

**DETERMINATION OF THE KINETICS  
OF HYDROCARBON CRACKING IN A  
FLUIDIZED BED REACTOR.  
(CASE STUDY: BUTANE CRACKING)**

**BY**

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NIGERIA**

**OCTOBER 2003**

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

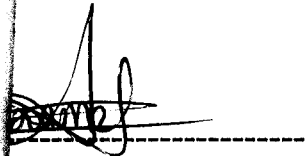
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## DECLARATION

IBOANUGO IKECHUKWU CHUKWUEMEKA, declare that this  
research work has not been presented either in whole or part for the award of  
Bachelor of Engineering anywhere. All literature cited have been duly  
acknowledged in the reference.



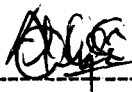
IBOANUGO IKECHUKWU C

20th October, 2003

DATE

## CERTIFICATION

It is to certify that I have supervised, read and approved this project titled "Determination of the kinetics of Hydrocarbon cracking in a fluidized bed reactor" which I find adequate both in scope and quality for the partial fulfillment of the requirements for the award of bachelor of engineering degree in chemical engineering.



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ENGR. M.A. OLUTOYE

31/10/2003

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DATE

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DR. F. ABERUAGBA

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DATE

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EXTERNAL EXAMINER

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DATE

## DEDICATION

I dedicate this research work to the family of Mr. & Mrs. K.O Igboanugo.

## ACKNOWLEDGEMENT

To Almighty God, I render my insurmountable appreciation and thanks for His Grace and divine favour that sees me through life endeavours. I thank all my lecturers for their support in my academic pursuits, especially my supervisor Engr. M.A Olutoye.

I also wish to acknowledge my room mates Stanley and Daniel, all my classmates, my friends, Paye, Imoh, Kaase, Akanimoh, Ashem, Adah, Andah, the Nzedinma's and myself. Together we achieved many feats and we will be there in future to celebrate our greatness and success.

## ABSTRACT

The determination of the kinetics of any chemical process is a very vital aspect in any chemical engineering study. Thus, the aim of this research work is to study the kinetics of butane cracking, presenting a kinetic model which shows a reaction mechanism having its derived hypothetical rate expression corresponding to a rate expression obtained experimentally, with the resistances controlling the catalytic reaction, and the effects of concentration, temperature, catalyst type and weight determined.

The research methodology involved charging different weights of zeolite catalyst into a prototype fluidized bed reactor with the products (the five major products were hydrogen, methane, ethane, ethylene, and propylene) collected in petroleum ether in sample bottles. The differential method of analysis of kinetic data was used and a first order rate constant  $k=2.85 \text{ m}^3/\text{hr.kg}$ , and a rate equation with respect to disappearance of butane,  $-R_b=(2.85 \text{ m}^3/\text{hr.kg}) (C_b, \text{ kmol}/\text{m}^3)$ , with its corresponding activation energy  $E=299.7 \text{ kJ}/\text{kmol}$  ( $54.9 \text{ kcal}/\text{gmol}$ ) obtained. Diffusion of butane gas through the gas film controlled the catalytic reaction, thus becoming the rate-limiting step.

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## CHAPTER ONE

### 1.0 GENERAL INTRODUCTION

Availability of natural gas, petroleum and petroleum products as well as their production processes has become key factors in the development of our society and the world. Petroleum was first discovered in Nigeria in 1956 at Oloibiri in the Niger-river delta by Shell-BP petroleum development company, Nigeria, and ever since, Nigeria has become sub-Saharan Africa's most rapidly developing country.

Petroleum and natural gas consists of complex hydrocarbon compounds. These hydrocarbons are organic compounds containing only carbon and hydrogen atoms, and they are a very large group with many members having great industrial importance, serving as fuels, sources of energy and raw materials for chemical and petrochemical industries.

Cracking is one of the refining and conversion process used to produce better quality fuels and other hydrocarbon products.

Basically, cracking is a process in which high molecular weight hydrocarbons are split into hydrocarbons with lower molecular weight. Over the years, thermal cracking processes have been modified to catalytic cracking to suit different raw materials and have been applied to a wide range of industrial and laboratory reactors.

Since the onset of catalytic cracking, there has been a gradual replacement of natural clays as catalysts with synthetic clays i.e. the amorphous silica-aluminas, which in turn have been largely replaced by the synthetic crystalline zeolites. These improved catalysts greatly increase the rate of chemical reaction without themselves (i.e. the catalysts) being affected by the reaction.

In the quest to advance and optimize petroleum refining and conversion with catalytic cracking as a stepping stone, many modifications have been suggested in reactor design and the fluidized bed reactor is now widely used for gas-solid catalyzed system which applies to cracking of butane over zeolite catalysts. The fluidized bed utilizes the principles of fluidization in which gas-solid and liquid-solid system have the solid phase subjected to behave more or less like a fluid by the upward movement of gas or liquid stream through the bed of solid particles.

For any particular chemical process such as hydrocarbon cracking, operating under appropriate conditions, feed materials maybe transformed into new and different species as products. Chemistry is used to study such processes especially when chemical reactions are involved which leads to the establishment of the kinetics of the process. Thus, chemical kinetics is the study of the time dependent behaviour of chemically reacting systems with the

major concern of the measurement of the rates of reaction and their interpretation, also probing the more fundamental questions relating to the behaviour of the chemical reactions and the factors affecting or controlling the reaction or process.

### 1.1 JUSTIFICATION

This study was carried out and the importance and advantages of such study, which has no bounds, can be summarized as follows:

1. The gain of better understating of the kinetic model and reaction mechanism, of a very important industrial process i.e. the cracking of hydrocarbons present in different raw materials.
2. This understanding will provide a process engineer with the knowledge of the optimum conditions needed for maximum yield of the products at lower costs, with the attendant advantage of the fluidized bed reactor having a reduced-pollution effect.
3. A thorough understanding gained from the study will equip the design engineer to construct a more realistic and useful economic analysis of the process during detailed design stage.
4. Insight gained by this study will aid the semi-emperical approach in modeling the process and subsequently ensure proper control of the system.
5. Findings from this study can be corroborated with pilot plant studies on the project topic, thus enhancing scale up of pilot plants.

## 1.2 SCOPE

The scope of this study dwells on the following:

1. Proposing of a hypothetic kinetic model and a reaction mechanism from which a theoretical rate expression is obtained from the model.
2. The batch wise operation of the prototype fluidized bed reactor operating without a regenerator.
3. Finding the experimental rate equation based on the unit weight of catalysts with the method of differential analysis conforming to that of a plug flow reactor.
4. Evaluating the temperature dependent term i.e. rate constant  $k$ , and the activation energy  $E$  of the reaction.
5. Testing for the resistance that controls this gas solid catalyzed system with methods given in literature.

## 1.3 OBJECTIVES

1. To determine experimentally the rate equation for the disappearance of butane in its catalytic cracking carried out in a laboratory prototype fluidized bed reactor.
2. To propose a reaction mechanism and kinetic model fro the catalytic cracking of butane, investigating the agreement of the proposed kinetic model and the rate equation obtained.
3. To provide explanations on the effects of concentration, temperature, catalyst type and weight on the reaction rate of the catalytic cracking of butane.
4. To determine the resistances that control the catalytic reaction, thus giving the rate-limiting step of the catalytic reaction.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 BRIEF HISTORY

The conversion of petroleum to its many products bearing in mind the presence of the complex hydrocarbons in its mixture has brought about breakthroughs in scientific and engineering fields. Among the conversion process, cracking plays vital roles with the main objective of converting heavy petroleum distillates to lighter ones.

Thermal cracking, which is the earliest process, was achieved by the appropriate application of heat alone. It can also be referred to as pyrolysis. Its use began in 1912 (Encyclopedia of Science & Tech., 1982). Engineer Eugene Houdry in the 1920s showed that better quality product could be obtained by treating heavy distillates at high temperatures with acidified montmorillonite clays and this led to the introduction of industrial catalytic cracking in 1936 (Encyclopedia of chemical Tech., 1981). In 1926, W.W. Odell, developed a catalytic cracker based on the process of fluidizing a bed of particles, with the industrial fluidized catalytic cracking unit (FCCU), starting operations in Bay Town Texas in 1942 (Perry et al, 1997). Zeolite catalysts with time replaced the initial clays and the amorphous silica aluminas.

The development and breakthroughs in petroleum and petrochemical industries brings to the fore the pertinent need to study the chemical kinetics involved in the cracking of complex hydrocarbon mixtures. Kinetic parameters for the pyrolysis (thermal cracking) of n-butane has been reported by several investigators and they were observed to have their order of reaction vary between 1 and 1.5, and their activation energy within 219.7 kcal/gmol to 78.7 kcal/gmol. (SUSU. A.A, 1997).

#### 2.2 BUTANE

Of the diverse groups homologous series present within the family of hydrocarbons, butane falls into the group of paraffinic alkanes. It is a colorless, odorless, gaseous hydrocarbon with molecular formula  $C_4H_{10}$ , and it exists either as normal butane or isomeric butane. In terms of reactivity, butane undergoes only substitution and decomposition reactions. Butane can be used as the primary content in domestic gas. Cracked products of butane can be used in polymerization to obtain raw materials for petrochemical industries.

## 2.3 CRACKING

Cracking is a process widely used in the petroleum industry to split higher molecular weight hydrocarbon to lower molecular weight. Cracking can be thermal, hydrocracking or catalytic.

### 2.3.1 THERMAL CRACKING

This is a process in when the carbon-to-carbon bonds of hydrocarbons are broken by the action of heat alone. It consists essentially of the heating of petroleum or any of its fractions to a temperature (usually above 450°C) at which substantial thermal decomposition takes place. There are a number of refining processes based on thermal cracking; they generally operate at low pressures and high temperatures.

