EFFECT OF CONCENTRATION ON THE RATE OF PRODUCTION OF OXALIC ACID FROM THE BARK OF EUCALYPTUS CAMALDULENSIS

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EFFECT OF CONCENTRATION ON THE RATE OF PRODUCTION OF OXALIC ACID FROM THE BARK OF EUCALYPTUS CAMALDULENSIS AT 50^0C USING 3% AND 4% CONCENTRATION

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BEING

A RESEARCH PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGER STATE.

IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF BACHELOR OF ENGINEERING IN CHEMICAL ENGINEERING

NOVERMBER, 2004

DECLARATION

I here by declare that this work titled Effect Of Concentration On the Production Of Oxalic Acid From The Bark Of Eucalyptus Camaldulensis Using 3% And 4% Concentration At 50^0C is authentic and has not been presented elsewhere for the award of any degree or its equivalent. Works or Information from other publication are dully acknowledge.

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CERTIFICATION

This is to certify that this project titled Effect Of Concentration On the Production Of Oxalic Acid From The Bark Of Eucalyptus Camaldulensis Using 3% And 4% Concentration At 50^0C was carried out by, ELIJAH OLUWASEYE AREO of the department of Chemical Engineering, Federal University Of Technology, Minna under the supervision of Dr. K. R. Onifade.

..... 22/11/2004

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.....
Date

.....

External Supervisor

.....
Date

DEDICATION

To all people that have affected my life positively and to the unseen knees, unseen tears, unseen pains and travails, often unseen faces that daily bring me forth in life endeavour.

ACKNOWLEDGEMENT

All praises be to almighty God, the creator, the Giver of all kinds of knowledge, the Sustainer and the most Merciful for His protection on my life and His guidance in all my undertakings.

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My special appreciation goes to my parents for being there for me, may the lord grant you good health and long life to eat the fruit of your labour, also my regards to the entire member of the Areos, the Durodolas and the Awoniyis may the Lord continues to increase you.

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NOTATION AND DEFINITION OF TERMS

C_{Ao}	-	initial concentration of H_2SO_4
C_A	-	concentration of H_2SO_4 at any time time t
F	-	Fractional conversion of H_2SO_4
$_tF$	-	Fractional conversion at any time t
k	-	Rate constant
n	-	order of reaction

ABSTRACT

The kinetics studies on the rate of production of Oxalic acid from the bark of Eucalyptus camaldulensis was analysized using integral method and differetial method of analysis using solvent concentration of 3% and 4% H_2SO_4. 3% H_2SO_4 recorded a rate constant of 0.0389 (intergral) and 0.0375 (differential) and rate equation, $-r_A=0.0389C_A^2$(intergral) and $-r_A=0.0375\ C_A^2$ (differential) while four percent H_2SO_4 recorded a rate constant of 0.0446 (intergral) and 0.0478 (differential) and rate equation $-r_A=0.0446C_A^2$ (intergral) and $-r_A=0.0478C_A^2$(differential). The result revealed that rate order of reaction is the same for both percentage of H_2SO_4 and a better yeild recorded with four percent H_2SO_4 concentration.

CHAPTER ONE

1.0 INTRODUCTION

Man's effort in extracting useful raw materials and medicines from the parts of many plants has led way for the exploitation of trees. High percentage of raw materials are extracted from plants parts such as bark, stem, culm twing etc in form of acids, Tannins, drugs fibres etc.

Oxalic acid otherwise, called ettanedioc acid is a colourless crystalline, toxic organic compound belonging to the family of carboxylic acid, and found to occur in wood sorrel and can be obtained from calcium and potassium oxalate.

Oxalic acid was first prepared synetically by a swedish chemist carl wilhelm scheele as acetosellic acid in 1776 and in 1787 Antoine Laurant Lavoisier gave it the present name. It decomposition was determined in 1815 by piere Louise Dulong.

Investigation on Eucalyptus tree revealed that the bark of this tree contains calcium oxalate crystals. In the past, no good attempt had been made to exploit this discovery on a technical scale.

In recent times, research project works on the extraction of oxalic acid from the bark of Eucalyptus Camaldunesis have revealed that the acid can be extracted at the temperature of 50 °C and 60^0 C with dilute H_2S0_4 using batch method of extraction. Also, the process is dependent on several parameters such as, extraction time, solvent temperature, percolation, solvent concentraction, particle size range and the preparation of the materials.

However, the scope of this research work considered the effects of solvent concentration on the amount of oxalic acid produced from the bark of Eucalyptus Camaldunesis.

In other word, this led to the study of the kinetics of the production of oxalic acid from the bark of Eucalyptus Camaldunesis.

1.1 AIM AND OBJECTIVES

Objectives of this project include the following :

(1) To investigate the kinetics of the process with the emphasis on effect of solvent concentration on the process involved during the

production of oxalic acid when using 3% and 4% solvent concentration .

(2) To investgate the time at which better yield can be obtained

(3) To establish and obtain a satisfactory rate equation to repressent the process.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 SECTION ONE :Biology and Botany

2.1.1 Origin and characteristic of eucalyptus

Eucalyptus is a large genus of evergreen tree and shrubs natives to semi – tropical and warm temperate region of Australia, New Zealand, Tasmania and nearly Islands. There are more than 500 species and belong to the myrtle family (myrtaceae). Eucalyptus is prominent among Australia genera, commonly known as gum trees or stingy bark trees with many trees forming shade tree or forest plantations.

The characteristics of the bark vary greatly. The gum has smooth bark; boxes have coarse fibrous bark; peppermints have fine fibrous stingy bark have thick loose or rough bark that may be shed in strips or flakes.

Economically, Eucalyptus tree constitute most valuable group within the other myrtales. The leaves are leathery and hang obliquely or vertically. The flower petals cohere to form a cap when the flower expands. The fruit is surrounding by woody cap shape receptacle and contains numerous minute seeds, possibly the largest fruit from 5 –6 centimeter are produced by E. macrocarpa.

The tallest Eucalyptus may reach the height of 100metre (330ft) and a circumference of 7.5 metre. One specimen of E. Regnans is 114m (374ft) tall and is among the world's tallest trees. Other tall species include E. Marginate, E gigantea, E Obligua and E Ovata. The smallest species such as E. Erythranda and E. mitrata ,may be less than 2m (6.6 ft) tall.

The leave glands of many species contain a volatile aromatic oil known as Eucalyptus oil, its chief use is medicinal and it consistutes an active ingredient in expectorants and inhalants.

Also, the juvenile leaves are usually opposite, sessile (not stalked) and covered with whithish bloom. Adult leaves are alternate stalked, often suckle

shaped and lack whitish bloom. The leaves margins are not nearly always smooth, althougth a few species have wavy or slightly toothed edges.

2.1.2 Eucalyptus camaldulensis

Widely cultivated in plantations and growing self-sawn seed, variable and hybridizing with other species. Bark smooth, ash – coloured leaves narrowly lanceolate up to 25cm long and 4.0cm broad. slightly glaucous, mature leaves are 25cm long and 1.5cm broad, flowered peduncles 10 to 15mm, terete operculum, conical to rostrate, the fruit are 7 – 8 x 5-6mm, hemispherical with a broad raised values exerted in curved.

2.1.3 Utilization of eucalyptus species

(a) Alkaloid

This is obtained commercially from eucalyptus leaves or barks as drug rutin. Rutin is an important drug for therapeutics. Alkaloid are also chemically basic compounds with an important physiological activity in medicine e.g. analgesics.

(b) Clove oil

The family yields the most valued species – clove oil from syzygium aromaticum, Eucalyptus oil, is well known for flavouring expectorant and antiseptics.

(c) Charcoal

Apart from the use in production of Bread and Goldsmith in most African countries, it is excellent household fuel. It does not smoke and it is relatively save to use. Most Eucalyptus carbonized easily, providing good commercial charcoal. It yields about 7,900 calories per kilogram against 4,700 kilogram for wood.

(d) Essential oil

The chief suppliers of essential oil are Australia, Congo (Kinshasa), Spain and Portugal. This is obtained from the bark, leaves and wood of Eucalyptus species, which are used in many industries. Among the terpene

and ketone derivatives in the oils are Cineole, used in veterinary medicines and piperitone, used in manufacture of synthetics thymol and methanol. The oil used in making perfumes includes geraniol, citronellal and citral.

(e) Fuel wood

Eucalyptus wood is exclusively used in Australia and other countries around the world as fuel. Plantations and other forest resource of the family can supply a substantial part of the household fuel needed by the low and middle classes.

(f) Honey

Among the major source of income in Australia is Eucalyptus honey, a total of about 17 million Kilogram is being exported annually. Some species are important sources of nectar and pollen for honey bees. It is also used for domestic purposes, because large part of Eucalyptus honey is being consumed.

(g) Ornamentals

As ornamentals, Eucalypts are grown for their attractive form and foliage, colorful flowers or decorative bark.

(h) Pulp and Paper

The bark of many species is used in papermaking and is suitable for use in pulp industry. Economically, the world production of pulp from eucalyptus is over one million tones annually.

(i) Oxalic acid

Oxalic acid is widely used as an acid rinse in Laundries. It forms a series of salt and can be extracted from eucalyptus bark, from which oxalate salt is formed.

Presently, it can be extracted from the bark of eucalyptus camaldulensis and it also used in laboratories and chemical industries.

(j) Resin

Resin is defined as any natural or synthetic organic compound consisting of a non – crystalline or viscous liquid substance. They are also insoluble in water but soluble in alcohol, spirit and high temperature.

Eucalyptus species (especially the leaves and wood) contain resin which is used as component of varnishes.

The Eucalyptus species yield what is known as Botany Kino an astringent dark – redish resin, obtained in a semi –fluid state from incisions made in tree trunk. The gumming resin is used in medicine as an astringent and to treat diarrhea, which is obtained from eucalyptus longirostic. When present in leaves especially the blue gum (Eucalyptus globulus) contains strong smelling oil used in medicine as antiseptic worm and other intestinal parasite excellent. And when in wood, it adds to its strength and durability

(k) Tannin

Tannin is extracted from the bark of Eucalyptus and is chiefly used in the production of leather use in making shoes, bags etc. Tannin is also used in the manufacture of ink. They are also used in dyeing fabric and medical applications.

Tannins is used in the treatment of some diseases and as antidote for flavour in some tea. The hard and durability of eucalyptus wood as contributed by tannin content in it. Economically, it is exported in large quantity in crude state in Australia.

(l) Timber

Eucalyptus wood is used as timber in fencing and buildings. The hard and tall wood is used in telephones and electric poles. The important timber species include E. mbeculate and E. Citriodora. It is used in the construction of furniture and cabinet work, and in making ships; floor for commercial and domestic purposes.

2.2 SECTION TWO : Oxalic acid Chemistry

2.2.1 Oxalic acid

It is otherwise known as Ethanedoic acid, it has the empirical formula $CO_2H.CO_2H$, The structural formula HOOC-COOH and molecular weight of 126 . 07. It is one of the important dicarboxylic acid and occurs in rhubarb, in sorrel and other plants of oxalis group.

2.2.2 Method of preparations.

(1) The obsolete : An industrial method which is now almost obslete is to heat saw – dust with a mixture of sodium and potassium hydroxides in iron pans at 200 – 220^0c in air. On cooling, the mass is extracted with

water and aqueous solution treated with a calcium hydroxide solution. The calcium oxalate, which is precipitated is collected by filtration and then decomposed by calculated quantity of dilute sulphuric acid. The prepicitated calcium sulphate is filtered off and the filtrate evaporated to crystallisation, oxalic acid dihytrate crystallized out.

(2) The Industrial : Oxalic acid is now prepared lindustrially by heating sodium formate rapidly to 360^0c

$$2HCO_2Na \rightarrow (CO_2Na)_2 + H_2$$

The free acid is obtained from sodium salt by procedure describe above in (1).

