experiment at 60°c $V_t$ (cm$^3$) | | | Experiment at 70°c $V_t$ (cm$^3$) | | |
|---|---|---|---|---|---|---|
| | 1$^{st}$ RUN | 2$^{ND}$ RUN | AVERAGE | 1$^{ST}$ RUN | 2$^{ND}$ RUN | AVERAGE |
| 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 20 | 8.50 | 7.90 | 8.20 | 7.50 | 7.50 | 7.50 |
| 40 | 7.40 | 8.10 | 7.80 | 7.00 | 7.20 | 7.10 |
| 60 | 7.90 | 7.50 | 7.70 | 6.90 | 6.70 | 6.80 |
| 80 | 7.30 | 7.60 | 7.50 | 6.50 | 6.90 | 6.70 |
| 100 | 7.40 | 7.20 | 7.30 | 6.10 | 6.90 | 6.50 |
| 120 | 7.10 | 6.90 | 7.00 | 6.80 | 6.40 | 6.40 |
| 140 | 6.20 | 6.50 | 6.40 | 6.20 | 5.90 | 6.10 |

Table 4.1 was use in determining the rate equation and order of reaction for the experiment at 60°C and for that at 70°C using both methods of integration and differentiation. Each of the steps is shown in the appendix while the resulting tables for each plot that was made are shown in the next subsection. It is however very important to note that both experiment were carried out at the same concentration of 2% $H_2SO_4$.

TABLE 4.2

| EXPERIMENT AT 60°C | | | | EXPERIMENT AT 70°C | | |
|---|---|---|---|---|---|---|
| Time(min) | Volume of used acid $V_t$ ($cm^3$) | Volume of unused acid V($cm^3$) | Conc. of unused acid $C_A$ ($mol/cm^3$) | Volume of used acid $V_t$ ($cm^3$) | Volume of unused acid V($cm^3$) | Conc. of unused acid $C_A$ ($mol/cm^3$) |
| 0.00 | 0.00 | 0.00 | 0.3750 | 0.00 | 0.00 | 0.3750 |
| 20 | 8.20 | 1.80 | 0.2897 | 7.50 | 2.50 | 0.2634 |
| 40 | 7.80 | 2.20 | 0.2747 | 7.10 | 2.90 | 0.2484 |
| 60 | 7.70 | 2.30 | 0.2709 | 6.80 | 3.20 | 0.2372 |
| 80 | 7.50 | 2.50 | 0.2634 | 6.70 | 3.30 | 0.2334 |
| 100 | 7.30 | 2.70 | 0.2559 | 6.50 | 3.50 | 0.2260 |
| 120 | 7.00 | 3.00 | 0.2447 | 6.40 | 3.60 | 0.2222 |
| 140 | 6.40 | 3.60 | 0.2220 | 6.30 | 3.70 | 0.2184 |

### 4.1.1 RESULT OF EXPERIMENT AT 60°c

The tables below are the tables that where generated from table 4.2 with all calculation details shown in the appendix .

TABLE 4.3: EXTENT OF CONVERSION TABLE

| TIME(minutes) | CONVERSION(X) | $C_A$(mol/cm$^3$) |
|---|---|---|
| 0 | 0.00 | 0.3750 |
| 20 | 0.2275 | 0.2897 |
| 40 | 0.2675 | 0.2747 |
| 60 | 0.2776 | 0.2709 |
| 80 | 0.2976 | 0.2634 |
| 100 | 0.3176 | 0.2559 |
| 120 | 0.3475 | 0.2447 |
| 140 | 0.4080 | 0.2220 |

TABLE 4.4: TABLE OF INTEGRAL ANALYSIS

| TIME(minutes) | $C_A$(mol/cm$^3$) | 1/$C_A$(cm$^3$/mol) | 1/$C_A$-1/$C_{AO}$(cm$^3$/mol) |
|---|---|---|---|
| 0.00 | 0.3750 | 2.67 | 0.00 |
| 20 | 0.2897 | 3.45 | 0.78 |
| 40 | 0.2747 | 3.64 | 0.97 |
| 60 | 0.2709 | 3.69 | 1.02 |
| 80 | 0.2634 | 3.80 | 1.13 |
| 100 | 0.2559 | 3.91 | 1.25 |
| 120 | 0.2447 | 4.09 | 1.42 |
| 140 | 0.2220 | 4.50 | 1.83 |

TABLE 4.5: TABLE OF DIFFERENTIAL ANALYSIS

| $C_A$(mol/dm$^3$) | -rA(mol\cm3 sec) | Log $C_A$ | -Log $r_A$ |
|---|---|---|---|
| 0.34 | 0.0041 | -0.47 | -2.39 |
| 0.2897 | 0.0022 | -0.54 | -2.66 |
| 0.27 | 0.0014 | -0.57 | -2.85 |

This table was obtain from the concentration (CA) against time (t) curve by picking some point on the curve and determining their slope (-r).