### 2.3.2 CATALYTIC CRACKING

In this process, the hydrocarbons are split to lower molecular weights in the presence of acidic inorganic substances called catalysts. This is the major process used throughout most of the world oil industry for the production of high-octane quality gasoline. Engineering advancement have brought about the transformation from the initial fixed bed catalytic cracking to moving beds and finally to fluidized bed catalytic cracking. During catalytic cracking, all-volatile carbonaceous materials are deposited on the catalyst surface as coke and turned off during regeneration.

Catalytic cracking has the advantages of producing maximum yields, improved quality products, reduced process time and increased rate of reaction by lowering the activation energy. With time, the catalyst lost their activity and this is the major disadvantage catalytic cracking.

## 3.3 HYDROCRACKING

This is a catalytic high-pressure process flexible enough to produce high octane gasoline or aviation jet fuel. The process is achieved by passing oil feed together with hydrogen at high pressure (6894Kpa - 17236Kpa) and moderate temperature (260 - 400°C) in contact with bifunctional catalyst comprising an acid solid and a hydrogenating metal component.

## 2.4 CATALYSTS

A catalyst is a substance that alters the rate of reaction of any chemical reaction of any chemical process. The use of catalysts enables the rate of reaction to be increased by thousands and sometimes millions of times by lowering the activation energy (i.e. energy required for bonds in the reactants to break so that reaction interactions can be initiated) with its selective property improving the efficiency and economics of the process.

Catalysts become deactivated when they lose their ability to crack the feed to lower boiling fractions. If deactivation is caused by a deposition and physical blocking of the surface it is termed FOULING, while removal of the solids deposited is termed REGENERATION. If the catalysts surface is slowly modified by chemisorptions (a chemical surface retention process in which weak chemical bonds are formed between liquid or gas molecules and a solid surface) on the active sites, which are not easily removed, then the process is called POISONING. If there is gradual wear away of the surface (ATTRITION) due to flow past the catalysts, the catalysts is said to be AGEING.

The activity of a catalyst is the ability to crack the feed to a lower boiling fraction.

Yield is the amount of specified product in a given process per mole of reactant consumed.

Selectivity is the number of moles of desired product formed per mole of undesired product formed.

Cracking catalysts must have the following essential properties:

- 1) A chemical composition capable of maintaining a high degree of acidity.
- 2) A physical structure of high porosity and large surface area for proper contacting with the reactant.
- 3) High selectivity and activity.
- 4) Mechanical durability for its industrial use.

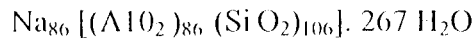
## ZEOLITES

The zeolites are aluminosilicates that contain alkali and alkali earth metals such as sodium, potassium and calcium as well as water molecules within their structural framework. They are relatively porous catalysts with cation exchange and reversible dehydration properties enabling them to act as molecular sieves i.e. having ability to separate molecular structures based on their size and/or for the selective adsorption of gases.

More than 30 distinct species of zeolite occur in nature with numerous zeolite being synthesized. These synthetic zeolites are preferred over natural ones because of their uniform chemical composition. These crystalline catalysts have cracking activity 50-100 times that of

amorphous catalysts permitting greater conversion with less coke deposition. They are more resistant to thermal degradation, having a configuration that allows for the recovery of heat of combustion.

A typical example of zeolite is the zeolite 13 x which has the formula:



And the other zeolites have a similar general formula and the choice of zeolites depends on cracking reaction to be undertaken (V.N Erikh et al, 1988).

## 2.6 FLUIDIZED BED REACTORS

Fluidization converts a bed of solid particles into an expanded suspended mass that has many properties of a fluid. This is achieved due to the fact that a fluid flowing upwards through a bed of solids exerts a certain force on the bed opposite to gravity. When gas is passed upwards through a bed of solid particles, friction causes a pressure drop. As the gas velocity is increased the pressure drop increases until it equals the weight of the bed divided by the cross-sectional area. At this point, the velocity is called minimum fluidizing velocity. The bed continues to expand uniformly until at some higher velocities when bubbles will form. At this point we have the minimum bubbling velocity, and the bubbling fluidized bed. Thus, the variation of inlet velocities, play an important role in the determination of the kinetics of the process.

For a fluidized bed reactor with an incorporated regenerator, the high rate of transfer of solids between the regenerator and the reactor permits a thermal balance between the exothermic burning of carbon in the regenerator and the endothermic cracking of the hydrocarbon feed in the reactor. The use of the reactor result in much lower gas and solid back mixing and an approach to plug flow reactor.

## 2.7 CHEMICAL KINETICS

Chemical kinetics involves the study of the modes and mechanism of reactions, the physical and energy changes involved, and the rate of formation of products. It searches for the factors that influence the rate of reaction, measures the rate and proposes explanation for the values found. The factors affecting the reaction rate could be the concentration of the reactants, the pressure, the temperature, the nature of catalyst involved if any, the type and nature of the reaction considering also the resistance controlling the process.



### 2.7.1 KINETIC MODELS

Reactions do not normally proceed as written. Reactant progress to products through a sequence of elementary steps that involves reactive intermediates. This progression of reactants to products through a sequence is known as REACTION MECHANISM. Thus, among the many objectives of any kinetic study is the determination of the reaction mechanism of the process reactions. This can be achieved by proposing a kinetic model for the steps involved in the reaction and obtaining a final rate of reaction whereby the rate of formation or disappearance of intermediates have been properly taken care of, with the reaction mechanism taking cognizance of the chemistry of the formation of intermediates with the attendant interactions which bring about the reactions chain initiation, propagation and termination.

To explain the kinetics of many processes, we assume that a sequence of elementary reactions are actually occurring, but that we can not measure or observe the intermediates formed because they are only present in minute quantities. Thus, we observe only the initial reactants and final products, or what appears to be a single reaction.

### 2.7.2 RATE OF REACTION

The rate of reaction is measured experimentally by following the concentration of some reactant or product involved in the reaction as a function of time as the reaction proceeds from a non-equilibrium state to an equilibrium state. It can be expressed as the rate of decrease of the concentration of a reactant or the rate of rate of increase of the concentration of the product. The rate of reaction can be written in many forms but based on volume of catalysts and weight of catalyst we have:

$$\dot{R}_i = \frac{1}{V_p} \frac{dN_i}{dt} = \frac{\text{(Moles of } i \text{ formed)}}{\text{(volume of particles) (time)}} \quad (1)$$

$$\text{And } R_i = \frac{1}{W} \frac{dN_i}{dt} = \frac{\text{(Moles of } i \text{ formed)}}{\text{(Weight of solid) (time)}} \quad (2)$$

$$\text{With } \dot{R}_i V_p = R_i W \quad (3)$$

Where  $\dot{R}_i$  = rate based on Volume of catalyst particles  
 $R_i$  = rate based on Weight of catalyst.

When we have a reaction involving Reactants A,B----, the rate of disappearance of A is given as:

$$-R_A = k C_A^a C_B^b \quad (4)$$

Where  $k$  = rate constant  
 $C_A$  = concentration of reactant A  
 $C_B$  = concentration of reactant B

We call the powers to which the concentrators are raised the Order to reaction.

ath order with respect to A

bth order with respect to B

nth order overall.

### 2.7.3 ARRIHENIUS' LAW

To obtain rate equations with a significant high accuracy there is need to correlate the experimental result with the theories involved in the determination of the kinetics of behind any process. Arrhenius law is a good approximation to other theories, in determining the temperature dependent term i.e. the rate constant  $k$ (Levenspiel, 1972).

For many reactions, the rate expression can be written as the product of the temperature dependent term and composition i.e.

$$R_i = f_1 (\text{temp}). f_2 (\text{composition}) \quad (5)$$

$$R_i = k f_2 (\text{composition}) \quad (6)$$

For such reactions, the rate constant has been found to be well represented by ARRIHENIUS LAW:

$$k = k_0 e^{-E/RT} \quad (7)$$

where  $k_0$  = frequency or pre-exponential factor

$E$  = activation energy

$R$  = gas constant

$T$  = temperature

This expression fits experiment over wide temperature ranges and is strongly suggested from various standpoints as being a good approximation to the true temperature dependency. (Levenspiel 1972).

## 2.7.4 RESISTANCES IN SOLID CATALYSED REACTIONS

In developing rate expressions for catalytic reactions we account for the various processes that may cause resistance to the reaction. For a single porous catalyst we may visualize these as follows:

**Gas film resistance:** Reactants diffuse from the main body of the fluid to the exterior surface of the catalyst.

**Pore diffusion resistance:** Due to the fact that the interior of the pellet contains so much more area than the exterior, most of the reaction takes place within the particle. Therefore reactants move from the pores into the pellets.

**Surface phenomenon resistance:** At some point in their wanderings, reactant molecules becomes associated with the surface of the catalysts. They react to give products which are then released to the fluid phase within the pores.

**Pore diffusion of products:** occurs when products move from the mouth of the catalysts pores unto the main gas stream.

**Resistance to heat flow:** for fast reactions accompanied by large heat release or absorption in which the flow of heat is not fast enough to keep the pellet isothermal.

## 2.7.4 INTERPRETATION AND ANALYSIS OF KINETIC DATA

The determination of the rate equation is usually a two-step procedure. First, the concentration dependency is found at fixed temperature, and temperature dependence of the rate constant is found yielding a complete rate equation.