(3) The Laborartory : The usual laboratory method for preparing oxalic acid is to oxidize sucrose with concentrated nitric acid in the presence of vanadium pentaoxide

$$C_{12}H_{22}O_{11} \xrightarrow[V_2O_5]{HNO3} 6(CO_2H)_2 + 5H_2O$$

(iv) In this thesis

Oxalic acid was extracted from the bark of Eucalyptus Camaldulesis which is contained in form of calcium oxalate. Sulphuric acid was used for extracting the oxalic acid.

CaC_2O_4	+	H_2SO_4	$\rightarrow$	$(CO_2H)_2$	+	$CaSO_4$
Calcium Oxalate		Sulphuric acid		Oxalic acid		Calcium sulphate

2.2.3 **Physical properties**

(i) Oxalic acid is colourless crystal, which affluences in air and crystallizes with two molecule of water of crystallization.

(ii) When heated to 200^0c, oxalic acid decomposes into CO_2, CO and water. $(CO_2H)_2 \rightarrow CO_2 + CO + H_2O$

while the dehydrated loses water when heated at 100 – 105^0C

(iii) Oxalic acid melt at 101.5^0C when hydrated while when anhydrous, the melting point is 189.5^0c and subliming at 150^oc

(iv) Oxalic acid is poisonous (toxic), soluble in water and ethanol but insoluble in $CHCL_3$.

(v) At the temperature of 20^0c, the solubility in g/100g water is 9.

(vi) The compound of oxalic acid has the specific grancity of 2.0.

2.2.4 Chemical properties

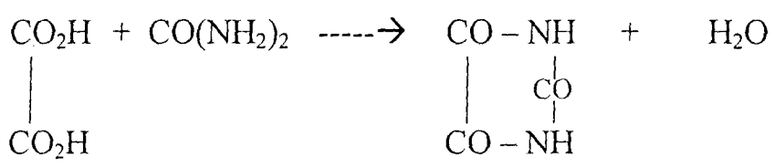
(I) When heated with concentrated tetraoxosulphate (VI) acid at 90%, oxalic acid is decomposed

$$(CO_2H)_2 \xrightarrow{H_2SO_4} CO_2 + CO + H_2O$$

(II) The anhydrate of oxalic acid is unknown, when anhydrous oxalic acid is reflected with ethanol, ethyl oxalate is formed

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

(III) Dicaboxylic acid react with urea in the presence of phosphory chloride to form cylic ureide, e.g. oxalic acid form parabamic acid (oxalylurea).



(IV) Oxalic acid oxidized by permanganate to form carbon dioxide and water.

$$(CO_2H)_2 + [O] \rightarrow 2CO_2 + H_2O$$

(V) It oxidized slowly by concentrated nitric acid when fused with potassiumhydroxide,it evolves hydrogen.

$$(CO_2H_2)_2 + 2KOH \rightarrow 2K_2CO_3 + H_2$$

(VI) Pyruvic is oxidized by warm nitric acid to oxalic acid

$$HOCH_2.H_2OH + 4(O) \rightarrow (CO_2H)_2 + CO_2 + H_2O$$

(VII) If excess phosphorous pentachloride is not used, oxalic acid decomposed possibly via the intermediate formation of the half acid chloride.

$$(CO_2H)_2 \rightarrow (CO_2H . COCL) \rightarrow CO_2 + CO + HCL$$

2.2.5 Economic uses of oxalic acid

Oxalic acid is widely used as an acid rinse in laundaries, where it is effectively used in removing rust and ink stain because it converts most insoluble ionic compounds into soluble complex ion. Also for the same reason, it is the chief constituent of many commercial preparation used for removing scale for radiator of automobile.

Oxalic acid is used for the manufacture of ink and for bleaching straw. Its antimony salt as mordents in printing and dyeing. It is also used in leather industries in manufacture of dyes and in preparation of related compounds such as glyoxalic acid and glycolic acid.

It is widely used in laboratories and domestic industries.The acid is also used in volumetric analysis for standardization of potassium permagnate solution. Its reducing properties lends it some useful industrial applications.

2.2.6 The risk and safety measure due to exposure to oxalic acid

Presently, there are various types of solid production that are produced by chemical and other allied industries, toxic product such as oxalic acid are used in various chemical and laboratory industies. It combines with calcium and magnesium ions in blood tossues, inhibiting the action of enzymes depending on those ions for activity.

Many human fallacies have been recorded following ingestion of little as sign of oxalic acid. The symptons appear rapidly and are marked by shock like sudden collapse and convulsive seizure. A marked renal tubules may appear, the result of convulsive seizure are thought to be of hypocaemia. Also, exposure to solution of oxalic acid of potassium oxalate to the skin may cause a localised pain and cyanosis in the finger or even gangrenous change. oxalic acid in solid form or in concentration can cause burn of the skin, eyes, or mucous memberances. It's concentration is a low as 5- 10% and can be irritating, if prolonged exposure was experienced.

Oxalic acid in solid form or its oxalate occurs in certain edible plants, notally spinach which contains 0.9% and may not be poisonous, but can serve to reduce the body's calcium supply, through its own oxalic acid content. The Rhubarb leaves contain as much as 1.2%. cases of fatal poisoning by ingestion of large quantities of rhubarb leaves have been recorded, even though the stalks are safe.

Safety of any person working with acid is important, as such protective glasses and wears must be provided to avoid content with eyes and skin. If concentrated oxalic salts are present in the atmosphere or in hot solutions, adequate ventilation should be given to the victim or proper respiratory protective device have to be worn.

Calcium oxalate crytals appear in neutral or alkaline urine, and in some cases. These will cohere to form slowly growing jagged – shaped (and consequently painful) urinary calculi or kidney stone. Oxalic acid has non – poisonous calcium chalk (e.g. chalk, plaster, whitewash etc). as its antidoles. Injury from inhalation of oxalic acid dust appears very rare.

Oxalic acid is a strong acid in nature exposure due to dust must be carefully controlley and work areas concentration held acceptable health limit.

2.3 SECTION THREE : KINETIC STUDY

2.3.1 Chemical kinetics

Chemical kinetics is the study of chemical reaction rates, how reaction rates are controlled and the pathway or mechanism by which a reaction proceeds from its reactants to its products. The rate of a chemical reaction may be expressed as a change in a reactant or product as function of time.

The mechanism is the squence of individual chemical events whose overall result produces the observed reaction.

However, mechanism also defined as all the individual collisional or elementrary process involving molecules (atom, radicals and ions) that take palce simulteanously of consecutively in producing the observed overall rate. Thus, mechanism of a reaction gives a detailed stereo – chemical picture of each step as it occurs.

Besides, chemical kinetics searches for the factors that influence the rate of reaction. It measures the rate and proposes explanations for the values found. Its study is important for a number of reasons :

(1) For physical chemist it is the tool for gaining insight into the nature of reacting systems, for understanding how chemical bonds are made and broken, and for estimating their energies and stability.

(2) For the organic chemist the value of chemical kinetics is greater still because the mode of reaction of compounds provides clues to their structure. Thus relative strength of chemical bonds and molecular structure of compounds can be investiagted by this tool.

(3) In addition, it is the basis for important theories in combustion and dissolution and provides a method to study heat and mass transfer and suggests methods for tackling rate phenomona in other fields of study.

(4) For the chemical engineering the kinetics of reaction must be known if he is to statisfactorily design equipment to effect these reactions on a technical scale of course, if the reaction is rapid enough so that the system essentiallly at equilibrium design is very much simplified. Kinetic information is not needed, and thermodynamic information alone is sufficient.

2.3.2 Concentration dependent term of a equation

Before we can find the form of the concentration term in a rate expression, we must distingush between different types of reaction. This distinction is based on the form and number of kinetic equation used to describe the progress of reaction.

Also, since we are concerned with the concentration – dependent term of the rate equation, we assume that the temperature of the system is kept constant.

(1) Single and multiple reactions

First of all, when material react to form products it is usually easy to decide after examing the stoichiometry, preferably at more than one temperature, whether we should consider a single reaction or a number of reactions to be occuring.

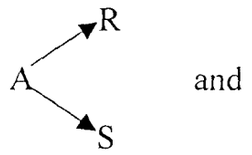
When a single stoichiometric equaiton and single rate equation are chosen to represent the progress of the reaction, we have a single reaction. When more than one stoichiometric equation is used to represent the observed changes, then more than one kinetic expression is needed to follow the changing composition of all the reaction components, and we have multiple reation.

Multiple reactions may be classified as :

(i) Series reactions

$$A \rightarrow R \rightarrow S$$

(ii) Parallel reactions, which are of two types



and

$A \rightarrow R$

$B \rightarrow S$

Competitive Side by Side

(2) Elementary and nonelementary reactions

Consider a single reaction with stoichiometric equation

$$A + B \rightarrow R$$

If we postulate that the rate controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B, then the number of collisions of molecules A with B is proportional to the rate equation. But at a given temperature the number of collision is proportional to the concentration of reactions in the mixture, hence the rate of disappearance of A is given by $-r_A = KC_AC_B$

Such reactions in which the rate equation corresponds to a stiochiometric equation are called elementary reactions.

When there is no correcpondence between stoichiometry and the rate then we have a nonelementary reactions. The classical example of a nonelementary reaction is that bewteen hydrogen and bromine.

$$H_2 + Br_2 \longrightarrow 2HBr$$

which has a rate expression :

$$r_{HBr} = \frac{K_1 [H_2] [Br_2]^{1/2}}{K_2 + [HBr] / [Br_2]}$$

Non-elementary reactions are explained by assuming that what we observe as a single reaction is in reality the overall effect of a sequence of elementary reactions. The reason for observing only a single reaction rather than two or more elementary reactions is that the amount of intermediates formed is negligibly small and therefore escapes detection.

(3) **Molecularity and order of reaction**

The molecularity of an elementary reaction is the number of molecules involved in the reaction, and this has been found to have

the values of one, two and occasionally three. Note that the molecularity refers only to an elementary reaction.

Often we find the rate of progress of a reaction, involving say material A, B, ...D, can be approximated by an expression of the following type :

$$r_A = KC_A^{a}C_B^{b} \ldots\ldots C_D^{d}, \qquad a + b + \ldots + d = n \ldots\ldots\ldots 1$$

Where a,b, ... d are not necessarily related to the stoichiometric coefficients. We call the powers to which the concentrations are raised the order of the reaction.

Thus the reaction is : ath order with respect to A

bth order with respect to B

nth order overall

since the order refers to the empirically found rate expression it can have a fractional value and need not be an integer. However, the molecularity of a reaction must be an integer since it refers to the mechanism of reaction, and can only apply to an elementary reaction.

rate constant K

When the rate expression for a homogeneous chemical reaction is written in the form of equation (1), the dimesions of the rate constant K for the nth-order reaction are

$$(\text{time})^{-1}\,(\text{concentration})^{1-n} \ldots\ldots\ldots 2$$

which for a first order reaction become simply

$(\text{time})^{-1}$

representation of a reaction rate

In expressing a rate we may use any measure to concentration, for example partial pressure, in which case

$$r_A = KP_A^{a}P_B^{b} \ldots\ldots P_D^{d}$$

Whatever measure we use leaves the often the order unchanged ; however, it will affect the rate constant K.

For brevity elementary reactions are often represented by an equation showing both the molecularity and the rate constant. For example

$$2A \xrightarrow{K_1} 2R \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

represents a bimolecular irreversible reaction with second – order rate constant K_1, implying that the rate of reaction is $-r_A = K_1 C_A^2$

At times it may be necessary to specify the component in the reaction to which the rate constant is referred. For example consider the reaction

$$B + 2D \xrightarrow{K_2} 3T \quad \text{.....(8)}$$

If the rate is measured in terms of B, the rate equation is $-r_B = K_2^{1} C_B C_D^2$

If the rate refers to D, the rate equation is

$-r_D = K_2^{11} C_B C_D^2$

or if it refers to the product T, then

$$-r_T = K_2^{111} C_B C_D^2$$

But from the stoichmetry

$$-r_B = -\tfrac{1}{2} r_D = \tfrac{1}{3} r_T$$

hence $K_2^{1} = \tfrac{1}{2} K_2^{11} = \tfrac{1}{3} K_3^{11}$

However, to avoid ambiquity when the stoichmetry involved different numbers of molecules of the various components, we mast specify the component being considered.