### 4.1.2 RESULTS OF EXPERIMENT AT 70$^{o}$c

TABLE 4.6: EXTENT OF CONVERSION TABLE

| TIME(minutes) | CONVERSION(X) | $C_A$ (mol/cm$^3$) |
|---|---|---|
| 0 | 0.00 | 0.3750 |
| 20 | 0.2976 | 0.2634 |
| 40 | 0.3376 | 0.2484 |
| 60 | 0.3669 | 0.2372 |
| 80 | 0.3776 | 0.2334 |
| 100 | 0.3973 | 0.2260 |
| 120 | 0.4075 | 0.2222 |
| 140 | 0.4376 | 0.2109 |

TABLE 4.7: TABLE OF INTEGRAL ANLYSIS

| TIME(minutes) | $C_A$(mol/cm$^3$) | 1/$C_A$(cm$^3$/mol) | 1/$C_A$ -1/$C^{Ao}$ (cm$^3$/mol) |
|---|---|---|---|
| 0.00 | 0.3750 | 2.67 | 0.00 |
| 20 | 0.2634 | 3.80 | 1.13 |
| 40 | 0.2484 | 4.03 | 1.36 |
| 60 | 0.2372 | 4.22 | 1.55 |
| 80 | 0.2334 | 4.29 | 1.62 |
| 100 | 0.2260 | 4.43 | 1.76 |
| 120 | 0.2222 | 4.50 | 1.83 |
| 140 | 0.2109 | 4.74 | 2.07 |

TABLE 4.8: TABLE OF DIFFERENTIAL ANALYSIS

| $C_A$ (mol/dm$^3$) | -rA (mol/sec cm$^3$) | log $C_A$ | -log $r_A$ |
|---|---|---|---|
| 0.30 | 0.0052 | -0.52 | -2.28 |
| 0.28 | 0.0038 | -0.55 | -2.42 |
| 0.26 | 0.0022 | -0.59 | -2.66 |

## 4.2 DISCUSSION OF RESULTS

The rate constant (k) obtained for 60°C using the integral and differential method of analysis differs by 0.0119 mol/sec cm$^3$. The order of reaction as obtained form differential method is 1.93, which is very close to second order and on approximation actually gives a second order.

In a similar way, comparing the results obtained for the experiment that was carried out at 70°C shows that the difference of 0.0558 mol/sec cm$^3$, which is quite high. But the order of the reaction obtained from both methods gives the order of the reaction to still be a second order.

In both experiments (at 60°C and 70°C) the value obtained for the order of reaction was all given to be approximately equal to two (2) Which implies a second order reaction. At 60°C the value of the rate constant (k) obtained by both integral and differential methods are low compared to those obtained at 70°C using this same methods. That is 0.0131 mol/sec cm$^3$ at 60°C as against 0.0152 mol/sec cm$^3$ at 70°C as given by integral method of analysis. And 0.025 at 60°C as against 0.071 mol/sec cm$^3$ at 70°C as given by differential method of analysis. These differences therefore show that at higher temperature the rate of reaction is higher.

Also comparing the extent of conversion of the reaction at 60°C and after 20 minutes of reaction the conversion was calculated to be equal to 22.76%.

At the end of each experiment (that is after 140minutes) the final conversion that was achieved by experiment at 60°C was still lower than that achieved after the same time interval by the experimental at 70°C.

The 0.0119mol/sec cm$^3$ difference between values of the rate constant experiment at 60°C as given under the comparison of results could be due to the higher accuracy the differential method has over the integral method. The same reason also holds for the remarkable high differenceof 0.0558mol/sec $cm^3$ obtain for the experiment at 70°C.

The high extent of conversion of 27.75% and 29.76%for 60°c and 70°C respectively after 20 minutes of each experiment, (i.e. 60°C and 70°C) is due to high concentration (present at the start of the reaction), bringing about high interaction between the reactant which means high of frequency collision (Ababio 1990).

For the experiment at 60°C, between the time interval of 20 minutes to40 minutes, 40minutes to 60minutes, 60 minutes to 80 minutes the extent of conversion between these intervals are 4%,2%,2%,3% and 6.1%respectively.There was an increase in the 80 to 100 minutes interval and then a sudden jump to 6.1% between 100 to 120 minutes interval.

So also, between time interval of 20 to 40 minutes, 40 to 60 minutes,60 to 80 minutes,80 to 100 minutes, 100 to 120 minutes and 120 to 140 minutes of experiment carried out at 70°C, the extent of conversion between such interval are 4%,3%,1.1%,2%,1% and 3% respectively. However throughout the experiment life no change in temperature from the fixed temperature was noticed. But it was noticed that these discrepancies in conversion most have occurred when there was poor or no stirring at all.