To explore the kinetics of catalytic reactions (exemplified in this study) the plug flow is commonly used where the axial mixing introduced by the flow between the solid particles is considered to be negligible, with the flow being orderly and no element of fluid overtaking or mixing with any other element ahead or behind.

### 2.7.4.1 INTEGRAL ANALYSIS

In integral analysis of kinetic data, a specific mechanism with its corresponding rate equation conforming to its flow pattern (i.e. either plug flow or mixed flow) is put to test by integrating the equation. In this approach a series of experimental runs with fixed initial concentration with catalyst weight and molar rate are obtained in such a manner that a wide range of the ratio of catalyst weight to molar rate is obtained with the conversion. The equation to be tested is selected and performance equation integrated according to its flow pattern. A graph of ratio of weight to molar rate is plotted against the integral performance

equation, if a straight line is obtained passing through the origin, then the equation satisfactorily fits the data.

#### 2.7.4.2 DIFFERENTIAL ANALYSIS

In this method, a series of experimental runs is made using a fixed feed but with varying molar rate and/or catalyst weight. A plot of conversion versus ratio of catalyst weight to molar rate is used to obtain slopes, which will be plotted against the corresponding concentration value. If this plot is linear and passes through the origin then the equation satisfactorily fits the data. Alternatively, the change in conversion at each concentration value is divided by the ratio of the weight to molar rate. The value obtained is plotted against the corresponding concentration value if the plot is linear and passes through the origin then it satisfactorily fits the data.

#### 2.7.4.3 DETERMINATION OF THE ACTIVATION ENERGY

From the Arrhenius equation  $k = k_0 e^{-E/RT}$ , the activation energy can be determined experimentally, by carrying out the reaction at several temperatures. Taking the natural logarithm of the Arrhenius equation then we have,

$$\ln k = \ln k_0 - \frac{E}{R} \left( \frac{1}{T} \right) \quad (8)$$

Plotting  $\ln k$  versus  $\left( \frac{1}{T} \right)$  at the different temperatures gives the intercept as  $\ln k_0$  and slope  $\frac{E}{R}$  of the resulting downward graph. Multiplying the value of the slope by the gas constant  $R$ , gives the activation energy  $E$  of the reaction.

#### 2.7.4.4 DETERMINATION OF THE RESISTANCE THAT CONTROLS THE REACTION

(a) **Gas film resistance:** to test whether film resistance controls, we compare  $k_{obs} V_p$  versus  $k_m S_{ex}$ .

$$\text{i.e. } \frac{\text{Observed rate}}{\text{rate if film resistance controls}} = \frac{k_{obs} V_p}{k_m S_{ex}} \quad (9)$$

$$\frac{k_{\text{obs}} V_p}{k_m S_{\text{ex}}} = \frac{\left( -\bar{R}_{\text{b,obs}} / C_{\text{bg}} \right) V_p}{k_m S_{\text{ex}}} \quad (10)$$

where  $k_{\text{obs}}$  = rate constant based on observed reaction rate

$V_p$  = volume of catalyst pellet

$k_m$  = mass transfer coefficient

$S_{\text{ex}}$  = unit exterior surface of catalyst pellet

$-\bar{R}_{\text{b,obs}}$  = reaction rate based on volume of catalyst

$C_{\text{bg}}$  = concentration of butane gas at inlet gas stream.

If  $k_{\text{obs}} V_p$  is much smaller than  $k_m S_{\text{ex}}$ , we ignore the resistance to mass transport through the film. If the two terms are of the same magnitude we suspect that the gas film resistance affects the rate (Levenspiel, 1972).

### (b) Strong Pore Diffusion:

for no pore diffusion resistance

$$\frac{\left( -\bar{R}_{\text{b,obs}} \right) L^2}{D_e C_{\text{bg}}} < 1 \quad (11)$$

for strong pore diffusion resistance

$$\frac{\left( -\bar{R}_{\text{b,obs}} \right) L^2}{D_e C_{\text{bg}}} > 1 \quad (12)$$

where  $D_e$  = effective thermal diffusivity

$L$  = characteristic length of catalyst pellet

$$L = \frac{\text{volume of pellet}}{\text{exterior surface area}} \quad (13)$$

### (c) Temperature Effects

(1) Film  $\Delta T$ : The whole pellet may be hotter (or cooler) than the surrounding fluid, and the temperature change is given as

$$\Delta T_{\text{Film}} = \frac{L \left( -\bar{R}b_{,\text{obs}} \right) (-\Delta H_r)}{h} \quad (14)$$

where  $(-\Delta H_r)$  = heat of reaction

$h$  = heat transfer coefficient

$$\text{but } \Delta H_r = \Delta H_f + R \int_{T_0}^T \frac{C_p}{R} dT \quad (15)$$

$$\Delta H_r = \Delta H_f + R \int_{T_0}^T \left( A + BT + CT^2 + DT^{-2} \right) dT \quad (16)$$

$C_p$  = Specific heat

A, B, C and D, are constants for determination of specific heat at reference temperatures (J.M Smith, 1996).

$\Delta H_f$  = change in standard heat of formation.

(2) Within Particle  $\Delta T$ : there may be temperature variations within the pellet and the expression is given as

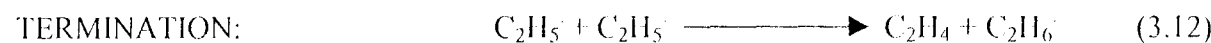
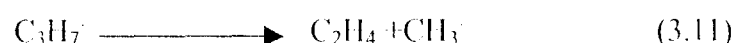
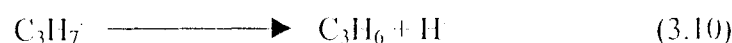
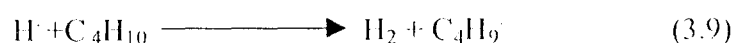
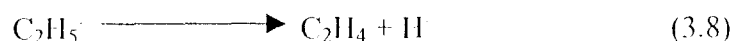
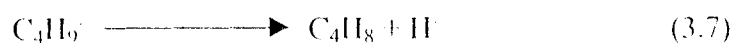
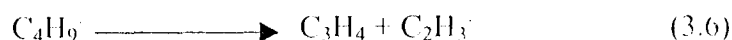
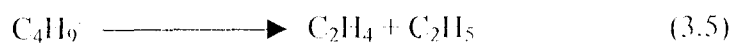
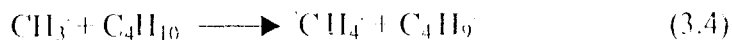
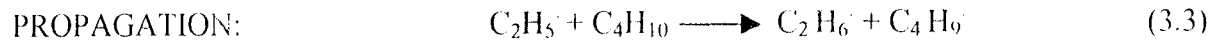
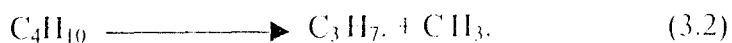
$$\Delta T_{\text{Particle}} = \frac{D_c \left( C_{bg} - 0 \right) (-\Delta H_r)}{K_{\text{eff}}} \quad (17)$$

$K_{\text{eff}}$  = effective thermal conductivity

## CHAPTER THREE

### 3.0 KINETIC MODEL FOR BUTANE CRACKING

The reaction mechanism for the cracking of butane involving the initiation, propagation and termination steps is illustrated below. The major products of the cracking reaction are hydrogen, methane, ethylene, ethane and propylene.



At the initiation stage the butane molecule's bond are broken to give radicals or intermediates.

At the propagation stage, the radical either undergoes bond cleavage and form products, or radicals still combine with the butane molecule to give products.

At the terminations stage two radicals combine to form the products and this leads to the end of the cracking reactions.

A three-step mechanism is hypothesized to explain the kinetics of the cracking of butane.

1. Diffusion of gaseous butane B through the film surrounding the catalyst pellet Z:



2. Penetration, diffusion and reaction within the pores of the catalyst to form products on catalyst surface



3. diffusion of products through the gas film surrounding the catalyst into the products stream.



Where B = butane

Z = catalyst

BZ = butane on catalyst surface

PZ = products on catalyst

P = products

From equations (3.14) to (3.16) the rate of butane cracking is hypothesized, starting with rate of formation of PZ, with square bracket used to indicate concentration.

$$R_{PZ} = k_3 [PZ] - k_4 [BZ] + k_6 [P][Z] - k_5 [PZ]$$

$$R_{PZ} = (k_3 - k_5) [PZ] - k_4 [BZ] + k_6 [P][Z]$$

Assuming that  $R_{PZ} = 0$ , since its concentration is very small, then

$$[PZ] = \left( \frac{k_6}{k_3 - k_5} \right) [P][Z] - \left( \frac{k_4}{k_3 - k_5} \right) [BZ] \quad 3.17$$

Also

$$R_{BZ} = k_1 [B][Z] - k_2 [BZ] + k_4 [PZ] - k_3 [BZ]$$

at  $R_{BZ} = 0$ , since its concentration is very small, then

$$[BZ] = \left( \frac{k_1}{k_3 + k_2} \right) [B][Z] + \left( \frac{k_4}{k_3 + k_2} \right) [PZ] \quad 3.18$$

$$\text{also } R_B = k_2 [BZ] - k_1 [B][Z] \quad 3.19$$

substituting (3.18) into (3.19)

$$R_B = \left( \frac{k_1 k_2}{k_3 + k_2} \right) [B][Z] + \left( \frac{k_2 k_4}{k_3 + k_2} \right) [PZ] - k_1 [B][Z] \quad 3.20$$

substituting (3.17) into (3.20)

$$R_B = \left( \frac{k_1 k_2}{k_3 + k_2} \right) [B][Z] + \left( \frac{k_2 k_4 k_6}{(k_3 - k_5)(k_3 + k_2)} \right) [P][Z] - \left( \frac{k_2 k_4}{(k_3 - k_5)(k_3 + k_2)} \right) [BZ] - k_1 [B][Z] \quad 3.21$$

With the assumption that  $k_2$  is very, very small then equation 3.21 reduces to

$$R_B = -k_1 [B][Z] \quad 3.22$$

Since the concentration of the catalyst is constant, let  $k = k_1 [Z]$

Where  $k$  = rate constant with respect to the disappearance of butane

$$-R_B = k [B] \quad 3.23$$



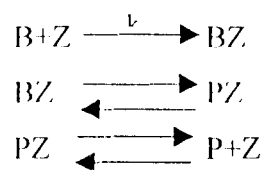
$$-R_B = k [B]$$

3.23

From equation (3.23) the hypothetical rate of disappearance of butane is

$$-R_B = k [B]$$

Thus, the three-step mechanism for butane catalytic cracking is:



## CHAPTER FOUR

### 4.0 RESEARCH METHODOLOGY

#### 4.1 EXPERIMENTAL DESIGN

To determine the kinetics of the cracking of butane over zeolite catalyst, this experiment was carried out using a prototype laboratory scale fluidized bed reactor with the aim of obtaining a rate expression for butane cracking with the temperature dependent term and concentration dependent term evaluated, and the resistance controlling the catalytic reaction determined.