To sum up, the condensed form of expressing the rate can be ambiquous. To eliminate any possible confusion, write the stoichiometric equation followed by the complete rate expression, and give the units of the rate constant.

2.3.3 **Interpretation of batch reaction data**

A rate equation chararcterizes the rate of reaction and its form may either be suggestion by theoretical consideration or simply be the result of an empirical curve – fitting procedure.

In any case the value of the constants of the equation can only be found by experiemt ; predictive methods are inadequate at present.

The determination of the rate equation is usually a two – step procedures ; first the concentration dependency is found at fixed temperature and then the temperature dependence of the rate constants is found, yielding the complete rate equation.

Equipment by which empirical information is obtained can be divided into two types, the batch and flow reactions. The batch reactor is simply a container to hold the contents while they react.

All that has to be determined is the extent of reaction at various times ; and this can be followed in a number of ways, for example :

(1) By following the concentration of a given component.

(2) By following the change in some physical property of the fluid such as the electrical conductivity or retractive index.

(3) By following the change in total pressure of a constant – volume system.

(4) By following the change in volume of a constant – pressure system.

The experiemental batch reaction is usually operated isothermally and at constant volume because it is easy to interpret the results of such runs. The reactor is a relatively, simple device adaptable to small – scale laboratory setups, and it needs but little auxilliary equipment or instrumentation.

Thus, it is used whenever possible for obtaining honogeneous kinetic data. This chapter deals with the batch reactor.

The flow reactor is used primarily in the study of the kinetics of hetergeneous reaction, though in a number of instaces it is used to complement and offers advantages over the batch reaction in the study of homogeneous reactions.

Reactions, and gas – phase reactions are examples of situations which may be more easily followed in flow reaction. .

There are two procedures for analyzing kinetic data, the integral and the differential methods. In the integral method of analysis we guess a particular form of rate equation and, after appropriate integrations and mathematical manipulations predict that the plot of a certain concentration function versus time should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained then the rate equation is said to satisfactorily fit the data.

In the differential method of analysis we test the fit of the rate expression to the data directly, and without an integration.

However, since the rate expression is a differential equation, we must first find $(^1/_V)(dN/dt)$ from the data before attempting the fitting procedure.

There are advantages and disadvantages to each method.

The integral method is easy to use and is recommended when testing specific mechanism, or relatively simple rate expressions, or when the data are so scattered that we cannot reliably find the derivatives needed in the differential method. The differential method is useful in more complicated situations but requires more accurate or larger amount of data.The integral method can be used to develop or build up a rate equation to fit the data.

In general, it is suggested that integral analysis be attempted first, and if not successful, that the differential method be tried. For complicated cases we may need to use special experiemetal methods which give a partial solution of the problem, or else flow reactors coupled with differetial analysis.

2.3.4 Integral method of analysis of data

General procedure :

The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted C verse t curve with the experiemental C verse t. data. If the fit is unsatisfactory, another rate equation is suggested and tested. The procedure may be summarized as follows :

(1) In a constant – volume system the rate expression for the disappearance of reactant A will be of the following form : $-r_A = \frac{dCA}{dt} = f(k,c)$

or in the more restricted case in which concentration depedent terms may be separated from the concentration – independent terms, we have :

$$-r_A = \frac{dCA}{dt} = f\,k\,(c) \quad \text{.....(6)}$$

(2) Equation (6) is rearanged to give

$$\frac{dCA}{f(c)} = kdt$$

Now f(c) only involves concentration of materials, which may be expressed in terms of C_A. Thus, eqn. (6) may be integrated either analytically or graphically to give

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{f(C)} = k\int_{o}^{t} dt = kt \quad \text{.....(7)}$$

(3) This concentration function is proportional to time, so a plot such as that of C_A $\frac{dC_A}{-C_{Ao} \quad f(C_A)}$

against time yields a straight line of slope k for this particular rate equation.

(4) From experimental determine numerical values for the integral of equation 7 and plot these at the corrresponding times.

(5) See whether these data fall on a reasonably straight line passing through the origin. If there is no reason to doubt this, then it may said that the particular rate eqaution being tested satisfactorily fits the data. If the data are better fitted by a curved line then this rate equation and its mechanism are rejected, and another rate equation is tried.

However, the integral method is especially useful for fitting simple reaction types corresponding to elementary reaction. A number of these forms are :

(a) Irreversible unimolecular – type first order reaction

Consider the reaction

A → productions

Suppose we wish to test the first – order rate equation of the following type,

$$-r_A = \frac{dCA}{dt} = kCA \quad \text{.....(8)}$$

Separating and integratring we obtain

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = k\int_{o}^{t} dt$$

$$\text{Or} \quad -\ln \frac{C_A}{C_{Ao}} = kt \quad \text{..... (9)}$$

Which is the derived result.

Now the fractional conversion X_A of a given reactant A is defined as the fraction of reactant converted into product or

$$X_A = \frac{N_{Ao} - N_A}{N_{Ao}}$$

Fractional conversion (or simply conversion) is a convenient so variable often used in place of concentration in engineering work ; therefore most of the results which follow will be presented in terms of both C_A and X_A.

For a constant density system V does not change so

$$C_A = \frac{N_A}{V} = \frac{N_{Ao}(1-XA)}{V} = C_{Ao}(1-XA)$$

and $-dC_A = C_{Ao}\, dX_A$

hence Eq.8 becomes

$$\frac{dX_A}{dt} = K(1-X_A)$$

by rearranging and integrating gives

$$\int_0^{XA} \frac{dX_A}{1-XA} = K \int_0^t dt$$

$$\text{or} - \ln(1-X_A) = kt.$$

(b) Irresversible Bimolecular – type second – order Reacties

Consider the reaction A + B → products

with the corresponding rate equation

$$-r_A = \frac{dC_B}{dt} = \frac{-dC_B}{dt} = KC_AC_B \quad \ldots\ldots\ldots\ldots 13$$

Noting that the amounts of A and B which have reacted at any time t are equal by given by $C_{Ao}X_A = C_B X_B$

Eq . 13 is rewritten in terms of X_A as

$$-r_A = C_{Ao}\frac{dX_A}{dt} = K(C_{Ao}-C_{Ao}X_A)(C_{Bo}-C_{Ao}X_A)$$

Letting $M = C_{Bo}/C_{Ao}$ be the initial molar ratio of reactants, we obtain

$$-r_A = \frac{dX_A}{dt} = KC_{Ao}^2(1-X_A)(M-X_A)$$

which on separation and formal integration becomes

$$\int_0^{X_A}\frac{dXA}{(1-X_A)(M-X_A)} = C_{Ao}K\int_0^t dt$$

this gives,

$$\text{In}\frac{1-XB}{1-XA} = \text{In}\frac{M-XA}{M(-XA)} = \text{In}\frac{C_BC_A}{C_{Bo}C_A} = \text{In}\frac{C_B}{MC_A}$$

$$= C_{Ao}(M-1)kt = (CB_o-CAo)\,kt,\ M \neq 1$$

Caution 1 : In the special case where reactants are introduced in the stoichiometric ratio the integrated rate expression becomes indeterminate and this requires taking limits of quotients for evaluation.

This difficulty is avoided if we go back to the original differential rate expression and solve it for this particular reactant ratio. Thus for the second – order reaction with equal initial concentration of A and B, or for the reaction 2A → products.

The defining second order differential equation becomes

$$-r_A = -\frac{dCA}{dt} = KC_A^2 = KC_{Ao}^2(1-X_A)^2$$

which on integrating yields

$$\frac{1}{CA} - \frac{1}{CAo} = \frac{1}{CAo}\frac{XA}{1-XA} = kt$$

Caution 2: The integrated rate expression depends on the stoichiometry as well as the kinetics. To illustrate, if the reaction A + 2B → product is first order with respect to both A and B, hence second order overall or

$$-r_A = \frac{dCA}{dt} = KC_AC_B = KC_{Ao}^2(1-X_A)(M-2X_A)$$

the integrated form is

$$\ln \frac{C_B C_{Ao}}{C_{Bo} C_A} = \ln \frac{M - 2X_A}{M(1 - X_A)} = C_{Ao}(M-2)kt, \; M \neq 2$$

with a stoichiometry reactant ratio the integrated form is

$$\frac{1}{C_A} - \frac{1}{C_{Ao}} = \frac{1}{C_{Ao}} \frac{X_A}{1-X_A} = 2kt, \quad M=2$$

Thus, special forms for the integrated expressions appear when the reactants are used in stoichiometric ratios, or when the reaction is not elementary.

(c) Empirical Rate Equations of nth order

When the mechanism of reaction is not known, we often attempt to fit the data with an nth – order rate equation of the form

$$-r_A = \frac{dCA}{dt} = KC_A^n$$

which on separation and integration yields

$$C_A^{1-n} - C_{Ao}^{1-n} = (n-1)kt \quad n \neq 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (29)$$

One curious feature of this rate form is that reactions with order $n > 1$ can never go to completion in finite time.

On the hand, for orders $n<1$ this rate form predicts that the reactant concentration will fall to zero and then become negative at some finite time, found from eq (29) as

$$t = \frac{C_{Ao}^{1-n}}{(1-n)\,k}$$

since the real concentration cannot fall below zero we should not carry out the integration beyond this time for $n < 1$, also as a consequence of this feature, in real systems the observed fractional order will shift upward to unity as a reactant is depleted.

d) <u>Zero order Reactions</u>

A reaction is of zero order when the rate of reaction is independent of the concentration of materials;

thus $-r_A = -\frac{dCA}{dt} = k$

integrating and nothing that can never become negative we obtain directly

$C_{Ao} - C_A = C_{Ao}.X_A = kt$ for $t < \frac{CA_o}{k}$

which means that the conversion is proportional to time.

As a rule reactions are of zero order only in certain concentration ranges – the higher concentrations. If the concentration is lowered far enough we usually find that the reaction becomes concentration dependent, in which case the order rises from zero.

In general, zero order reactions are those whose rates are determined by some factor other than the concentration of the reacting materials e.g. the intensity of radiation within that vat for photochemical reactions, or the surface available in certain solid catalyzed gas reactions. It important, then, to define the rate of zero order reactions so that this factor is included and properly accounted for.

2.3.5 Differential method of analysis of data

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derived dci/dt and testing the goodness of fit of the equation with experiment.

We may plan the experimetal program to test the complete rate equation in question, or to test and fit separately the various parts of the rate equation which are then combined to give the complete rate equation. These two procedures are outlined in turn.

The analysis of the complete rate equation by the differential method may be summarized as follows.

(1) Hypothesizes a mechanism and from it obtain a rate equation. As with integral analysis, it will be of the form

$$-r_A = \frac{-dCA}{dt} = f(k,c)$$

or

$$-r_A = \frac{-dCA}{} = k\,f(c)$$

dt

(2) From experiment obtain concentration – time data and plot them.

(3) Draw a smooth curve through these data

(4) Determine the slope of this curve at suitable, selected concentration values. These slopes, dC_A/dt are the rates of reaction at these compositions.

(5) Evaluate f(c) for each composition

(6) Plot – (dC_A/dt) versus f(c), if we obtain a straight line through the origin the rate equation is consistent with the data; if not then another equation should be tested.

The crucial operations in this procedure are steps 3 and 4 even a slight uncertainty in the slope of the fitted curve will result in a large uncertainty in evaluate slopes. It is therefore recommended that the CA version t data be plotted on a large piece of paper, that smooth curves be carefully fitted freehand to the data, independently by a number of people, and resultant slopes be averaged.