# CHAPTER FIVE

## 5.1 CONCLUSION

Both integral and differential methods of analysis provide a rate equation. But the integral method was only use to confirm the conformity of the laboratory data to the second order rate, while the differential method was use to develop the specific rate equation. And haven judge differential method of analysis as to be more accurate (J.M Smith 1980), it is therefore adopted and hence equation 5.1 and 5.2 are the required rate equations

$$-r_A = 0.025C_A^{1.93} \quad (5.1)$$

$$-r_A = 0.071C_A^{2.04} \quad (5.2)$$

The above equation 5.1 represents the rate equation for the experimental data at 60°C and equation 5.2 represent the experimental data at 70°C. And with the extent of final conversion at 60°C and that at 70°C being 27.75% and 29.76% respectively, brings this work to a clear deductive conclusion.

And so in conclusion, the rate constant (k) depends on temperature of the reaction. The rate constant (k) increases in value with increase in temperature and hence the rate of reaction is faster at higher temperature of 70°C, but the order of reaction remains the same. Hence, greater quantity of oxalic acid will be produce at 70°C than at 60°C for the same production time. Temperature therefore has a significant effect on the rate of production of oxalic acid from the bark of eucalyptus camaldulensis.

## 5.2 RECOMMENDATION

It is recommended that another research work should be done on the effect of stirring so as to gain more insight to the factors that affect production of oxalic acid from the bark of eucalyptus camaldulensis.

# REFERENCES

Smith J. M (1980) Chemical reaction kinetics
Mc Graw hill international publisher

Otave Levenspil (1999) chemical engineering kinetics
Oregon state university (USA)

SHAFI` I.S.(1998) Production of oxalic acid from the bark of eucalyptus camaldulsis.
B. Eng thesis.

W.G Brecks, R.J.C Brown J.D.McCowan (1989). Chemistry for science and engineering ( 2nd edition )
McGaw hill Ryerson ltd.

Mohammed Abdulkardir (2003) Kinetic study for the production of oxalic acid from eucalyptus camaldulensis.
B. Eng thesis.

Brooker.M and Kleinig D. (1996) Eucalyptus : A guide to identification.
Reed publisher, Australia.

# APPENDIX 1

(A). Conversion of 2% $H_2SO_4$ to molar concentration

% Concentration of original acid =98%

% Concentration of acid to be diluted = 2%

$\therefore M_1V_1 = M_2V_2$

$M_1$ =% conc. of 98% acid

$M_2$ = % conc. of 2% acid

$V_1$ = volume of 98% acid ($cm^3$)

$V_2$ = volume of 2% acid ($cm^3$) =500$cm^3$

$\Rightarrow V_1 = 2 \times 500/98 = 10.20CM^3$

$\Rightarrow$10.20$cm^3$ of $H_2SO_4$ (98%) is added to 489.80$cm^3$of distilled water to obtain 500$cm^3$ of 2%$H_2SO_4$. Therefore 20.40$cm^3$ will be required for 1000$cm^3$ of 2% $H_2SO_4$.

Molecular mass of $H_2SO_4$ =98g

Density of conc. acid =1.84g/$dm^3$

Volume = mass/ density = 98/1.84 =53.26

For 98% conc.

Vol =100 × 53.26/98 = 54.40$cm^3$

$\therefore$ 54.40 in 1000$cm^3$ =1mol/$dm^3$

$\therefore$ 20.40 in 1000$cm^3$ =0.3750mol/$dm^3$ .

B). Conversion of 4% KOH to molar concentration

4% conc. 4gis present in 100$cm^3$ of water

$\therefore$ 40g is present in 100$cm^3$of water

To calculate for molar solution,

Molar mass of KOH =56g

$\therefore$ 56% of KOH in 1000$cm^3$0f water =1mol/$dm^3$

$\Rightarrow$ 40g of KOH in 1000$cm^3$ of water = 0.7143 mol/$dm^3$

# APPENDIX 2

Appendix 2 shows the calculation steps use in obtaining table 4.2 It however important to take note of the equation below as reference would be made to them.

$H_2SO_4 + CaC_2O_4 \rightarrow (CO_2H)_2 + CaSO_4$ (1)

$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + H_2O$ (2)

$2KOH + H_2SO_4 \rightarrow K_2SO_4 + H_2O$ (3)

Equation (1) is the equation of the original reaction for producing oxalic acid, equation (2) is the quenching reaction and equation (3) is the titrimetric equation.

## EXPERIMENT AT 60$^{0}$c

### After 20 minutes

1000cm$^3$ contains o.375 mole $H_2SO_4$

1.8cm$^3$ contains 0.000675 mole $H_2SO_4$.