The parameters of the experimental set-up are;

- i. Reactor internal diameter,  $d_{int} = 0.0853\text{m}$
- ii. Reactor external diameter,  $d_{ext} = 0.27\text{m}$
- iii. Catalyst diameter,  $d_p = 250\mu\text{m}$
- iv. Catalyst density,  $P = 1.12\text{g/cm}^3$

For the batch process with a constant reaction time of 5 minutes, the variables are

- i. Catalyst weight
- ii. Gas flow-rate
- iii. Gas pressure
- iv. Temperature

#### 4.2 EQUIPMENT / APPARATUS AND MATERIALS

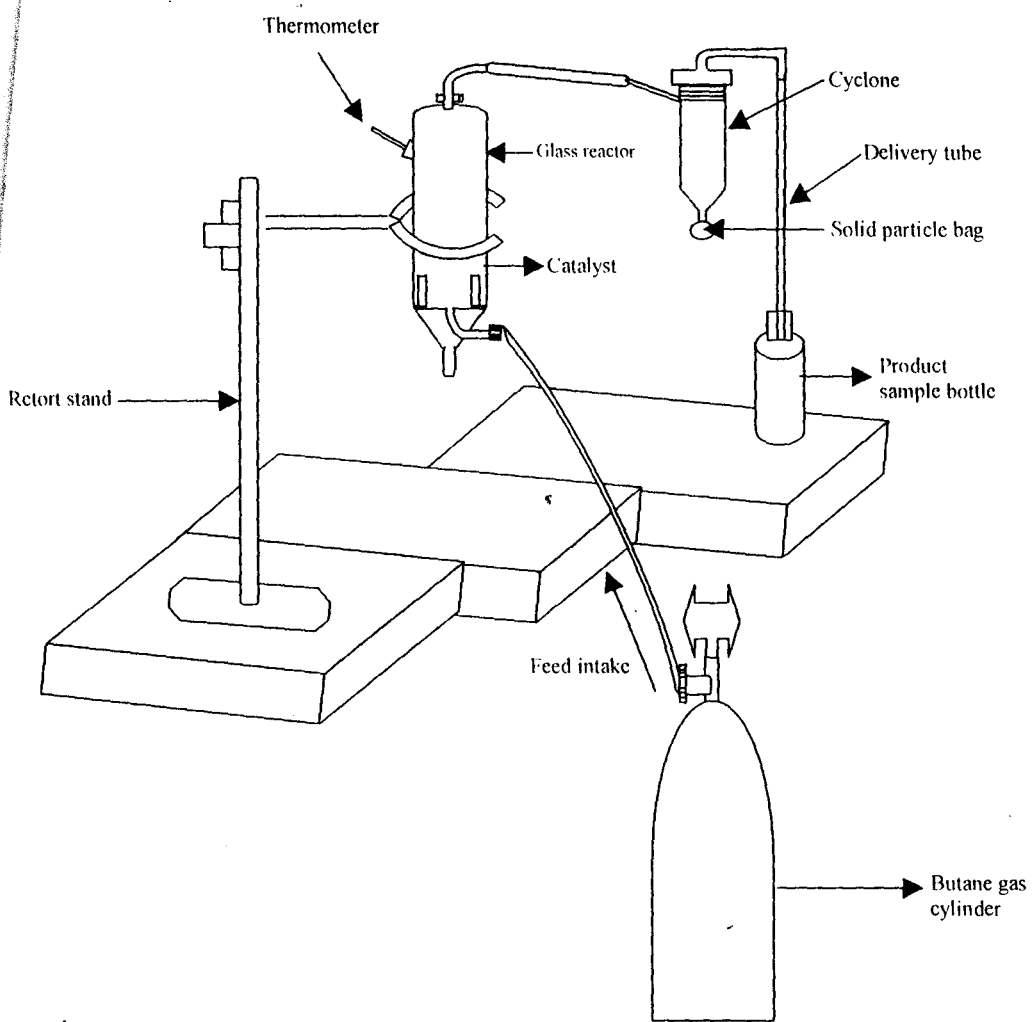
The equipments used as shown in the diagram (fig 4.1) are

- a. Prototype fluid catalytic reactor.
- b. Cyclone
- c. Gas cylinder
- d. Thermometer
- e. Retort stand and clamp
- f. Sample bottles
- g. Stop watch
- h. Weighing balance
- i. Measuring cylinder
- j. Heat regulator

##### Materials Used

- a. Butane gas
- b. Petroleum ether
- c. Zeolite catalyst.

### 4.3 DIAGRAM



#### 4.4 EXPERIMENTAL PROCEDURE

- a. 50g of the zeolite was charged into the reactor.
- b. A 25ml of petroleum ether (40-60°C) was measured and poured into the sample bottle and connected to the cyclone through a delivery tube as shown in the diagram.
- c. The reactor was heated to a temperature of 42°C using the heat regulator.
- d. The butane gas control valve was opened and the gas flow-rate maintained at 2-litres/min and gas pressure of 1.6bar.
- e. After 5minutes of reaction, the cracked product was collected in the petroleum ether. The gas valve was then closed and the sample bottle detached and labeled S1R1 (S indicates the temperature range, and R indicates catalyst weight).
- f. A fresh 25ml petroleum ether (40-60°C) was poured into a new sample bottle and connected to the apparatus. A catalyst weight of 60g was charged into the reactor. The flow-rate was increased to 2.5litre/min and pressure increased to 1.8bar, with heat supplied from the heat regulator. The cracked product was collected in petroleum ether. After 5mins, the gas valve was then closed and the sample bottle detached and labeled S1R2.
- g. For S1R3, a fresh 25ml petroleum ether (40-60°C) was poured into a new sample bottle and connected to the apparatus with the catalyst weight of 70g charged into the reactor. The flow rate was increased to 3litres/min and pressure increased to 2.0bar. The cracked products was collected in petroleum ether, detached and labeled S1R3.
- h. The experiment was repeated with petroleum ether (60-80°C) and steps (a) to (g) taken and product obtained labeled as S2R1, S2R2 and S2R3.
- i. The cracked products were analyzed at Kaduna refinery laboratory using a gas chromatograph with the liquid-injection method giving the percentage composition of the cracked products.

## CHAPTER FIVE

### 5.0 RESULTS AND DISCUSSION OF RESULTS

#### 5.1 RESULTS

Parameters given for the experiment are:

Diameter of zeolite particle,  $d_p = 250 \times 10^{-6} \text{m}$

Density of zeolite,  $\rho = 1.12 \text{g/cm}^3 = 1120 \text{kg/m}^3$

Diameter of fluidized reactor = 0.0853m

From appendix (A2), the clear calculations give the tables presented below.

**Table 5.1: run S1R1**

W=0.05kg      v=2000cm<sup>3</sup>/min      P=1.6bar.

S/no	Temp (°C)	C <sub>b,in</sub> (kmol/m <sup>3</sup> )	X <sub>b,in</sub>	C <sub>b,out</sub> (kmol/m <sup>3</sup> )	X <sub>b,out</sub>	C <sub>b,aves</sub> (kmol/m <sup>3</sup> )	ΔX <sub>b</sub>	$\frac{\Delta X_b}{W/F_{bo}}$
1	42	0.0611	0.0542	0.0247	0.6176	0.0429	0.5630	0.0847
2	45	0.0605	0.0635	0.0244	0.6223	0.0425	0.5588	0.0841
3	49	0.598	0.0743	0.0241	0.6269	0.0420	0.5526	0.0832
4	54	0.0589	0.0882	0.0238	0.6316	0.0414	0.5434	0.0818
5	58	0.0581	0.1006	0.0235	0.6362	0.0408	0.5356	0.0807

**Table 5.2: Run S1R2**

W= 0.06kg      v=2500cm<sup>3</sup>/min      P=1.8bar

S/no	Temp (°C)	C <sub>b,in</sub> (kmol/m <sup>3</sup> )	X <sub>b,in</sub>	C <sub>b,out</sub> (kmol/m <sup>3</sup> )	X <sub>b,out</sub>	C <sub>b,aves</sub> (kmol/m <sup>3</sup> )	ΔX <sub>b</sub>	$\frac{\Delta X_b}{W/F_{bo}}$
1	41	0.0689	0.0523	0.0223	0.6933	0.0456	0.641	0.1164
2	47	0.0677	0.0688	0.0219	0.6988	0.0448	0.630	0.1144
3	51	0.0668	0.0812	0.0216	0.7029	0.0442	0.6217	0.1129
4	54	0.0662	0.0894	0.0214	0.7056	0.0438	0.6162	0.1119
5	59	0.0652	0.1032	0.0211	0.7098	0.0432	0.6066	0.1102