CHAPTER THREE

3.0 EXPERIMENTAL METHODOLOGY

3.1 Equipments And Materials

1. Eucalyptus Camalduensis bark
2. Mortal, pestle and grinder
3. Electric weighing balance (analytical weighing balance)
4. Sieving machine (mesh size: 0.25mm, 0.05mm, 0.71mm, 0.85mm, 1mm)
5. Hot plate magnetic stirrer
6. Beakers and funnels
7. Filter papers and fibre clothes
8. Measuring cylinders
9. Volumetric flask: 1000ml and 500ml
10. Burettes, Pipettes (10ml) and retort stand
11. Sample of sulphuric acid (H_2S0_4)
12. Sample of potassium hydroxide (KOH)
13. Distilled water (Deionized water)

3.2 Size Reduction

This is a process whereby particles of solid are been broken or cut into smaller pieces. However, the fresh sample of Eucalyptus Camaldunensis, which was obtained from the national Forestry Department of the federal Ministry of Environmental in Minna, was sun dried.

When a constant weight was attained, after eight days of drying the bark of the Eucalyptus was manually crushed using wooden mortar and pestle into smaller sizes. In order to obtain smaller sizes of the particles, the sample was then grinded using a grinder.

3.3 Screen Analysis

Screening is defined as the method of separating particles according to sizes. When the solid particles are dropped on the screening surface, the fine particles pass through the screen opening, while the oversized or bigger particles remain at the top.

Sieving machine which contains series of different mesh sizes were arranged in decreasing order, that is largest particle sizes were put at the top while the smallest sizes fall below. The stack was placed on the analyzer and with the aid of electric vibrator (Vibration rate amplitude 7m), mechanical shaken took place for specific time of about ten minutes, thus, the crushed samples were screened by the screen analyzer into series of sieves. The mesh size used ranging from 0.25mm – 1.0mm.

3.4 Experimental Procedure

50g of the sieved sample of 0.25mm was measured into a beaker and 500cm^3 of 3% H_2SO_4 was added. The beaker was placed over a hot plate magnetic stirrer set at 50°C. Thermometer was used to monitor the temperature rises.

20minutes from the time the temperature became stable at 50°C, about 15cm^3 of the reacting minutes was drawn for analysis. The 15cm^3 of the reacting mixture was filtered to obtain a clear filtrate. 10cm^3 of prepared 6% potassium hydroxide (KOH) was then reacted with 10cm^3 of the filtrate. This was to stop the reaction between the Calcium Oxalate in the bark and H_2SO_4 producing the Oxalic acid (quenching).

The resulting mixture was titrated with part of the prepared 3% H_2SO_4 using Phenolphthalein as indicator. The volume of acid used (Titre value) was recorded. The experiment was run for 140 minutes with time interval of 20 minutes.

Similarly, the above procedure was repeated using 4% H_2SO_4 and 8% potassium hydroxide (KOH) for quenching. Result obtained in each case was tabulated and presented in the tables.

3.5 Experimental Analysis

3.5.1 Integral method of analysis

Using the nth order kinetics

$$-r_A = -\frac{dC_A}{dt} = KC_A^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

On Integration, this yields

$$C_A^{1-n} - C_{A0}^{1-n} = K(n-1)t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

For any functional conversion in any time t_f, the above equation can be re-written as

$$t_f = \frac{(F^{1-n}-1)}{k(n-1)} C_{A0}^{1-n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

Where $F = C_A/C_{Ao}$

Taking Logarithm of both sides

$$\text{Log } t_f = \text{Log}\left[(F^{1-n}-1)/K(n-1)\right] + (1-n)\log C_{Ao} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

This expression shows that a plot of log t_f vs. log C_{Ao} should give a straight line of slope 1-n.

Using a fractional conversion of 0.9, this equation can be re-written as:

$$\text{Log } t_f = \text{Log}\left[(0.9^{1-n}-1)/K(n-1)\right] + (1-n)\log C_{Ao} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

3.5.2 Differential Method of analysis

Using the nth order kinetics

$$-\frac{dC_A}{dt} = KC_A^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.7$$

taking logarithms of both sides

$$\log(-dC_A/dt) = \log k + n\log C_A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.8$$

of log $(-dC_A/dt)$ vs. $\log C_A$ should give a straight line with n as slope and logk as intercept on the $\log(-dC_A/dt)$ axis

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION OF RESULTS

4.1 Tables of results

TABLE 4.1.1 Drying rate table of the bark of eucalyptus camaldulensis

Day	Time started (am)	Time stopped (pm)	Duration (hr)	Starting weight (kg)	Stopped weight (kg)	Moisture lost (kg)
1.	10.30	5.30	7	5.964	4.388	1.567
2.	10.30	5.30	7	4.388	4.202	0.186
3.	10.30	5.30	7	4.202	3.190	1.012
4.	10.30	5.30	7	3.190	2.348	0.842
5.	10.30	5.30	7	2.348	1.998	0.350
6.	10.30	5.30	7	1.998	1.911	0.087
7.	10.30	5.30	7	1.911	1.896	0.015
8.	10.30	5.30	7	1.896	1.896	0.000

TABLE 4.1.2 Results obtained from experiment for 3% concentration at 50°C

Time(min)	Titre value (cm^3)	Volume of Acid reacted (cm^3)	Concentration of acid reacted (Mol/dm^3)
0	0.00	0.00	0.5633
20	5.01	0.80	0.4906
40	6.55	2.04	0.4208
60	7.01	2.50	0.3949
80	8.41	3.90	0.3160
100	8.71	4.20	0.2991
120	9.19	4.68	0.2721
140	9.36	4.85	0.2625

TABLE 4.1.3 Result obtained using integral method of analysis

T (min)	Log (t)	C_A (mol/dm^3)	C_{AO} (mol/dm^3)	Log C_{AO}
0	0.000	0.5633	0.6259	-0.2035
20	1.300	0.4906	0.5451	-0.2635
40	1.602	0.4208	0.4676	-0.3301
60	1.778	0.3949	0.4388	-0.3577
80	1.903	0.3160	0.3511	-0.4546
100	2.000	0.2991	0.3323	-0.4785
120	2.074	0.2721	0.3023	-0.5196
140	2.146	0.2625	0.2917	-0.5351

TABLE 4.1.4 Result obtained using the different method of analysis.

C_A(mol/dm^3)	Slope (-dC_A/dt)	Log (-dC_A/dt)	Log C_A
0.5633	0.00708	-2.15	-0.2493
0.434	0.00398	-2.40	-0.3625
0.368	0.00234	-2.63	-0.4342
0.316	0.00170	-2.77	-0.5003
0.272	0.00110	-2.96	-0.5654

TABLE 4.1.5: Results obtained from experiment for 4% concentration at 50°C

Time (min)	Tite value (cm^3)	Volume of acid reacted (cm^3)	Concentration of acid reacted (mol/dm^3)
0	0.00	0.00	0.7510
20	5.21	0.70	0.6617
40	6.36	1.85	0.5754
60	6.85	2.34	0.5386
80	7.96	3.45	0.4552
100	8.52	4.01	0.4132
120	8.95	4.44	0.3809
140	9.21	4.70	0.3613

TABLE 4.1.6 Result obtained using Integral method of analysis.

T (min)	Log (t)	C_{AO} (mol/dm^3)	Log C_{AO}
20	1.300	0.5117	-0.291
40	1.602	0.4169	-0.380
60	1.778	0.3707	-0.431
80	1.903	0.3273	-0.485
100	2.000	0.3076	-0.512
120	2.079	0.3020	-0.520
140	2.146	0.2818	-0.552

TABLE 4.1.7 Result obtained using the differential method of analysis

C_A(mol/dm^3)	Slope (-dC_A/dt)	Log (-dC_A/dt)	Log C_A
0.7510	0.00239	-1.62	-0. 1244
0.5633	0.00955	-2.02	-0.2493
0.434	0.00457	-2.34	-0.3625
0.368	0.00275	-2.56	-0.4342
0.316	0.00199	-2.70	-0.5003
0.272	0.00120	-2.92	-0.5654

However, when 3% concentration of acid solvent was used, the reaction was represented with the following rate equations:

Using Integral method of analysis equation 4.1 was obtained

2.21

$$-r_A = 0.0398\ C_A \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

Also, with the differential method of analysis, the reaction was represented with equation 4.2 as shown below.

2.22

$$-r_A = 0.0375\ C_A \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.2$$

Thus, equation 4.1 was obtained using table (4.1.3) and equation (3.6) whereas; equation 4.2 was obtained using equation (3.8) and table (4.1.4).

However, the value obtained for the rate constants using Integral method of analysis and differential method of analysis are 0.0389min^{-}

^{1} and 0.0375 min^{-1} respectively, also values obtained for the order of reaction are 2.21 and 2.22 using the Integral and differential method of analysis respectively.

Meanwhile, when 4% concentration of Acid was used, the reaction is represented by the following rate equation:

$-r_A = 0.0446 C_A^{2.12} mol/dm^{-3} min^{-1}$ 4.3

$-r_A = 0.0478 C_A^{2.12} mol/dm^{-3} min^{-1}$ 4.4

However, the value obtained for the rate constants using Integral method of analysis and differential method of analysis are 0.0446min^{-1} and 0.0478min^{-1} respectively, also, value obtained for the order of reaction is 2.12 which is the same for both analysis. Finally, results are tabulated and summarized in the table 4.2.1.

TABLE 4.1.8: The summary of results.

Used Concentration at 50°C	Methods of Analysis	Rate Constant (min^{-1})	Order of Reaction	Rate equation ($mol/dm^{-3}min^{-1}$)
3% H_2So4	Integral	0.0389	2	$-r_A = 0.0389\ C_A^{2.21}$
	Differential	0.0375	2	$-r_A = 0.0375\ C_A^{2.22}$
4% H_2So4	Integral	0.0446	2	$-r_A = 0.0446\ C_A^{2.12}$
	Differential	0.0478	2	$-r_A = 0.0478\ C_A^{2.12}$

4.2 Discussion of Results

From the analysis of the results, it was observed that the production of Oxalic acid from the bark of Eucalyptus Camaldulensis has different rate constants which are (0.0389, 0.0446)min^{-1} at 3% and 4% H_2SO4 concentration using Integral method and (0.0375, 0.0478)min^{-1} using differential method respectively, thus an approximately the same value was obtained using both methods of analysis. Also, it was observed that an approximately the same value of order of reaction which is second order of reaction was obtained for both integral and differential method of analysis. Also by comparing the rate equations obtained (equation 4.2 and equation 4.4) which are obtained by using differential method of analysis at 3% and 4%

concentration of H_2SO4 respectively, it was observed that the rates were higher at 4%compared to the rates at 3% concentration, it was then observed that the rate equation is proportional to the concentration of solvent used.

However, from the table (4.1.4) and table (4.1.7) it was noticed that the gradient gets less as the reaction proceeds, also, the rate of reaction was observed to be decreasing with time with the highest rate at the initial concentration where the concentration was high and similarly, it shows that there was low reactivity as reaction proceeds and this may due to the fact that at the early stages of the reaction there will be high contact between the reactants, that is the frequency of collision is concentration dependent, therefore, as the reaction proceeds and the concentration of the reactant decreases, there tends to be reduction in the frequency of collision of reactants and therefore the reduction in the concentration of the reactant consumed.

However, it was shown that both the differential and Integral method of analysis provide a satisfactory method for evaluating the rate equation for the production of oxalic acid from the bark of Eucalyptus Camaldunesis in which Integral method has advantage for a few numbers of data over that of differential method which requires large numbers of data.

CHAPTER FIVE

5.1 CONCLUSION

From the results of the experiment carried out, Oxalic acid can be obtained from the bark of Eucalyptus Camaldunesis due to the Calcium oxalate salt contained in the bark.