From stoichiometry of quenching reaction,1 mole $H_2SO_4$ reacts with 2 mole KOH.

0.000675 moles $H_2SO_4$ will react with

0.000675 × 2 =0.00135 moles KOH

Similarly,

1000cm$^3$ contains 0.7143 moles of KOH

since quenching reaction is at ratio 1:2 moles of KOH needed for quenching is 0.007143 - 0.00135 = 0.005793 moles KOH

Mole of $H_2SO_4$ quenched =0.005793/2 =0.0028965 $H_2SO_4$

But 10cm$^3$ of filtrate contain 0.2897 mole /dm$^3$ $H_2SO_4$

### After 40 minutes

1000CM$^3$ contains 0.3750 $H_2SO_4$
2.2 cm$^3$ contains 0.000825 $H_2SO_4$
from equation (2), 0.000825 will react with
0.000825 × 2 = 0.00165 moles of KOH
Similarly,
1000cm$^3$ contains 0.7143 moles KOH
and 10cm$^3$ contains 0.007143
KOH for quenching = 0.07143 – 0.001725 = 0.005418
$H_2SO_4$ quenched = 0.005418/2 = 0.002709 moles $H_2SO_4$
10cm$^3$ filtrate contains 0.002709
and 1000cm$^3$ contains 0.2709mole /dm$^3$ $H_2SO_4$

### After 80 minutes

1000cm$^3$ contains 0.3750 moles $H_2SO_4$
2.5cm$^3$ contains 0.0009375 moles $H_2SO_4$
from equation (2) 0.0009375 moles $H_2SO_4$ will react with
0.0009375 × 2 = 0.001875 moles KOH
Similarly,
1000cm$^3$ contains 0.7143 moles KOH and 10cm$^3$ contains 0.007143 moles KOH
KOH for quenching = 0.007143 – 0.001875 = 0.005268moles
$H_2SO_4$ quenched = 0.005268/2 = 0.002634 moles $H_2SO_4$
$\Rightarrow$ 1000cm$^3$ contains 0.2709 moles/ dm$^3$ $H_2SO_4$

### After 100 minutes

1000cm$^3$ contains 0.375 moles $H_2SO_4$
2.7cm$^3$contain 0.001013 moles $H_2SO_4$
From equation (2) 0.001013 will react with
0.001013 × 2 =0.02026 moles KOH
Similarly,
1000cm$^3$ contains 0.7143 moles KOH
And 10cm$^3$ contains 0.007143 moles KOH

KOH for quenched =0.007143 -0.002026 = 0.005117

$H_2SO_4$ quenched =0.005117/2 = 0.002559 moles $H_2SO_4$

⇒ 1000cm$^3$ will contain 0.2559 mol/dm$^3$

After 120 minutes

1000cm$^3$ contains 0.3750 moles

3.0 cm$^3$contains 0.001125

From equation (2) 0.001125moles $H_2SO_4$ will react with

0.001125 × 2 =0.00225 moles KOH

Similarly,

1000cm$^3$ contains 0.7143 and 10cm$^3$ contains 0.007143

KOH for quenching =0.007143 – 0.00225 = 0.004893 moles KOH

$H_2SO_4$ quenched = 0.004893/2 = 0.002447

⇒1000cm$^3$ contains 0.2447 mol/dm$^3$ $H_2SO_4$

After 140 minutes

1000cm$^3$ contain 0.3750 moles $H_2SO_4$

3.6cm$^3$ contains 0.00135 moles $H_2SO_4$

From equation (2)

0.00135 × 2 = 0.0027moles KOH

Similarly,

10cm$^3$ contains 0.007143

KOH for quenching = 0.007143 – 0.00270 = 0.004443

$H_2SO_4$ quenched =0.004443/2 = 0.00222 moles $H_2SO_4$

⇒ 1000cm$^3$ contains 0.222mol/dm$^3$ $H_2SO_4$

## EXPERIMENT AT 70°C

### After 20 minutes

1000cm$^3$ contains 0.3750 mole $H_2SO_4$
2.5cm$^3$ contains 0.009375 mole $H_2SO_4$
0.009375 moles $H_2SO_4$ wil react with
0.009375 $\times$ 2 = 0.001875 moles KOH
Similarly,
10cm$^3$ contains 0.007143 moles KOH
KOH for quenching =0.007143 – 0.001875 = 0.005268
$H_2SO_4$ quenched = 0.005268/2 = 0.002634 moles $H_2SO_4$
$\Rightarrow$ 1000CM$^3$ contains 0.2634mol/dm$^3$ $H_2SO_4$