Table 5.3: Run S1R3

$W=0.07$  kg

$v=3000$  cm<sup>3</sup>/min

$P=2.0$  bar

S/no	Temp (°C)	$C_{b,in}$ (kmol/m <sup>3</sup> )	$X_{b,in}$	$C_{b,out}$ (kmol/m <sup>3</sup> )	$X_{b,out}$	$C_{b,aves}$ (kmol/m <sup>3</sup> )	$\Delta X_b$	$\frac{\Delta X_b}{W/F_{bo}}$
1	43	0.0761	0.0570	0.0186	0.7695	0.0474	0.7125	0.1475
2	47	0.0752	0.0682	0.0183	0.7732	0.0468	0.705	0.1460
3	52	0.0742	0.083	0.0181	0.7757	0.0461	0.6927	0.1434
4	55	0.0733	0.0917	0.0179	0.7782	0.0456	0.6863	0.1421
5	59	0.0725	0.1016	0.0177	0.7807	0.0451	0.6791	0.1406

Table 5.4: Run S2R1

$W=0.05$  kg,

$v=2000$  cm<sup>3</sup>/min

$P=1.6$  bar

S/no	Temp (°C)	$C_{b,in}$ (kmol/m <sup>3</sup> )	$X_{b,in}$	$C_{b,out}$ (kmol/m <sup>3</sup> )	$X_{b,out}$	$C_{b,aves}$ (kmol/m <sup>3</sup> )	$\Delta X_b$	$\frac{\Delta X_b}{W/F_{bo}}$
1	62	0.0574	0.1115	0.0205	0.6827	0.0390	0.5712	0.08856
2	66	0.0568	0.1207	0.0202	0.6873	0.0385	0.5666	0.08785
3	70	0.0561	0.1316	0.0200	0.6904	0.0381	0.5588	0.08664
4	74	0.0555	0.1409	0.0198	0.6935	0.0377	0.5526	0.08568
5	78	0.0548	0.1517	0.0195	0.6981	0.0372	0.5464	0.08471

Table 5.5: Run S2R2

$W=0.06$  kg

$v=2500$  cm<sup>3</sup>/min

$P=1.8$  bar

S/no	Temp (°C)	$C_{b,in}$ (kmol/m <sup>3</sup> )	$X_{b,in}$	$C_{b,out}$ (kmol/m <sup>3</sup> )	$X_{b,out}$	$C_{b,aves}$ (kmol/m <sup>3</sup> )	$\Delta X_b$	$\frac{\Delta X_b}{W/F_{bo}}$
1	62	0.0646	0.1114	0.0152	0.7909	0.0399	0.6795	0.1234
2	65	0.0641	0.1183	0.0151	0.7923	0.0396	0.6740	0.1224
3	69	0.0633	0.1293	0.0149	0.7950	0.0391	0.6657	0.1209
4	74	0.0624	0.1417	0.0147	0.7978	0.0386	0.6562	0.1192
5	79	0.0617	0.1513	0.0145	0.8006	0.0381	0.6593	0.1178

**Table 5.6: Run S2R3**

W=0.07kg

v=3000cm<sup>3</sup>/min

P=2.0bar

S/no	Temp (°C)	C <sub>b,in</sub> (kmol/m <sup>3</sup> )	X <sub>b,in</sub>	C <sub>b,out</sub> (kmol/m <sup>3</sup> )	X <sub>b,out</sub>	C <sub>b,aves</sub> (kmol/m <sup>3</sup> )	ΔX <sub>b</sub>	$\frac{\Delta X_b}{W/F_{bo}}$
1	62	0.0718	0.1103	0.00822	0.8981	0.04001	0.7878	0.1631
2	66	0.0710	0.1202	0.00813	0.8993	0.0396	0.7791	0.1613
3	71	0.0699	0.1338	0.00800	0.9009	0.0390	0.7671	0.1588
4	75	0.0691	0.1437	0.00791	0.9020	0.0385	0.7583	0.1570
5	80	0.0681	0.1561	0.00779	0.9035	0.0379	0.7474	0.1547

**Table 5.7: Run S1R1 (for Arrhenius' plot)**

S/no	T(°C)	T(k)	1/T(1/k)	k(m <sup>3</sup> /hr.kg)	ln k
1	42	315	0.00317	1.974	0.6801
2	45	318	0.00314	1.979	0.6826
3	49	322	0.00311	1.981	0.6836
4	54	327	0.00306	1.976	0.6811
5	58	331	0.00302	1.978	0.6821

**Table 5.8: Run S1R1 (for Arrhenius' plot)**

S/no	T(°C)	T(k)	1/T(1/k)	k(m <sup>3</sup> /hr.kg)	ln k
1	41	314	0.00318	2.5526	0.9371
2	47	320	0.00313	2.5536	0.9375
3	51	324	0.00309	2.5543	0.9378
4	54	327	0.00306	2.5548	0.9380
5	59	332	0.00301	2.5509	0.9365

**Table 5.9: Run SIR2 (Arrhenius plot)**

S/no	T(°C)	T(k)	1/T(1/k)	K(m <sup>3</sup> /hr.kg)	ln K
1	43	316	0.00316	3.1119	1.1352
2	47	320	0.00313	3.1197	1.1377
3	52	325	0.00308	3.1106	1.1348
4	55	328	0.00305	3.1162	1.1366
5	59	332	0.00301	3.1175	1.1370

**Table 5.10: Run SIR2 (Arrhenius plot)**

S/no	T(°C)	T(k)	1/T(1/k)	K(m <sup>3</sup> /hr.kg)	ln K
1	62	335	0.002988	2.2708	0.8201
2	66	339	0.002950	2.2818	0.8250
3	70	343	0.0022915	2.2740	0.8215
4	74	347	0.002282	2.2727	0.8210
5	78	351	0.002849	2.2772	0.8229

**Table 5.11: Run SIR2 (Arrhenius plot)**

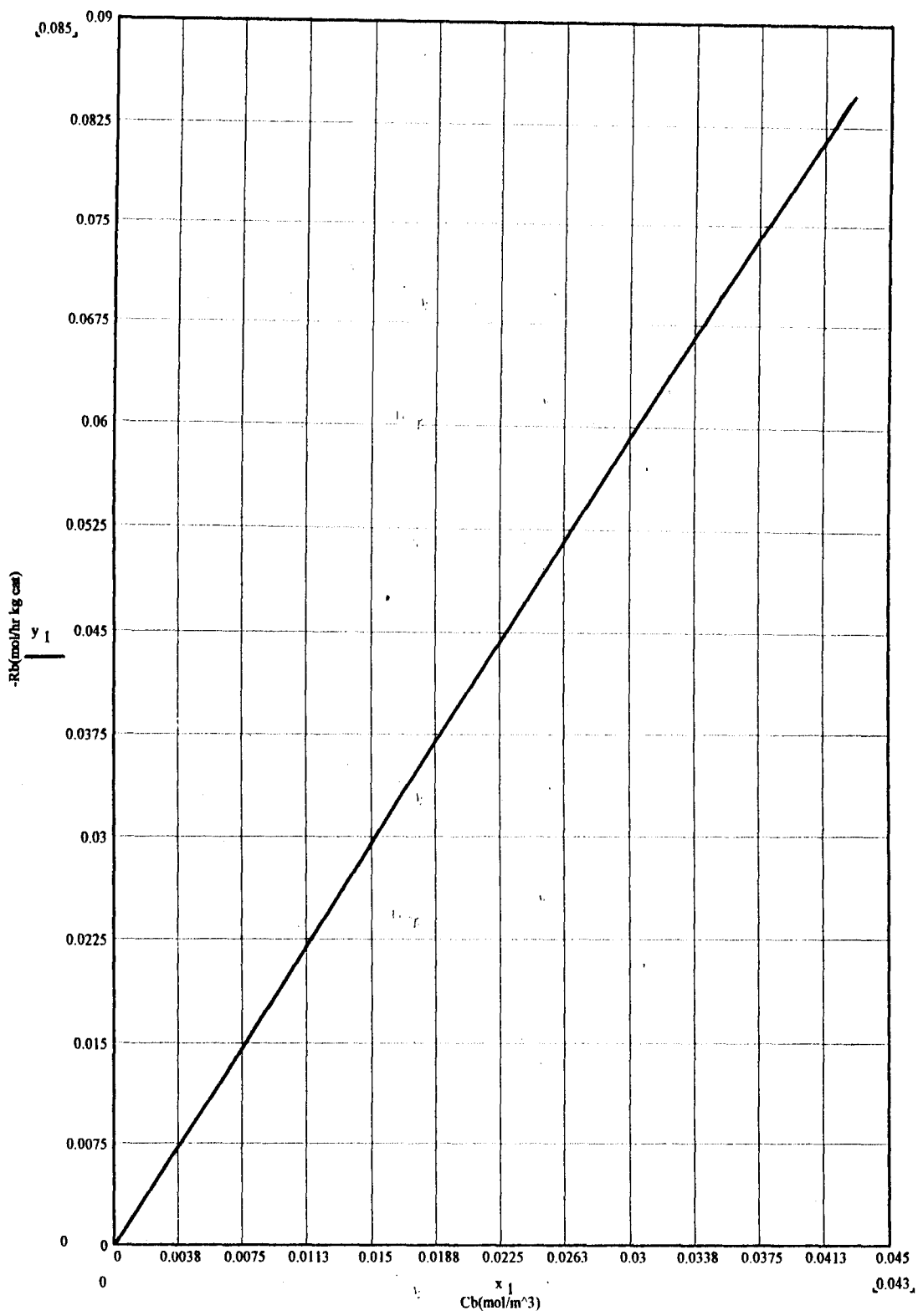
S/no	T(°C)	T(k)	1/T(1/k)	K(m <sup>3</sup> /hr.kg)	ln K
1	62	335	0.002985	3.0927	1.1291
2	65	338	0.002959	3.0909	1.1285
3	69	342	0.002940	3.0921	1.1288
4	74	347	0.002882	3.0881	1.1276
5	79	352	0.002841	3.0919	1.1288