However, a rate equation that links the rate of reaction to the concentration of solvent was established. That is via the rate equation obtained, the rate of reaction was shown to be proportional to the concentration of solvent, which means that the rate of reaction was found to be increased when the solvent concentration increased. Also the rate constants were not the same because different solvent concentrations were used. That is at 3% H_2SO_4 concentration rate constant obtained were (0.0389 and 0.0375) min^{-1} for Integral and Differential method of analysis respectively. While at 4% H_2SO_4 concentration (0.0446 and 0.0478)min^{-1} were obtained for Integral and Differential method respectively.

Therefore, it can be concluded that the mechanism of production of this Oxalic acid involved one-step reaction; its rate was affected by both reactants and has second order of reaction. Also, it is concluded that oxalic acid can be extracted from the bark of Eucalyptus Camaldunesis with better yield at 4% concentration of the solvent.

5.2 RECOMMENDATION

The recommendation includes:

1. Having studied the Kinetics involved in the production of this Oxalic acid then, it is recommended that a chemical plant be designed for the small scale production of Oxalic acid from Eucalyptus Camaldunesis
2. There is a need for other species of Eucalyptus to be tried for Oxalic acid production, to see if better results could be obtained.

3. Further investigation should be carried out to evaluate the purity of this acid produced in the laboratory and the purity of the one produced commercially.
4. Further investigation should be made to ascertain which catalyst especially local one that can enhance the yield of Oxalic acid from the bark of Eucalyptus plants.

REFERENCES

1. Keay, R.W.J; (1989): "Tree of Nigeria", Oxford science publisher, pp. 78.
2. Prof. V.H. Heywood- Consultant Editor, (1979): "Flowering Plants of the world", Oxford university press, London, pp. 151-162.
3. "Encyclopedia Americana", (1979), volume 10, pp 648, volume 28,pp. 69.
4. Smith J.M; (1980): "Chemical reaction kinetics", Mc Graw Hill international publishers, pp 34-86.
5. Levenspiel,O; (1999):"Chemical reaction engineering", John Wiley and sons ,Third Edition, Oregon state University, U.S.A.,pp 12-100.
6. Ababio,O.Y;(1990):"New school chemistry",
7. Lawal, O.; (April, 1996); "Production of oxalic acid from the bark of Eucalyptus Calmaldulensis", F.U.T., Minna, Niger state.
8. Salihu, H.s; (February, 1998); "Production of oxalic acid from the bark of Eucalyptus Calmaldulensis at 50°C and 4 % concentration", F.U.T., Minna.
9. Prof. Perry, R.H and Green, D.; (1987): "Chemical Engineer's Handbook" 6th Edition, Mc Graw Hill Book company.
10. Necker,C., D and Doyke, P.M;(1985): "Organic chemistry ", pp. 48.
11. Wolfe, D.H; (1991): "Essential of general organic and biological chemistry", pp. 306 and 311.
12. Scott, H.F; (1992): "Elements of chemical reaction engineering, university of Michigan, U.S.A, pp.69.

APPENDICES

APPENDIX A

1. Preparation and conversion of 3% H_2So4 to Molar Concentration

% concentration of original Acid = 98%

% concentration of diluted Acid = 3%

.

.. Using, $M_1V_1 = M_2V_2$

Where, M_1 = % concentration of 98% acid

M_2 = % concentration of 3% acid

V_1 = Volume of 98% acid (cm^3)

V_2 = Volume of 3% acid (cm^3)

Then, $V_1 = \frac{M_2 V_2}{M_1}$

$= \frac{3 \times 500}{98}$

$= 15.31 cm^3$

This means that $15.31 cm^3$ of 98% H_2So4 will be present in $500 cm^3$ of water

OR

It means that 30.62 cm^3 of 98% H_2So4 will be present in 1000 cm^3 of water.

However, using the formula

$$C = \frac{10\ dp}{M}$$

Where, C = Concentration in mol/dm^3 of diluted acid

P = Purity level

D = Density

M = molecular weight H_2So4

Thus, d = $1.84 g/dm^3$

M = 98

P = 3%

$$C = \frac{10 \times 3 \times 1.84}{98} = 0.5633\ mol/dm^3$$

2. Preparation and conversion of 6% KOH to Molar Concentration

For 6% concentration, 6g is present in $100cm^3$ of water

60g is present in $1000cm^3$ of water

But for Molar solution,

Molar Mass of KOH = 56g

$\therefore$ 56g of KOH in $1000^3cm = 1mol/dm^3$

Then, 60g of KOH in $1000cm^3$ of water $= \frac{60}{56} mol/dm^3$

$= 1.0714mol/dm^3$

3. Preparation and conversion of 4% H_2So4 to Molar Concentration

Using, $M_1 V_1 = M_2 V_2$

M1 = % concentration of 98% acid = 98%

M2 = % concentration of 4% acid = 4%

V1 = Volume of 4% acid = $500cm^3$

V2 = Volume of 98% acid = ?

Then, $V1 = \frac{M_2 V_2}{M_1} = \frac{4 \times 500}{98}$

$= 20.41cm$

This means that $20.4cm^3$ of 98% H_2So4 will be present in $500cm^3$ of water.

However, using $C = \frac{10\ pd}{M}$

Where $d = 1.84g\ 1dm^3$

P = 4%

M = 98

$\therefore C = \frac{10 \times 4 \times 1.84}{98} = 0.7510mol/dm^3$

4. Preparation and conversion of 8% KOH to Molar Concentration

For 8% concentration, 8g is present in $100cm^3$ of water.

$\therefore$ 80g is present in $1000cm^3$ of water

But for Molar solution,

Molar mass of KOH = 56g

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

The, 80g of KOH in $1000cm^3$ of water $= \frac{80}{56} mol/dm^3$

$= 1.4286mol/dm^3$

APPENDIX B

Conversion of Titre Value to Volume of Acid Reacted

Considering equations below

$2KOH + H_2SO4 \longrightarrow K_2SO_4 + 2H_2O$ 5.1

Using $\frac{M_A V_A}{M_B V_B} = \frac{a}{b}$ 5.2

Volume of excess KOH is obtained as thus:

V_A = $5.31cm^3$ (titre volume after 20mins)

M_A = $0.56\ 33mol/dm^3$

M_B = $1.0714mol/dm^3$

V_B = ?

a = 1; b = 2

Then, $VB = \frac{M_A V_A . b}{M_B . a}$

$= \frac{0.5633 \times 5.31 \times 2}{1.0714}$

$= 5.5836\ cm^3$ = Volume of KOH unreacted during quenching

$\therefore 10 - 5.5836 = 4.4164cm^3$ = Volume of KOH reacted.

To obtain volume of unreacted H_2SO_4 during production of Oxalic acid equation 5.2 is reused since reaction will take place between H_2SO_4 and KOH.

i.e. $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$ 5.3

Then, using $VA = \frac{M_B V_B a}{M_A b}$

Where V_B will be Volume of KOH reacted during quenching

$V_B = 10 - 5.5836$

$= 4.4164cm^3$

$V_A = 1.0714 \times 4.4164 \times 1$

0.5633×2

$= 4.2cm^3$ (unreacted H_2SO4)

Then, $5 - 4.2 = 0.8cm^3$ = reacted H_2SO_4 during the production of Oxalic acid

That is, volume of H_2SO4 reacted during the production by considering Equation 5.4 below.

$CaC_2O_4 + H_2SO_4 \longrightarrow (COOH)_2 + CaSO_4$ 5.4

i.e. by Stoichiometric,

1 mole of CaC2O4 will require 1 mole of H_2SO4 to produce.

1 mole of (COOH)2 and 1 mole of CaSO4.

Then using $V_A = \frac{M_B V_B a}{M_{Ab}}$

Where V_b will be volume of KOH reacted during qunching

$V_B = 10 - 5.5836$

$= 4.4164cm^3$

$V_A = \frac{1.0714 * 4.4164 * 1}{0.5633 * 2}$

$= 4.2cm^3$ (unreacted H_2SO_4)

then, $5 - 4.2 = 0.8cm^3$ = reacted H_2SO_4during the production of oxalic acid

that is, volume of H_2SO_4 reacted during the production by considering equation 5.4 below

$CaC_2O_4 + H_2SO_4 \text{ ---> } (COOH)_2 + CaSO4$ 5.4

i.e by stichiometry,

I mole of CaC_2O_4 will required I mole of H^2S^o4 to produce I mole of $(COOH)_2$ and 1 mole of CaSO4 :

After 40 mins.

Considering equation below :

$2\ KOH + H_2SO_4 \text{ ---> } K_2SO_4 + 2H_2O$

Using = $\frac{M_A V_A}{M_A V_b} = \frac{a}{b}$

Volume of excess KOH is obtained as thus :

V_A = 6.55cm^3 (titre value)

M_A = 0.5633 mol/dms^3

M_B = 1.0714mil/dm^3

V_B = ?

a = 1

b = 2

then $V_B = \frac{M_A V_A . b}{M_B .a} = \frac{0.5633 \times 6.55 \times 2}{1.0714 \times 1}$

= 6.8875 cm^3 = volume of KOH unreacted during qunching

: . 10 – 6.8875 = 3.1125 cm^3 = volume of KOH reacted during qunching

To1 obtain volume of unreacted H^2S^o4 during production of oxalic acid equation (5.2) is used again.

i.e $H_2S_o4 + 2\ KOH$ --- $K_2SO_4 + 2H_2O$

$V_A = \frac{M_B V_B a}{M_A b}$ where V_B now become 3.1125 cm^3

$V_A = \frac{1.0714 \times 3.1125 \times 1}{0.5633 \times 2}$ = 2.96cm^3 = unreacted H_2SO_4

Therefore, 5 – 2.96 = 2.04cm^3 = reacted H_2SO_4 during the production.

After 80 mins.

2 KOH + H^2S^o4 ---> K_2SO_4 + $2H_2O$

Using = $\frac{M_A V_A}{M_B V_B} = \frac{a}{b}$ 5.2

Where V_A = 8.41cm^3 (tite value

M_A = 0.5633 mol/dms^3

M_B = 1.0714mil/dm^3

V_B = ?

a =1 ; b = 2

then $V_B = \frac{M_A V_A . b}{M_B . a} = \frac{0.5633 \times 8.41 \times 2}{1.0714 \times 1}$

$= 8.8433\ cm^3$ = unreacted KOH

: . $10 - 8.8433 = 1.1\ 567\ cm^3$ = reacted KOH

To obtain volume of unreacted H_2SO_4 during production equation (5.2) is used again.

i.e $H_2SO_4 + 2\ KOH \rightarrow K_2SO_4 + 2H_2O$

$V_A = \frac{M_B V_B . a}{M_B . b}$ where $V_B = 1.1567\ cm^3$

$V_A = \frac{1.0714 \times 1.1567}{0.5633 \times 2} = 1.1cm^3$ = (unreacted H_2SO_4

Therefore, $5 - 1.1cm^3 = 3.9cm^3$ volume ofH_2SO_4 that has reacted during production.

After 120 mins.

$2\ KOH + H_2SO_4 \text{--->} K_2SO_4 + 2H_2O$

Using = $\frac{M_A V_A}{M_B V_B} \frac{a}{b}$ 5.2

Where $V_A = 9.19cm^3$ (tite value

$M_A = 0.5633\ mol/dms^3$

$M_B = 1.0714mil/dm^3$

$V_B = ?$

a=1 ; b = 2

then $V_B = \frac{M_A V_A . b}{M_B . a} = \frac{0.5633 \times 9.19 \times 2}{1.0714 \times 1}$

$= 9.66\ cm^3$ = unreacted KOH

: . $10 - 9.66 = 0.34\ cm^3$ = reacted KOH

To obtain volume of unreacted H_2SO_4 during production equation (5.2) is used again.

i.e $H_2SO_4 + 2\ KOH \rightarrow K_2SO_4 + 2H_2O$

$V_A = \frac{M_B V_B . a}{M_B . b}$ where $V_B = 0.34$

$V_A = \frac{1.0714 \times 0.34}{0.5633 \times 2} = 0.32cm^3$ = (unreacted H_2SO_4

Therefore, $5 - 0.32cm^3 = 4.68cm^3$ volume of H_2SO_4 that has reacted during production.