### After 40 minutes

1000 cm$^3$ contain 0.3750 moles $H_2SO_4$
2.9cm$^3$ contain 0.001088
0.001088mole $H_2SO_4$ will react with
0.001088 x 2 = 0.002176moles KOH
Similarly,10cm$^3$ contains 0.007143moles KOH
KOH for quenching = 0.007143 -0.00217 = 0.004967
$H_2SO_4$ quenched = 0.004967/2 =0.002484
$\Rightarrow$ 1000cm$^3$ contains 0.2484mol/dm$^3$

### After 60 minutes

1000cm$^3$ contain 0.3750 moles $H_2SO_4$
3.2 cm$^3$ contain 0.0012moles $H_2SO_4$
0.0012 moles $H_2SO_4$ will react with
0.0012 x 2 =0.0024 moles KOH
Similarly, 10cm$^3$ contains 0.007143 moles KOH
KOH for quenching =0.007143 - 0.0024 = 0.004743
$H_2SO_4$ quenched = 0.004743/2 = 0.002372
$\Rightarrow$ 1000cm$^3$ contains 0.2372mol/dm$^3$ $H_2SO_4$

After 80 minutes

1000cm$^3$ contains 0.3750 moles $H_2SO_4$

3.3 cm$^3$ contains 0.001238 moles $H_2SO_4$

0.001238 will react with

0.001238 x 2 = 0.002475 mole KOH

Similarly, 10cm$^3$ contains 0.007143 moles KOH

KOH for quenching = 0.007143 -0.002475 = 0.004668

$H_2SO_4$ quenching = 0.004668/2 =0.002334

⇒ 1000cm$^3$ contains 0.2334mol/dm$^3$ $H_2SO_4$

After 100 minutes

1000cm$^3$ contains 0.3750 moles $H_2SO_4$

3.5cm$^3$ contains 0.0013125 moles $H_2SO_4$

0.0013125 will react with

0.0013125 x 2 =0.002624 moles KOH

Similarly, 10cm$^3$ contains 0.007143

KOH for quenching = 0.007143 - 0.002624 = 0.004519

$H_2SO_4$ quenched = 0.004519/2 = 0.002260 moles $H_2SO_4$

⇒ 1000cm$^3$ contains 0.2260mol/dm$^3$ $H_2SO_4$

After 120 minutes

1000cm$^3$ contains 0.3750 moles $H_2SO_4$

3.6cm$^3$ contains 0.00135

0.00135 will react with 0.00135 x 2 = 0.0027moles KOH

Similarly, 10cm$^3$ contains 0.007143

KOH for quenching = 0.007143 - 0.0027 = 0.004443 moles KOH

$H_2SO_4$ quenched = 0.004443/2 = 0.002222

⇒ 1000cm$^3$ contains 0.2222mol/dm$^3$ $H_2SO_4$

After 140 minutes

1000cm$^3$ contains 0.3750 moles $H_2SO_4$

$3.9cm^3$ contains 0.01463 moles $H_2SO_4$

0.01463 will react with 0.01463 x 2 = 0.002926 moles KOH

Similarly, $10cm^3$ contains 0.007143 moles KOH

KOH for quenching = 0.007143 – 0.002926 = 0.004217 moles KOH

$H_2SO_4$ quenched = 0.004217/2 =0.002109

$\Rightarrow$ $1000cm^3$ contains $0.2109mol/dm^3$ $H_2SO_4$

## APPENDIX 3

This appendix is showing the calculations by which table 4.3 and 4.7 for 60°C and 70°C respectively where obtained.