**Table 5.12: Run SIR2 (Arrhenius plot)**

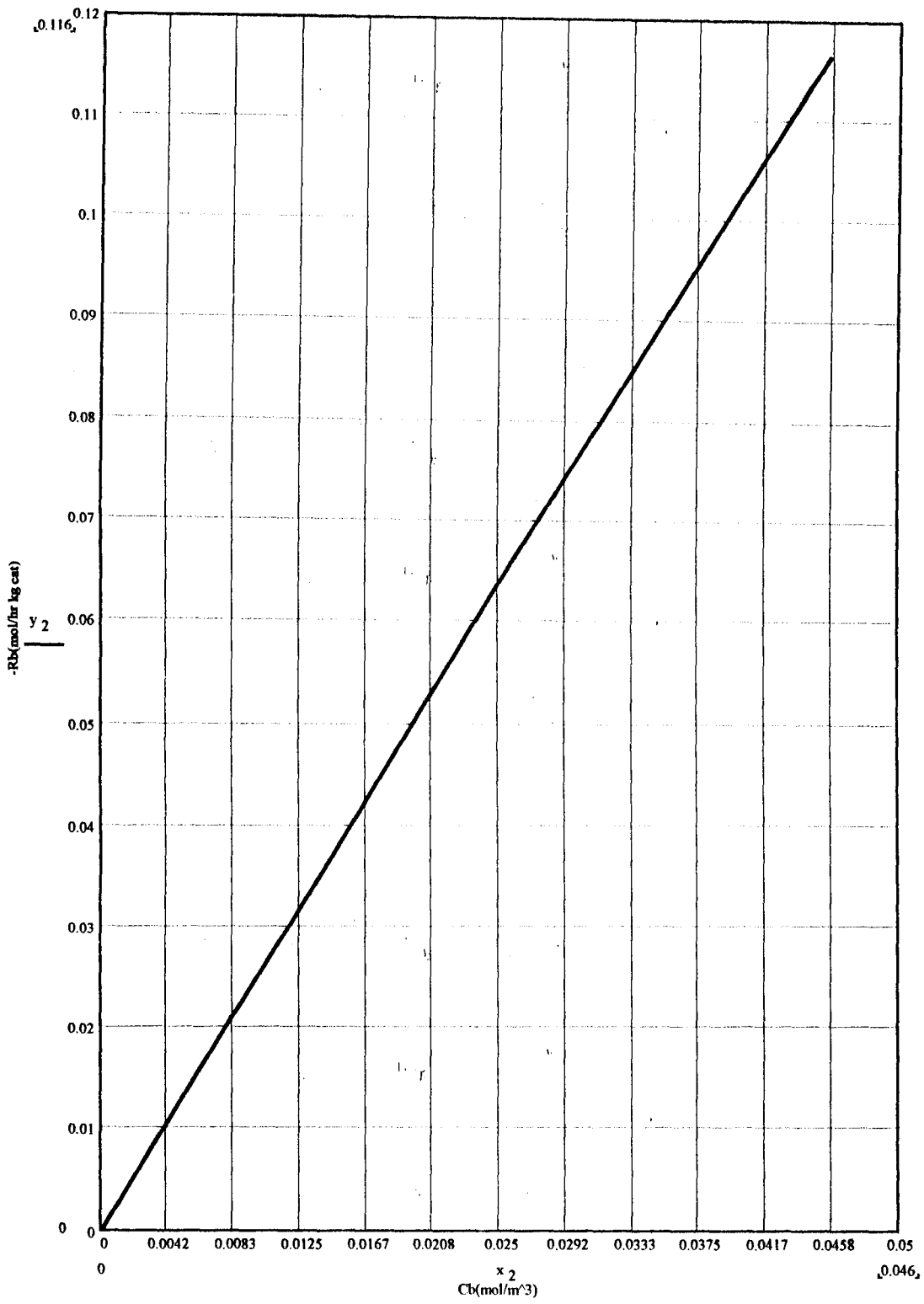
S/no	T(°C)	T(k)	1/T(1/k)	K(m <sup>3</sup> /hr.kg)	ln K
1	62	335	0.002985	4.0765	1.4052
2	66	339	0.002950	4.0733	1.4044
3	71	344	0.002907	4.07179	1.4041
4	75	348	0.002874	4.0779	1.4056
5	80	353	0.002833	4.08179	1.4065



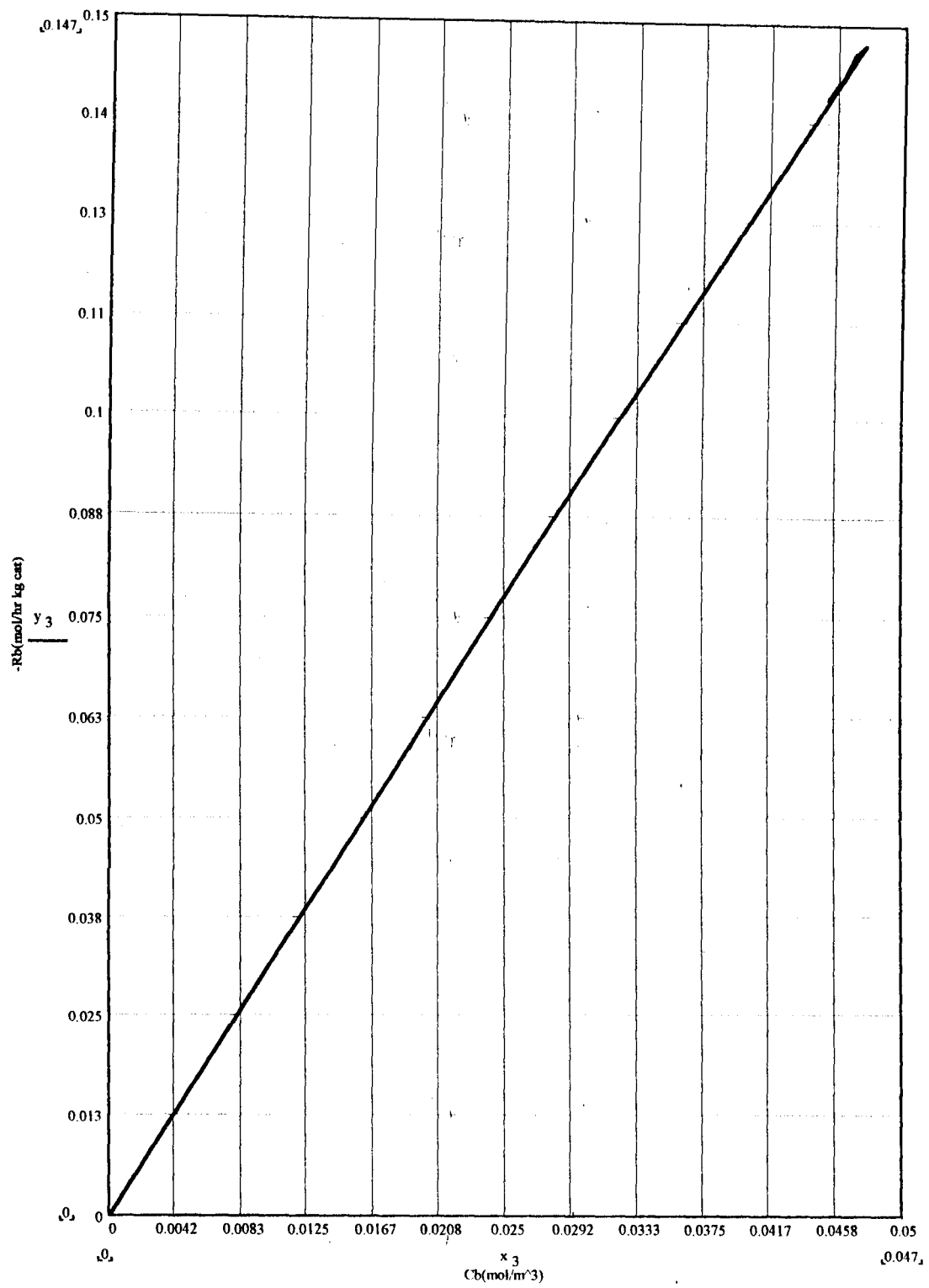
ables 5.1 to 5.6 were used to plot the graphs of rate versus concentration with the line of best fit drawn for the coordinates. Also, tables 5.7 to 5.12 were used to plot the graphs of  $\ln k$  versus  $1/T$  i.e. (Arrhenius plot) with the line of best fit drawn to obtain a linear curve.