After 140 mins.

$2\,KOH + H_2SO_4 \text{--->} K_2SO_4 + 2H_2^o$

Using = $\frac{M_A V_A}{M_B V_B} = \frac{a}{b}$ 5.2

Where $V_A = 9.46cm^3$ (tite value

$M_A = 0.5633\ mol/dms^3$

$M_B = 1.0714mil/dm^3$

$V_B = ?$

$a = 1\ ;\ b = 2$

then $V_B = \frac{M_A V_A . b}{M_B . a} = \frac{0.5633 \times 9.46 \times 2}{1.0714 \times 1}$

$= 9.95\ cm^3$ = unreacted KOH

$\therefore\ 10 - 9.95 = 0.05\ cm^3$ = reacted KOH

To obtain volume of unreacted H_2SO_4 during production equation (5.2) is reused.

i.e $H_2SO_4 + 2\,KOH \rightarrow K_2SO_4 + 2H_2O$

$V_A = \frac{M_B V_B . a}{M_B . b}$ where $V_B = 0.05$

$V_A = \frac{1.0714 \times 0.05}{0.5633 \times 2} = 0.15cm^3$ = (unreacted H_2SO_4

Therefore, 5 – 0.15cm3 = 4.85cm3 which is the volume of H_2SO_4 that has reacted during production.

APPENDIX C

1. Expression of Data as a function of concentration using simple calculations :

After 20mins:

Since $1000cm^3$ of Acid contains 0.5633 moles H_2SO_4

$\therefore$ $0.8cm^3$ of acid will contain $\frac{0.8 \times 0.5633}{1000}$ moles of H_2SO_4

$= 0.45064 \times 10^{-3}$ moles of H_2SO_4

but fron the quenching reaction 1 mole H_2SO_4 requires 2 moles of KOH

$\therefore$ 0.45064×1^{-3} moles of H_2SO_4 will require $2 \times 0.45064 \times 10^{-3}$ moles KOH

$= 0.90128 \times 10^{-3}$ moles KOH

Also, $1000cm^3$ contain 1.0714 moles of KOH

$10com^3$ will contain $\frac{1.0714 \times 10}{1000}$ moles of KOH

$= 10.714 \times 10^{-3}$ moles of KOH

Moles of KOH required for qunching

$= 10.714 \times 10^{-3} - 0.90128 \times 10^{-3}$

$= 9.81272 \times 10^{-3}$ moles

Moles of H_2SO_4 quenched $= \frac{9.81272 \times 10^{-3}}{2}$

$= 4.90636 \times 10^{-3}$ moles

This implies that:

$10cm^3$ of filtrate contains 4.90636×10^{-3} moles

$\therefore$ $1000cm^3$ filtrate will contain $\frac{1000 \times 4.9063 \times 10^{-3}}{10}$

$= 0.4906ml/dm^3$

After 40mms

Since $1000cm^3$ of Acid contains 0.5633 moles H_2SO_4

2.04 of acid will contain $\frac{2.04 \times 0.5633}{1000}$ moles of H_2SO_4

$= 1.14913 \times 10^{-3}$ moles H_2SO_4

but from the quenching reaction

1 mole H_2SO_4 require 2 moles of KOH

1.14913×10^{-3} moles H_2SO_4 will require $2 \times 1.14913 \times 10^{-3}$ moles KOH

$= 2.2983 \times 10^{-3}$ moles KOH

Also,

$1000cm^3$ contain 1.0714 moles of KOH

$10cm^3$ will contain $\frac{1.0714 \times 10}{1000}$ moles of KOH

$= 10.714 \times 10^{-3}$ moles KOH

moles of KOH required for quenching

$= 10.714 \times 10^{-3} - 2.2983 \times 10^{3}$

$= 8.41574 \times 10^{-3}$

mols of H_2SO_4 quenched $= \frac{8.41574 \times 10^{-3}}{2}$

$= 4.20787 \times 10^{-3}$ moles

=> $10cm^3$ of filtrate contain 4.2078 x 10-3 moles

$1000\ cm^3$ of filtrate contain $\frac{1000 \times 4.2078 \times 10^{-3}}{10} = 0.42079\ mol/dm^3$

After 80mms

Since $1000cm^3$ of Acid contains 0.5633 moles H_2SO_4

$\therefore$ $3.9cm^3$ of acid will contain $\frac{3.9 \times 0.5633}{1000}$ moles of H_2SO_4

$= 2.1969 \times 10^{-3}$ moles H_2SO_4

but from the quenching reaction

1 mole H_2SO_4 require 2 moles of KOH

2.1969×10^{-3} moles H_2SO_4 will require $2 \times 2.1969 \times 10^{-3}$ moles KOH

$= 4.39374 \times 10^{-3}$ moles KOH

Also,

$1000cm^3$ contain 1.0714 moles of KOH

$10cm^3$ will contain $\frac{1.0714 \times 10}{1000}$ moles of KOH

$= 10.714 \times 10^{-3}$ moles KOH

moles of KOH required for quenching

$= 10.714 \times 10^{-3} - 4.3937 \times 10^{3}$

$= 6.32026 \times 10^{-3}$

mols of H_2SO_4 quenched $= \frac{6.32026 \times 10^{-3}}{2}$

$= 3.16013 \times 10^{-3}$ moles

=> $10cm^3$ of filtrate contain 3.16013 x 10-3 moles

1000 cm^3 of filtrate contain $\frac{1000 \times 3.16013 \times 10^{-3}}{10} = 0.316013$ mol/dm^3

After 140mms

Since $1000cm^3$ of Acid contains 0.5633 moles H_2SO_4

$\therefore$ $4.85cm^3$ of acid will contain $\frac{4.85 \times 0.5633}{1000}$ moles of H_2SO_4

$= 2.7320 \times 10^{-3}$ moles H_2SO_4

but from the quenching reaction

1 mole H_2SO_4 require 2 moles of KOH

2.7320×10^{-3} moles H_2SO_4 will require $2 \times 2.7320 \times 10^{-3}$ moles KOH

$= 5.46401 \times 10^{-3}$ moles KOH

Also,

$1000cm^3$ contain 1.0714 moles of KOH

$10cm^3$ will contain $\frac{1.0714 \times 10}{1000}$ moles of KOH

$= 10.714 \times 10^{-3}$ moles KOH

moles of KOH required for quenching

$= 10.714 \times 10^{-3} - 5.46401 \times 10^{3}$

$= 5.2499 \times 10^{-3}$

mols of H_2SO_4 quenched $= \frac{5.2499 \times 10^{-3}}{2}$

$= 2.6249 \times 10^{-3}$ moles

=> $10cm^3$ of filtrate contain 2.6249 x 10-3 moles

1000 cm^3 of filtrate contain $\frac{1000 \times 2.6249 \times 10^{-3}}{10} = 0.2625$ mol/dm^3 H_2SO_4

APPENDIX D

1 Integral Method of Analysis

from thr graph of log t vs log C_{AO} as shown in graph (v)

slope is obtained as thus:

$$\text{slope} = \frac{\Delta \log t}{\Delta \log C_{AO}}$$

$$= \frac{1.66 - 0.6}{-0.6 + 0.4}$$

$$= 3.11776$$
$$= \underline{3.12}$$

Also, Slope = n –1 = -3.12

$$n = 1 - 3.12$$

$$n = \underline{2.12}$$

To Evaluate the rate Constant :

The intercept on graph (v) is taken to be 0.4 and n = 2.12 is sustituted in equation

$$\text{Log}\left[(0.9^{1-n} - 1)/K(n-1)\right] = \text{intercept.}$$

$$\frac{0.9^{1-2.12} - 1}{K(2.12 - 1)} = \log^{-1}(0.4)$$

$$\frac{0.9^{-1.12} - 1}{1.12k} = 2.51189$$

$$\frac{0.125248}{1.12 \times 2.51189} = k$$

2. *Using Differential Method of Analysis*

$$\text{Slope} = n = \frac{(-1.6 + 2.3)}{(-0.105 + 0.435)}$$

$$= \frac{0.7}{0.33}$$

$$= 2.1212$$
$$= \underline{2.12}$$

Also obtained from the graph (vi) is intercept which is –1.32

i.e Log k = -1.32

$k = \log^{-1}(-1.32)$
$= \underline{0.04786}$

3. *Integral Method of Analysis*

from the graph of log t agianst loc C_{AO} as shown in graph (II)

slope is obtained as thus :

$$\text{slope} = \frac{\Delta \log t}{\Delta \log C_{AO}}$$

$$= \frac{1.74 - 0.6}{0.045 - 0.4}$$

$$= \frac{1.14}{0.355}$$

$$= 3.211$$
$$= \underline{3.21}$$

but $n - 1 = \text{slope}$

$n - 1 = -3.21$

$n = 1 - 3.21$

$n = 2.21$

To Evaluate the rate Constant :

The intercept on graph (II) is taken to be 0.46 and n is calculated to be $n = 2.21$, by substitution it into equation then, k is obtained.

i.e $\text{Log}\left[(0.9^{1-n} - 1)/K(n-1)\right] = \text{intercept.}$

$$\frac{0.9^{(1-2.21)} - 1}{k(2.21 - 1)} = \log^{-1}(0.46)$$

$$\frac{(0.9^{-1.21} - 1)}{1.21k} = 2.8840$$

$$k = \frac{0.1360}{1.21 \times 2.8840}$$

$$k = \frac{0.1360}{3.4897}$$

$$k = \underline{0.0389}$$

4. *Using Differential Method of Analysis*

$$\text{slope} = n = \frac{(-2.0 + 2.5)}{(0.425 - 0.2)}$$

$$n = \frac{0.5}{0.225}$$

$= 2.2222$
$= 2.22$

Also obtain from the graph (III) is intercept which is -1.43

therefore, log k = intercept

$$\log k = -1.43$$

$$k = \log^{-1}(-1.4)$$

$$k = 0.03715$$

APPENDIX E

Calculating Slope :

The following slopes are obtained from the graph C_A against t as shown in graph (I) at differents chosen concentration