### For 60°C

t = 0

$X_A = (C_{Ao} - C_A)/C_{Ao}$

$X_A = (0.3750- 0.3750)/0.3750 = 0.00$

t =20 minutes

$X_A = (0.3750-0.2897)/0.3750 = 0.2275$

t =40 minutes

$X_A = (0.3750-0.2747)/0.3750 = 0.2675$

t =60 minutes

$X_A = (0.3750-0.2709)/0.3750 = 0.2776$

t = 80 minutes

$X_A = (0.3750-0.2634)/0.3750 = 0.2976$

t =100 minutes

$X_A = (0.3750-0.2559)/0.3750 = 0.3176$

t =120 minutes

$X_A = (0.3750-0.2447)/0.3750 = 0.3475$

t =140 minutes

$X_A = (0.375-0.2220)/0.3750 = 0.4080$

For 70°C

t = 0

$X_A$ = (0.3750-0.3750)/0.3750 = 0.00

t =20 minutes

$X_A$ = (0.3750-0.2634)/0.3750 = 0.2976

t = 40 minutes

$X_A$ = (0.37580-0.2484)/0.3750 = 0.3376

t = 60 minutes

$X_A$ = (0.3750-0.2334)/0.3750 = 0.3776

t = 100 minutes

$X_A$ = (0.3750-0.2334)/0.3750 = 0.3973

t =120 minutes

$X_A$ = (0.3750-0.2222)/0.3750 = 0.4075

t = 140 minutes

$X_A$ = (0.375-0.2109)/0.3750 = 0.4376

## APPENDIX 4

Integral Method Of Analysis At 60°C

Scale of graph

X-axis, 1cm represents 10minutes

Y-axis, 5cm represents 1 $dm^3$/mol

Slope = $(y_1 - y_2)/(x_1 - x_2)$

But, slope = k = rate constant

And so,

Slope = (1.3 - 0.79)/ (100 – 61) = 0.0131

Integral Method Of Analysis At 70°C

Similarly,

Slope = (1.83 – 0.6)/ (120 - 39) = 0.0152

## APPENDIX 5

This appendix shows the calculations, which table 4.5 and 4.8 where obtained from the curve of $C_A$ against time (t), for 60°C and 70°C respectively. That is the differential method.

Now taking a slop at any given point from the plot of $C_A$ against time (t).

### For 60°C

At 0.34mol/dm$^3$

$-r_A = (0.365-0.25)/ (28-0) = 0.0041$

At 0.2897mol/dm$^3$

$-r_A = (0.34-0.24)/ (64-0) = 0.0022$

At 0.27mol/dm$^3$

$-r_A = (0.313-0.2)/ (79-0) =0.0014$

### For 70°C

At 0.3mol/dm$^3$

$-r_A = (0.345-0.20)/ (28-0) = 0.0052$

At 0.28mol/dm$^3$

$-r_A = (0.33-0.2)/ (34-0) = 0.0038$

At 0.26mol/dm$^3$

$-r_A = (0.3-0.2)/(45-0) = 0.0022$

Now finding the values of k and n from the slope of the graph $\log r_A$ against $\log C_A$.