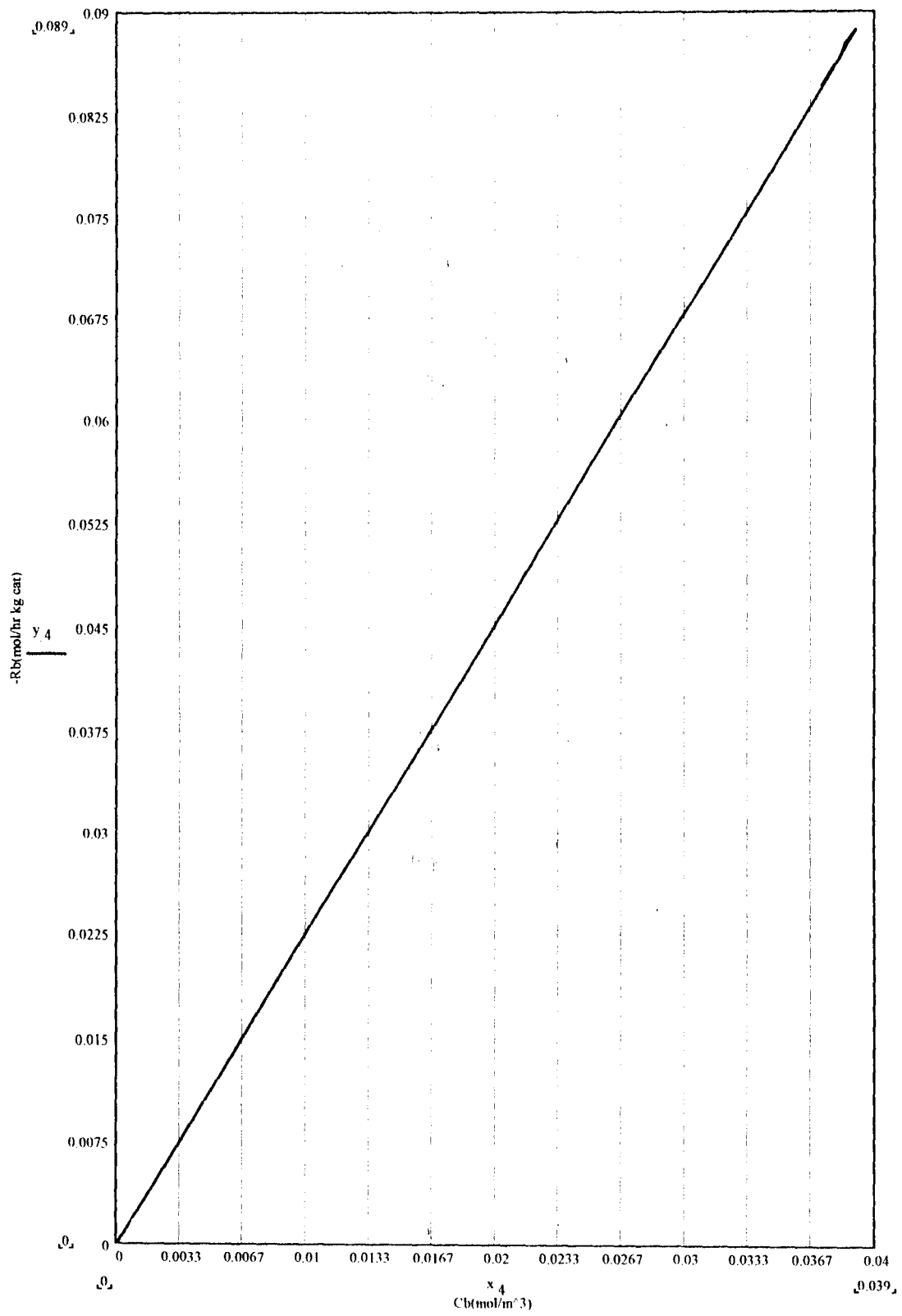
Graph of Rate Vs Concentration(SIR1)



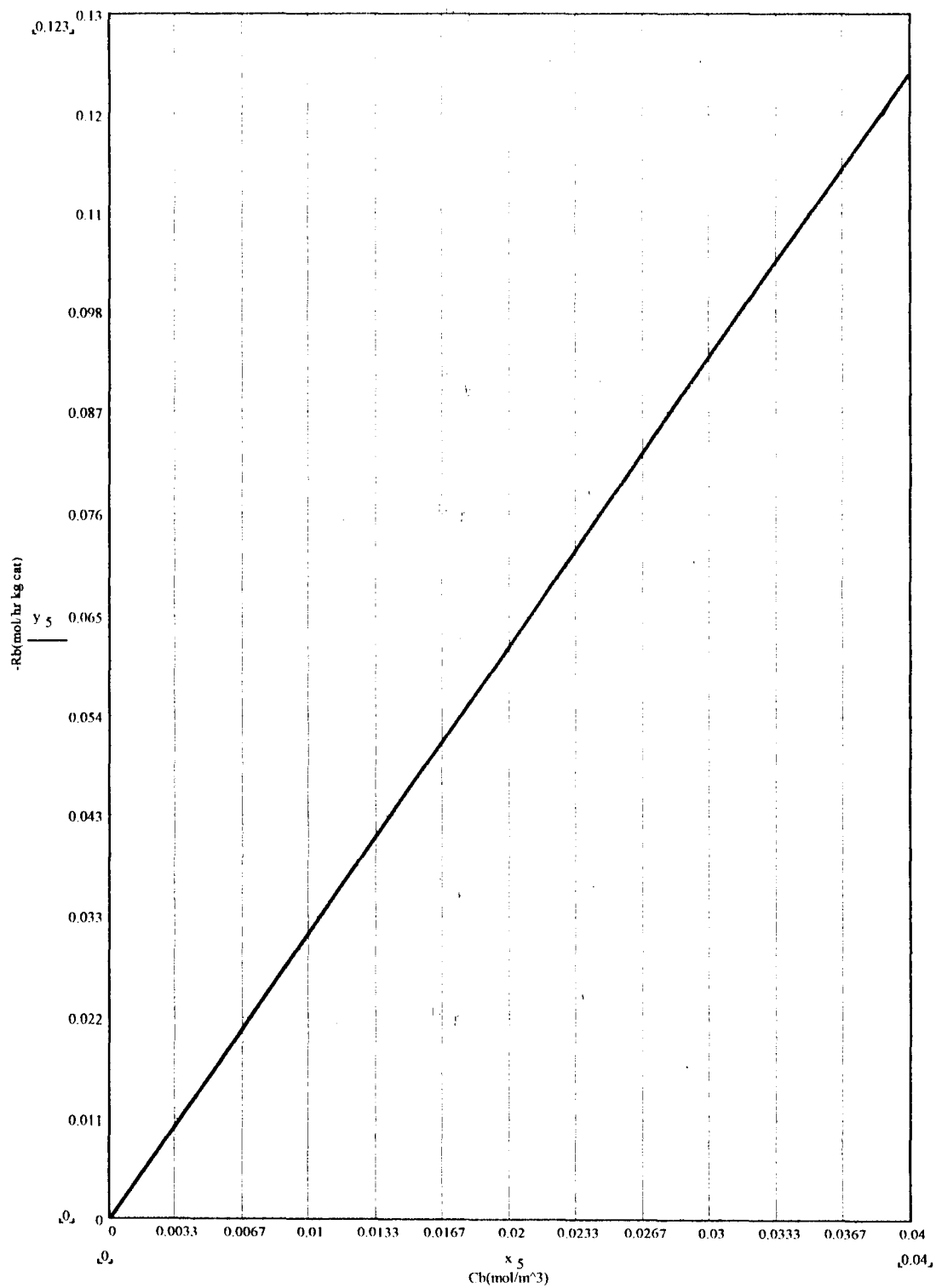
Graph of Rate Vs Concentration(S1R2)



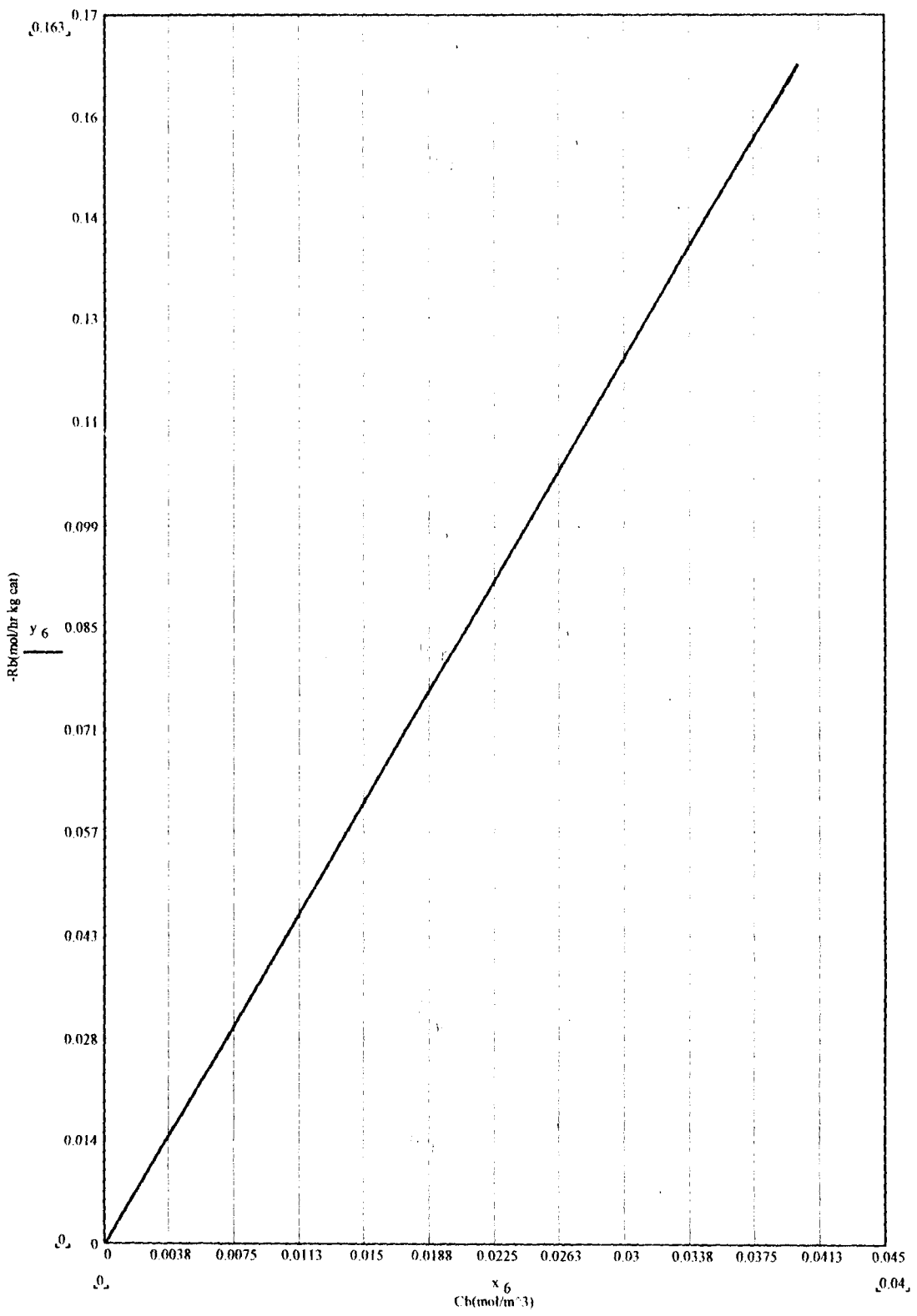
Graph of Rate Vs Concentration(SIR3)