At 0.5633 mol/dm^3

$$\text{Slope} = \frac{\Delta C_A}{\Delta t}$$

$$= \frac{0.5633 - 0.5}{0 - 8.95}$$

$$= -0.00708$$

At 0.434 mol/dm^3

$$\text{Slope} = \frac{\Delta C_A}{\Delta t}$$

$$= \frac{0.45 - 0.39}{19 - 35}$$

$$= -0.00398$$

At 0.368 mol/dm^3

$$\text{Slope} = \frac{\Delta C_A}{\Delta t}$$

$$= \frac{0.38 - 0.336}{43 - 63}$$

$$= -0.00234$$

At 0.316 mol/dm^3

$$\text{Slope} = \frac{\Delta C_A}{\Delta t}$$

$$= \frac{.328 - 0.3}{70 - 87}$$

$$= -0.00170$$

At 0.272 mol/dm^3

$$\text{Slope} = \frac{\Delta C_A}{\Delta t}$$

$$= \frac{0.281 - 0.256}{110 - 135}$$

$$= -0.00110$$

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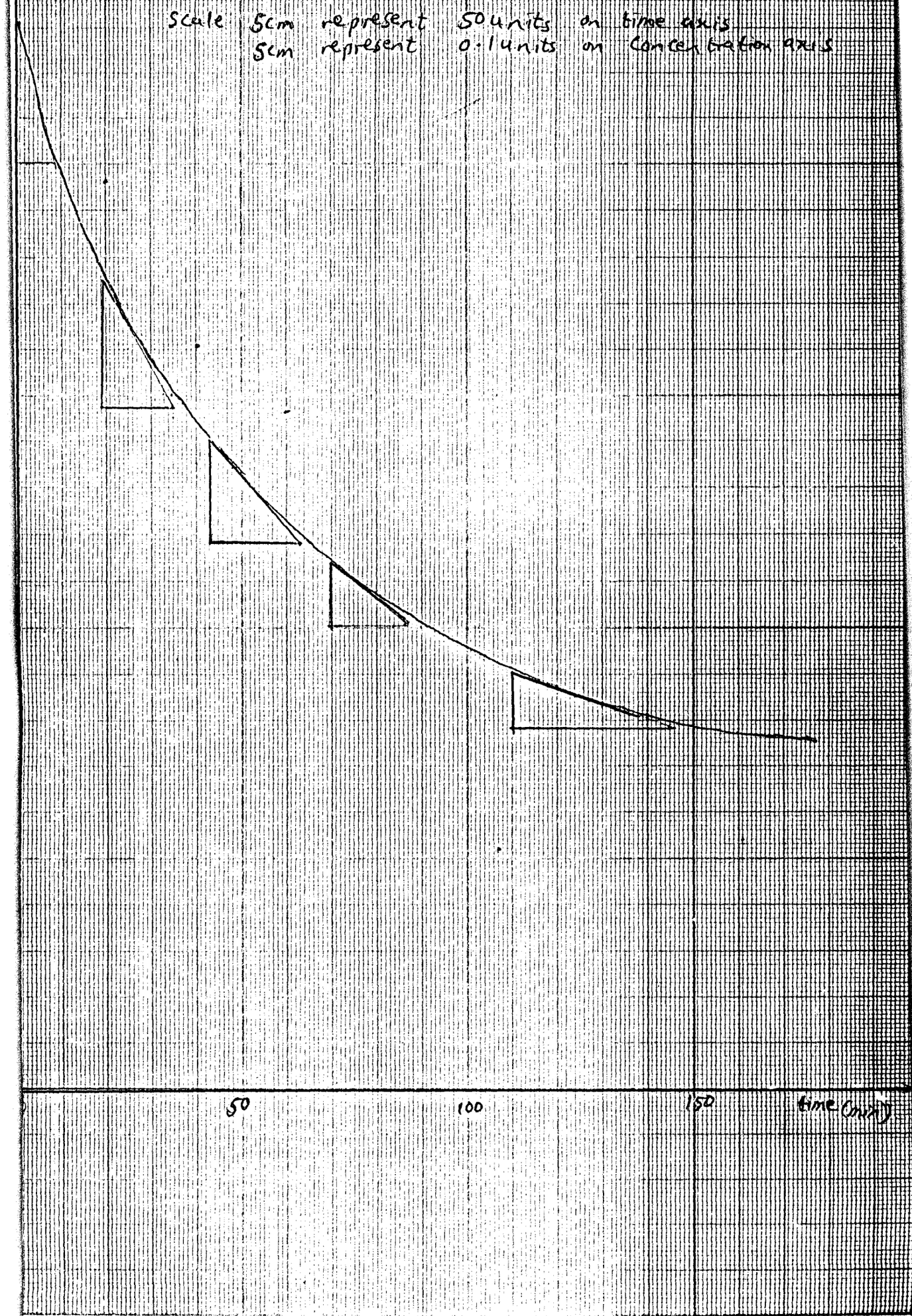
GRAPH I

Graph of Concentration (mol/dm³) against time (min)

Scale 5cm represent 50 units on time axis
5cm represent 0.1 units on concentration axis



F B S CONCEP

GRAPH II

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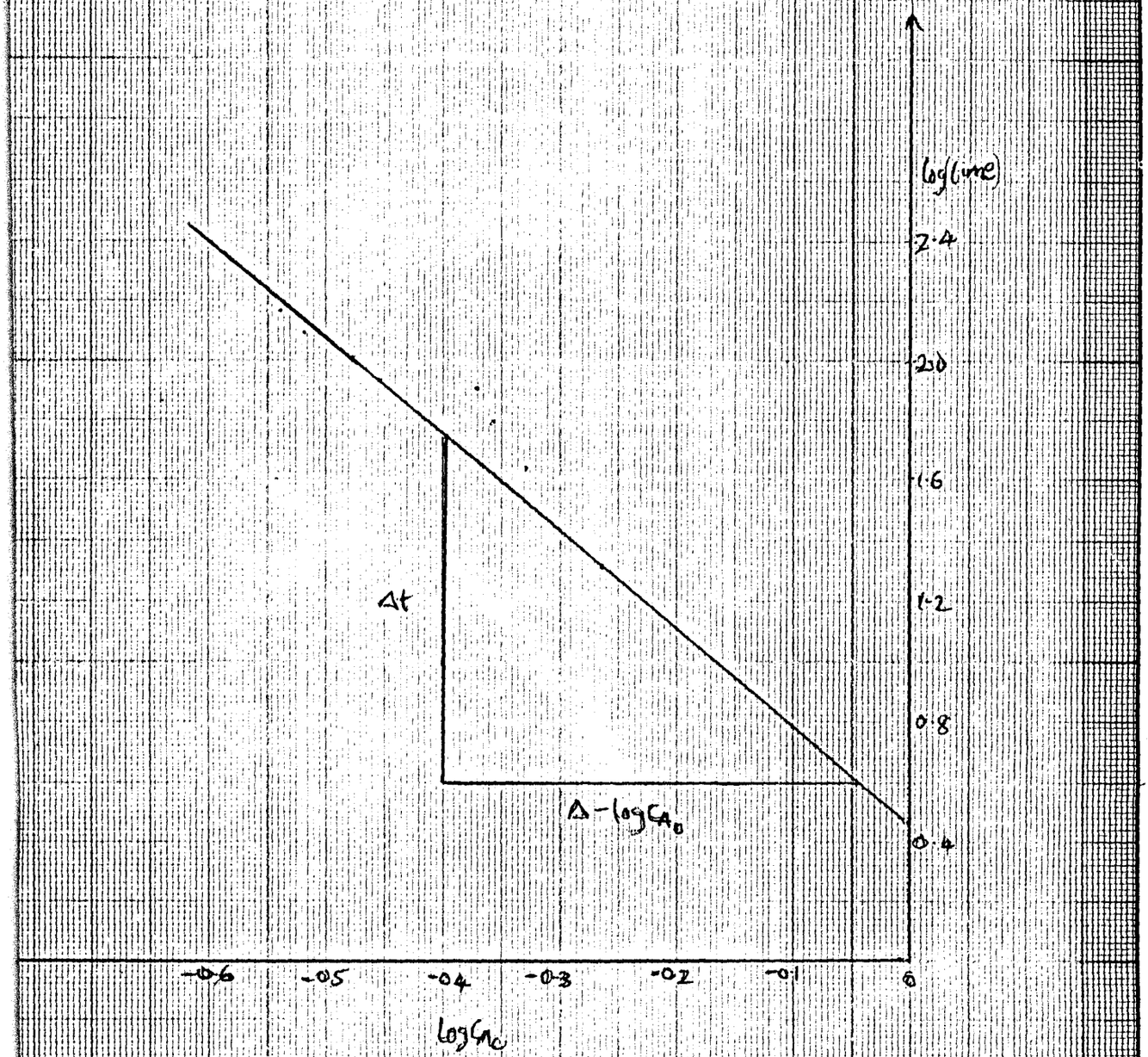
Graph of log t against log C_{A0}