Slope = (0-(-1.6))/ (0-(-0.83)) = 1.93

But n = slope = 1.93

Intercept on y-axis = k

And from $\log r_A = \log k + n \log C_A$

For this plot intercept = -1.6

$\therefore \log k = -1.6$

$k = 10^{(-1.6)} = 0.025$

k =0.025mol/sec cm$^3$

Similarly for experiment at 70°C

Slope = (0-(-1.15))/ (0-(-0.563)) = 2.04

Hence n = 2.04

Intercept on y-axis = -1.15

$\therefore$ logk = -1.15

k = $10^{(-1.15)}$ = 0.071 mol/sec $cm^3$

# INTEGRATION METHOD OF ANALYSIS

## A PLOT OF CONCENTRATION AGAINST TIME

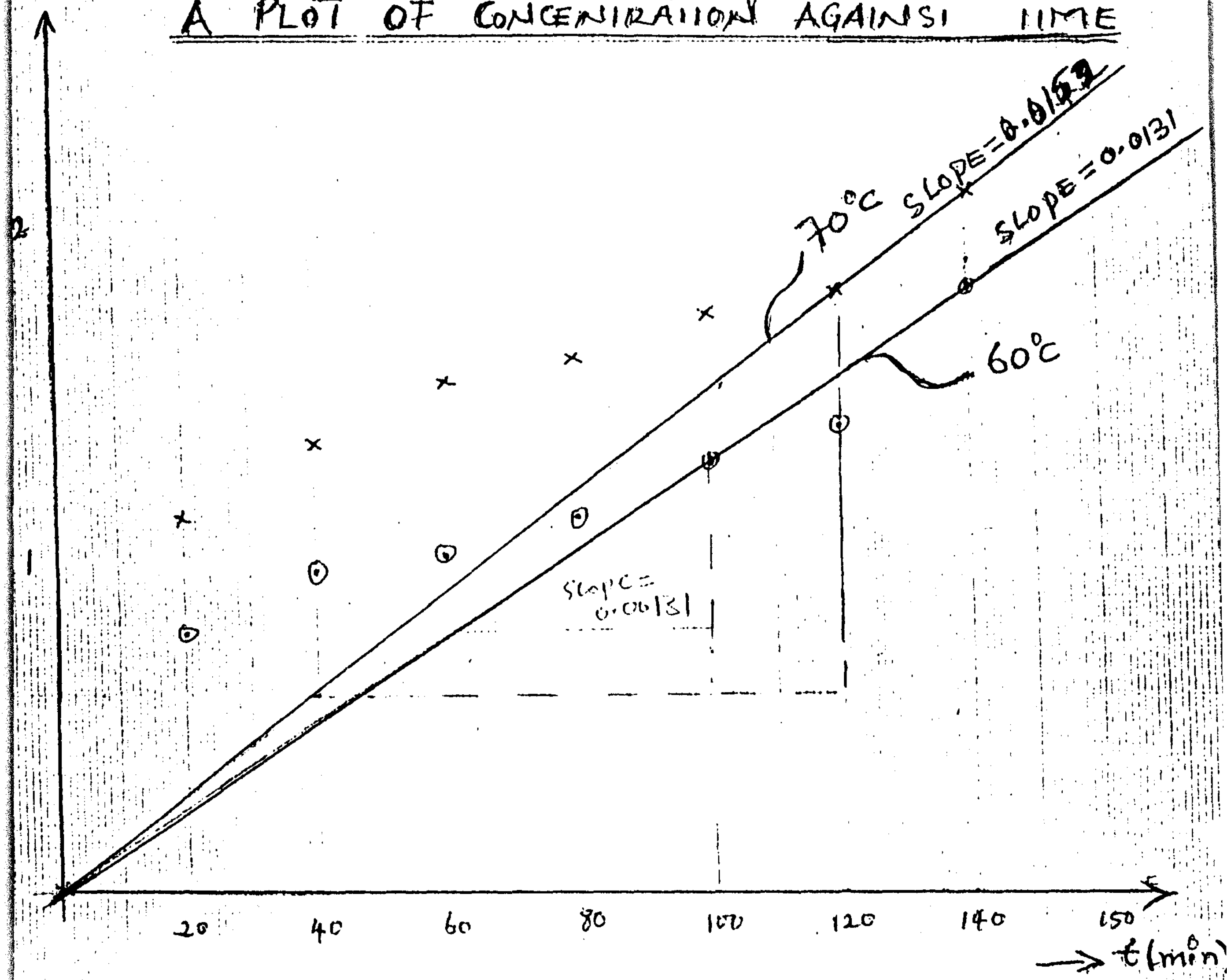

FIGURE 1

## A GRAPH OF CONCENTRATION CA AGAINST TIME (MINUTES)

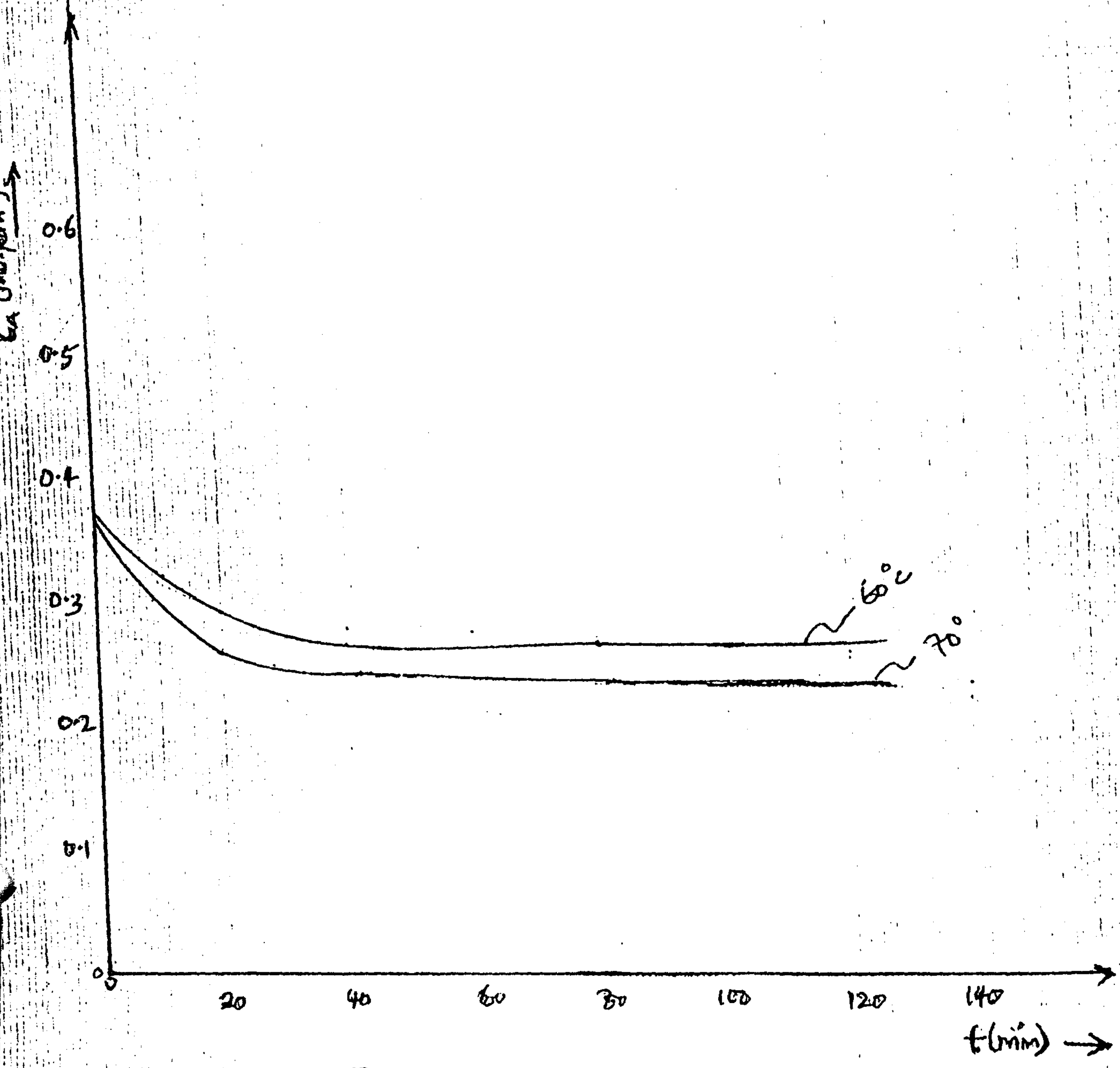

FIGURE 2

A GRAPH OF $r_A$ ($dC_A/dt$) AGAINST $C_A$

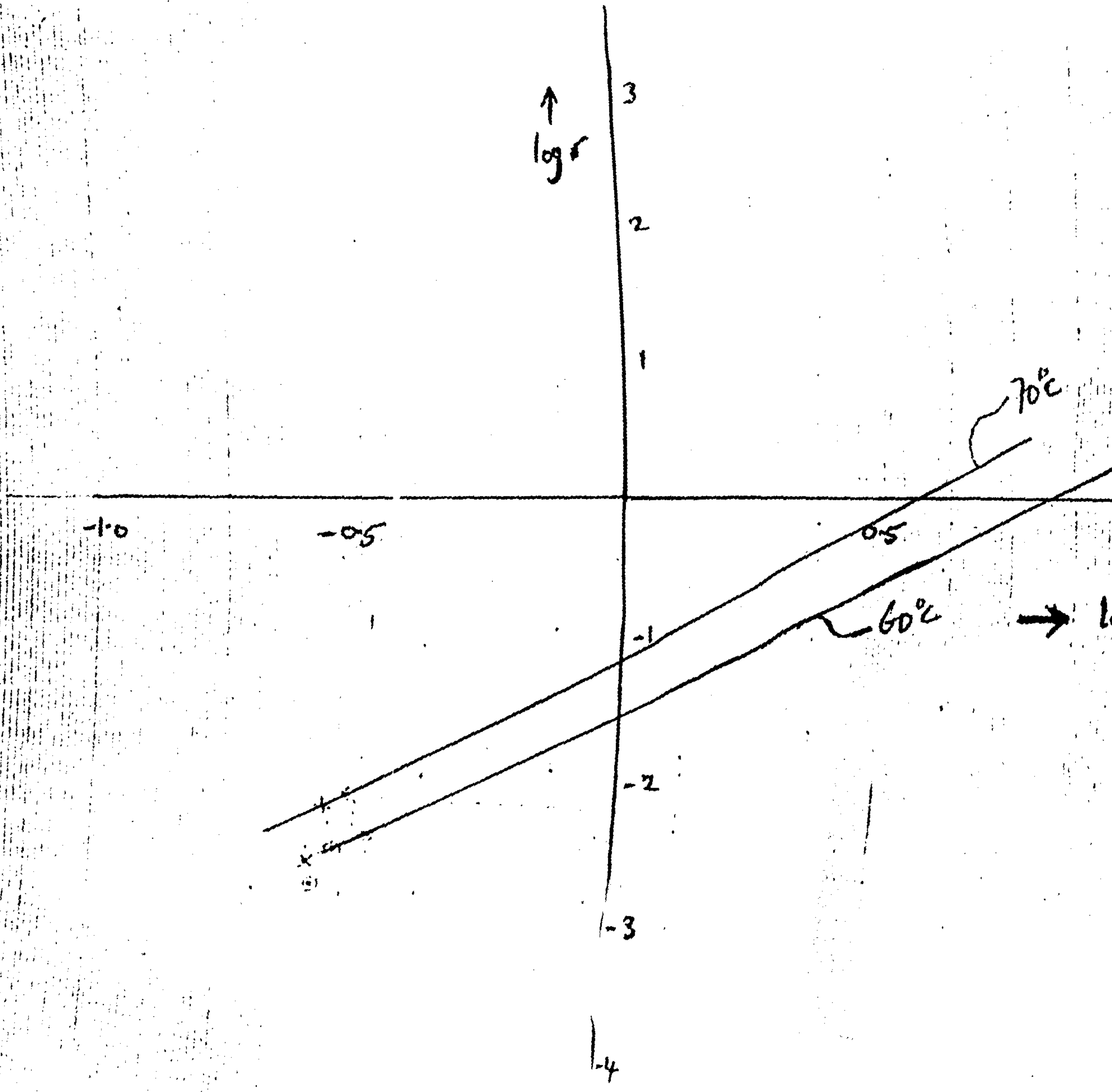

FIGURE 3