Scale 2cm represent 0.4unit on log(time) — axis

2cm represent −0.1unit on log C_{A0} — axis



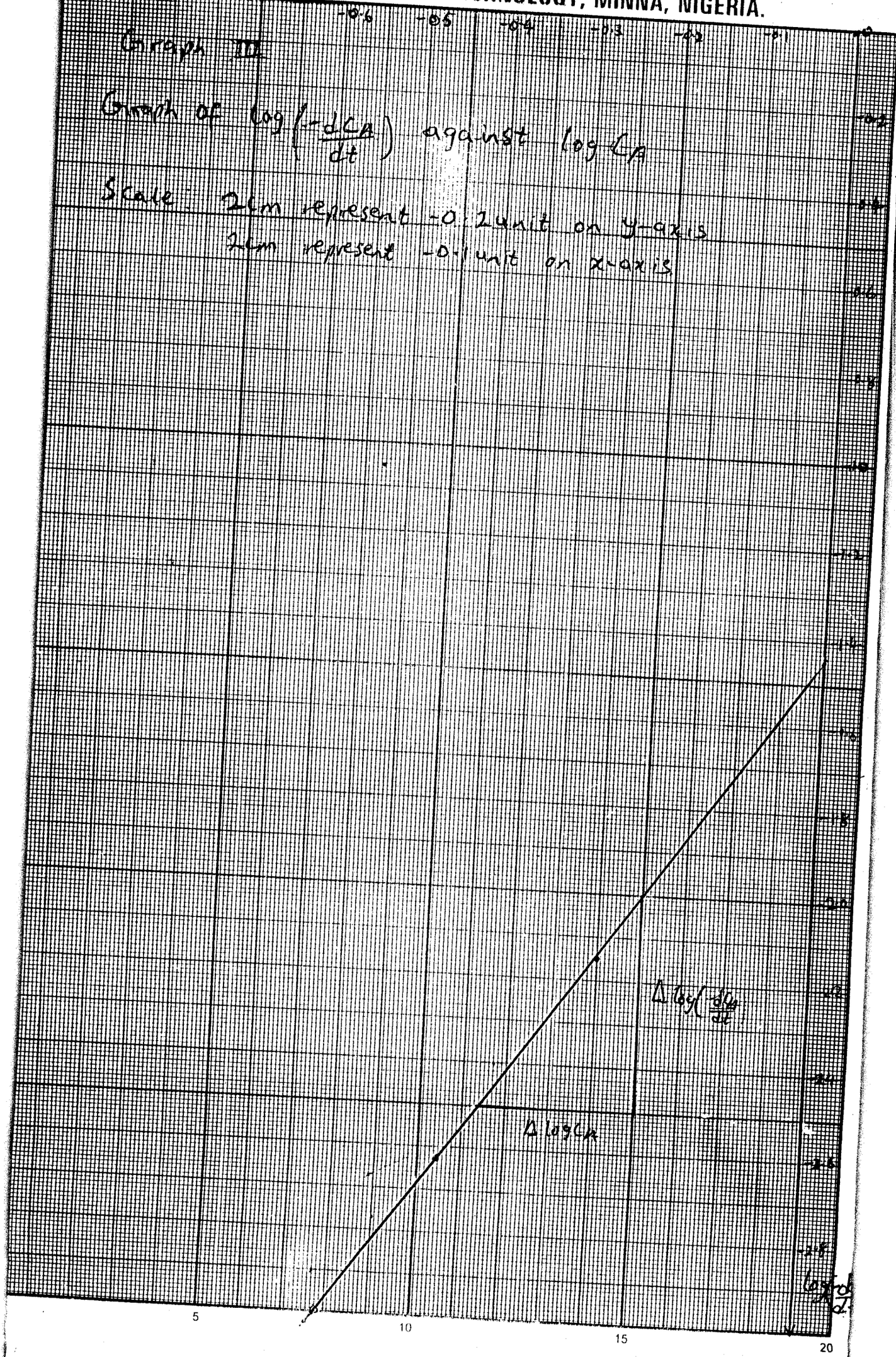
F.B.S CONCEPT

Graph III

Graph of $\log\left(-\frac{dC_A}{dt}\right)$ against $\log C_A$

Scale 2cm represent -0.2 unit on y-axis

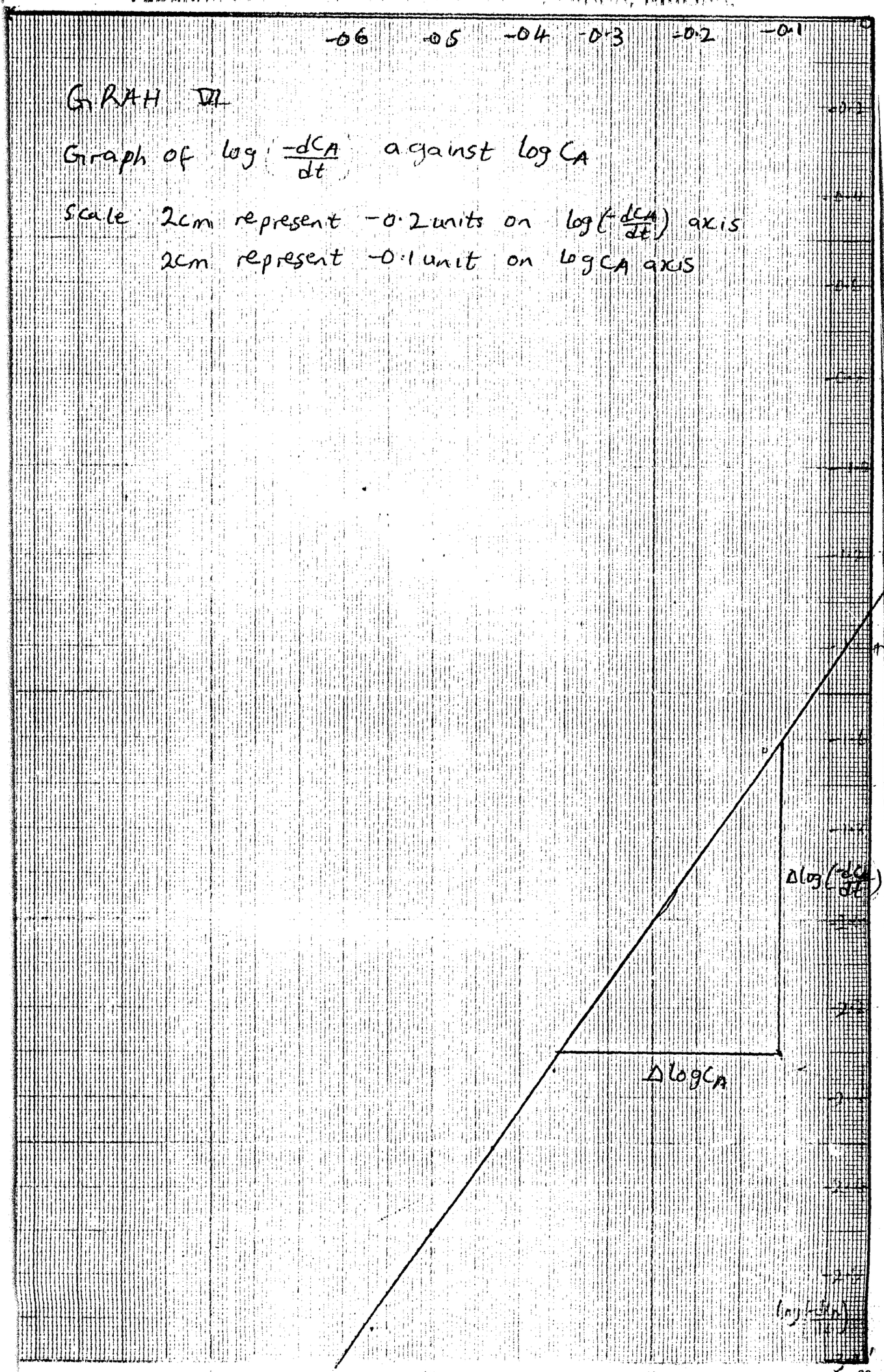
2cm represent -0.1 unit on x-axis



GRAPH III

Graph of $\log\left(\frac{-dC_A}{dt}\right)$ against $\log C_A$

Scale 2cm represent −0.2 units on $\log\left(-\frac{dC_A}{dt}\right)$ axis
2cm represent −0.1 unit on $\log C_A$ axis

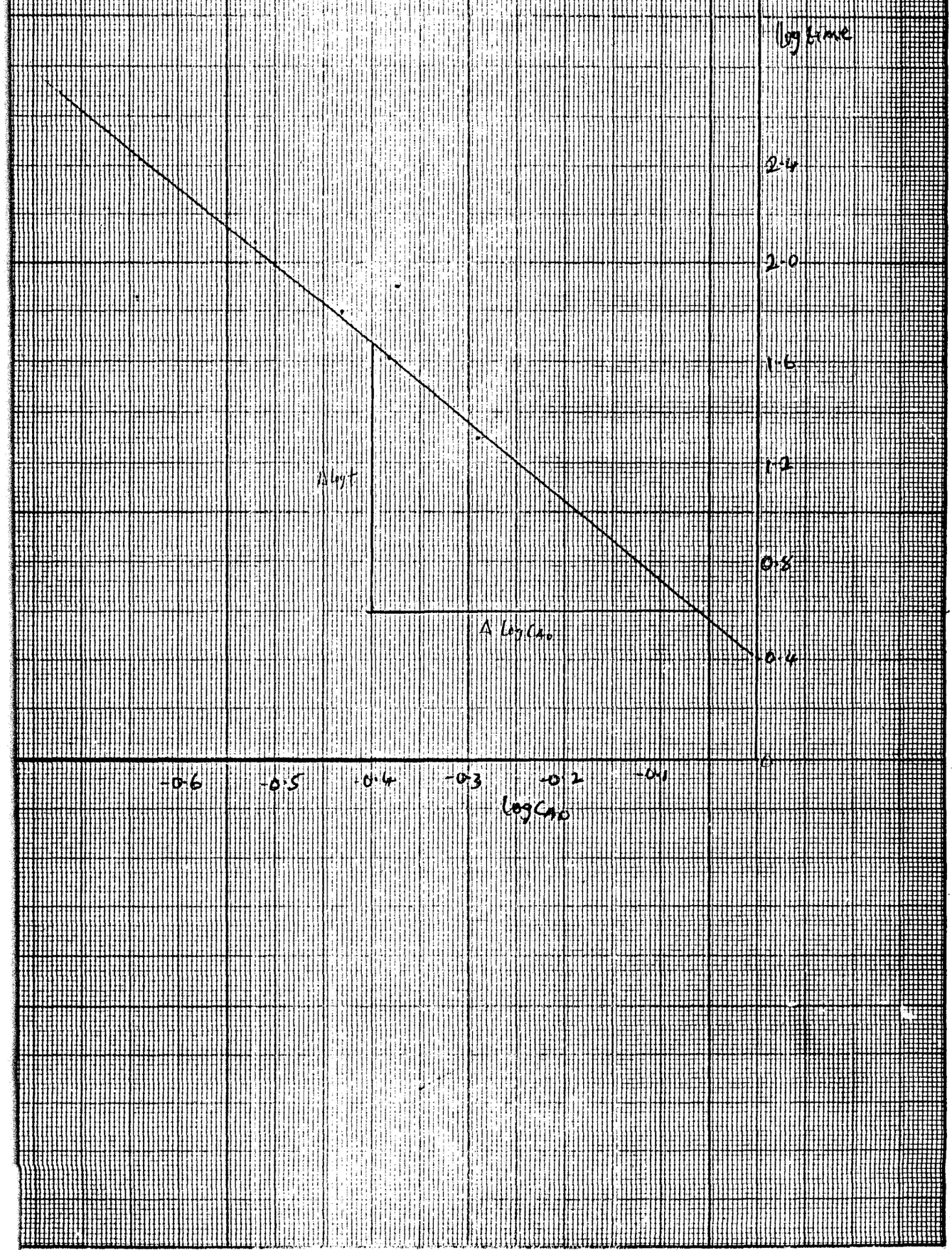


GRAPH I

Graph of log time against $\log C_{A0}$

Scale 2cm represent 0.4 unit on log t-axis

2cm represent 0.1 unit on $\log C_{A0}$-axis



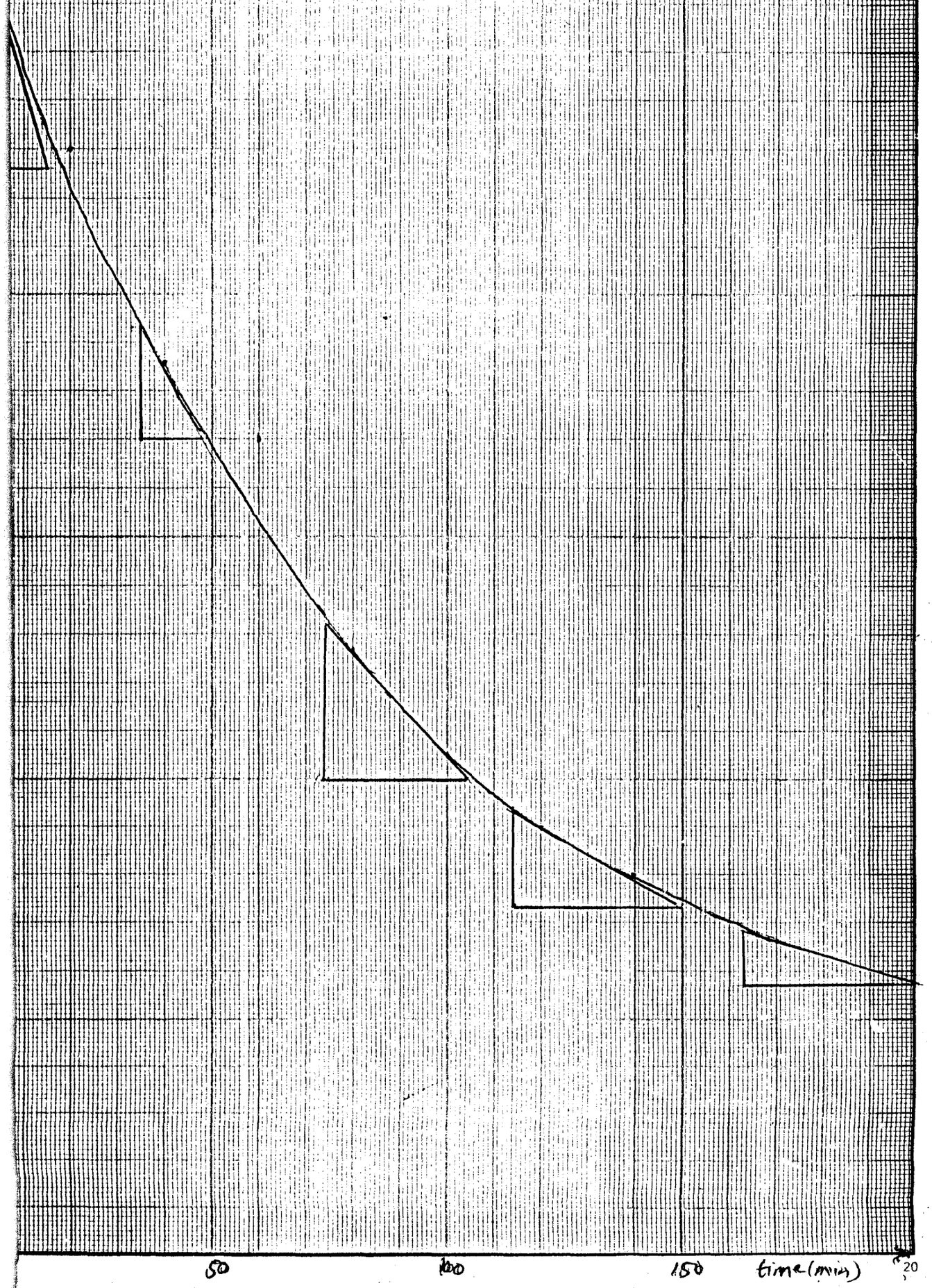
F. B. S CONCEPT

GRAPH IV

Graph of Concentration (mol/dm^3) against time (min)

Scale: 5cm represent 50units on time axis

5cm represent 0·1units on concentration axis



F.B.S CONCEPT