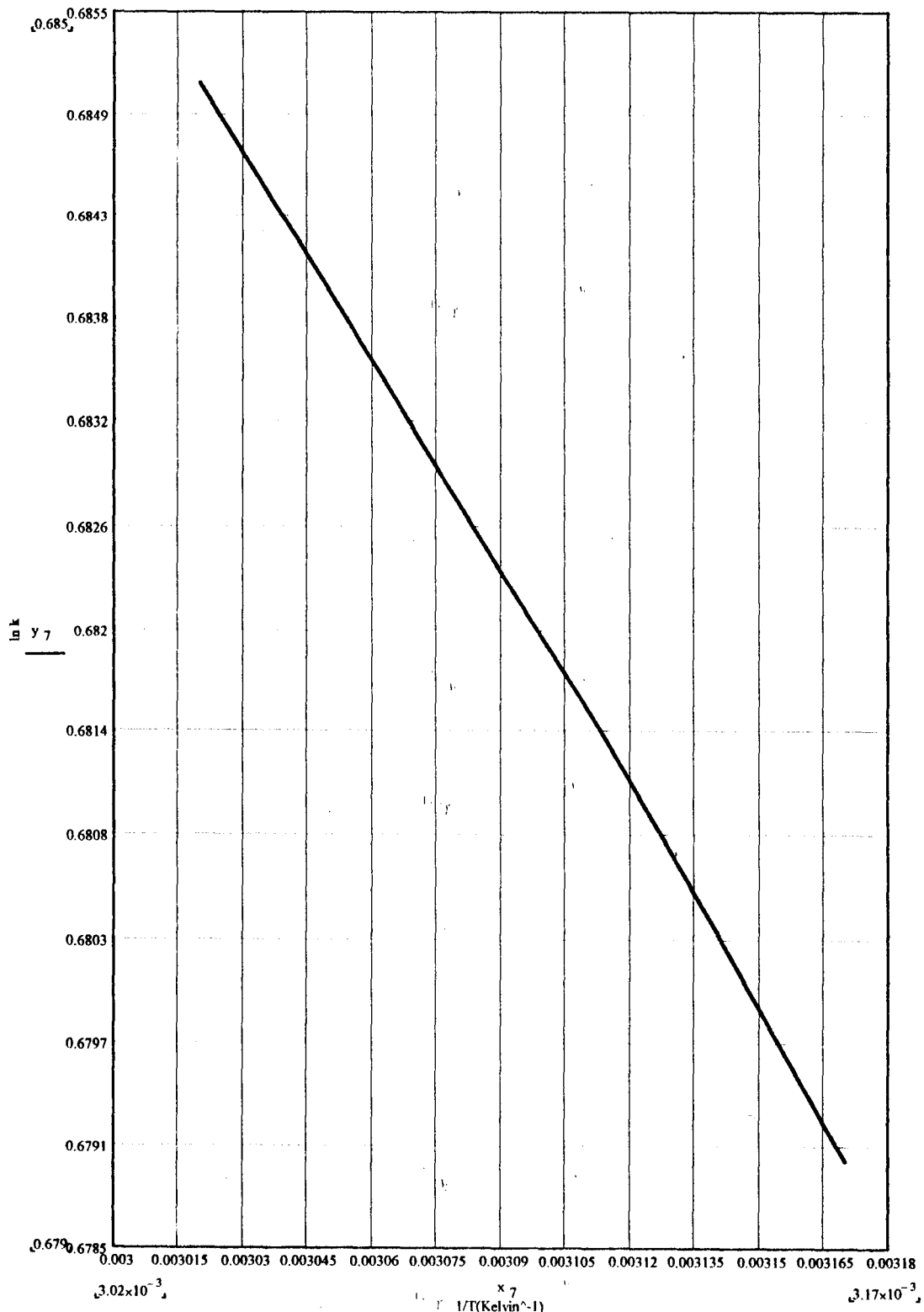
Graph of Rate Vs Concentration(S2R1)



Graph of Rate Vs Concentration(S2R2)

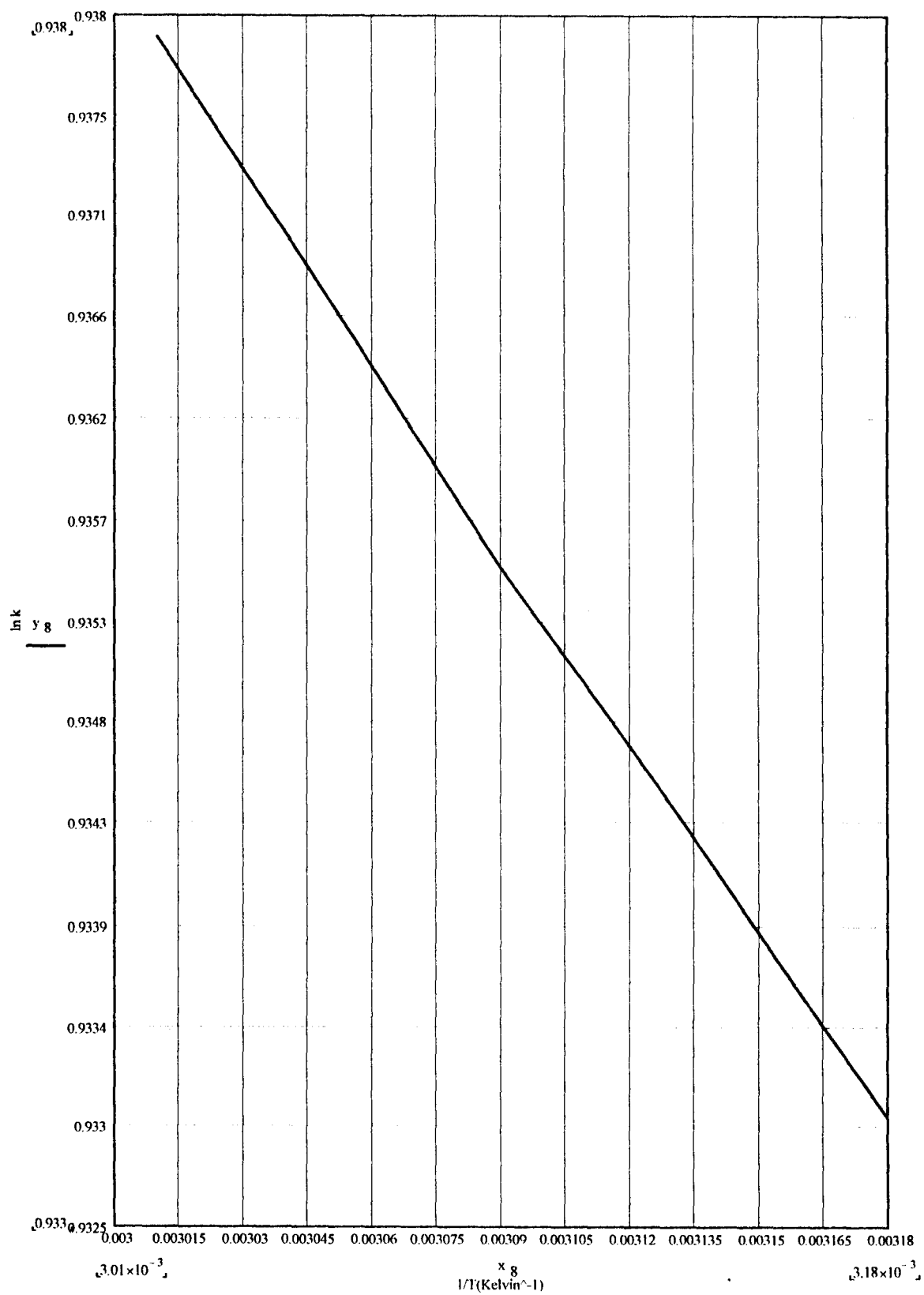


Graph of Rate Vs Concentration(S2R3)

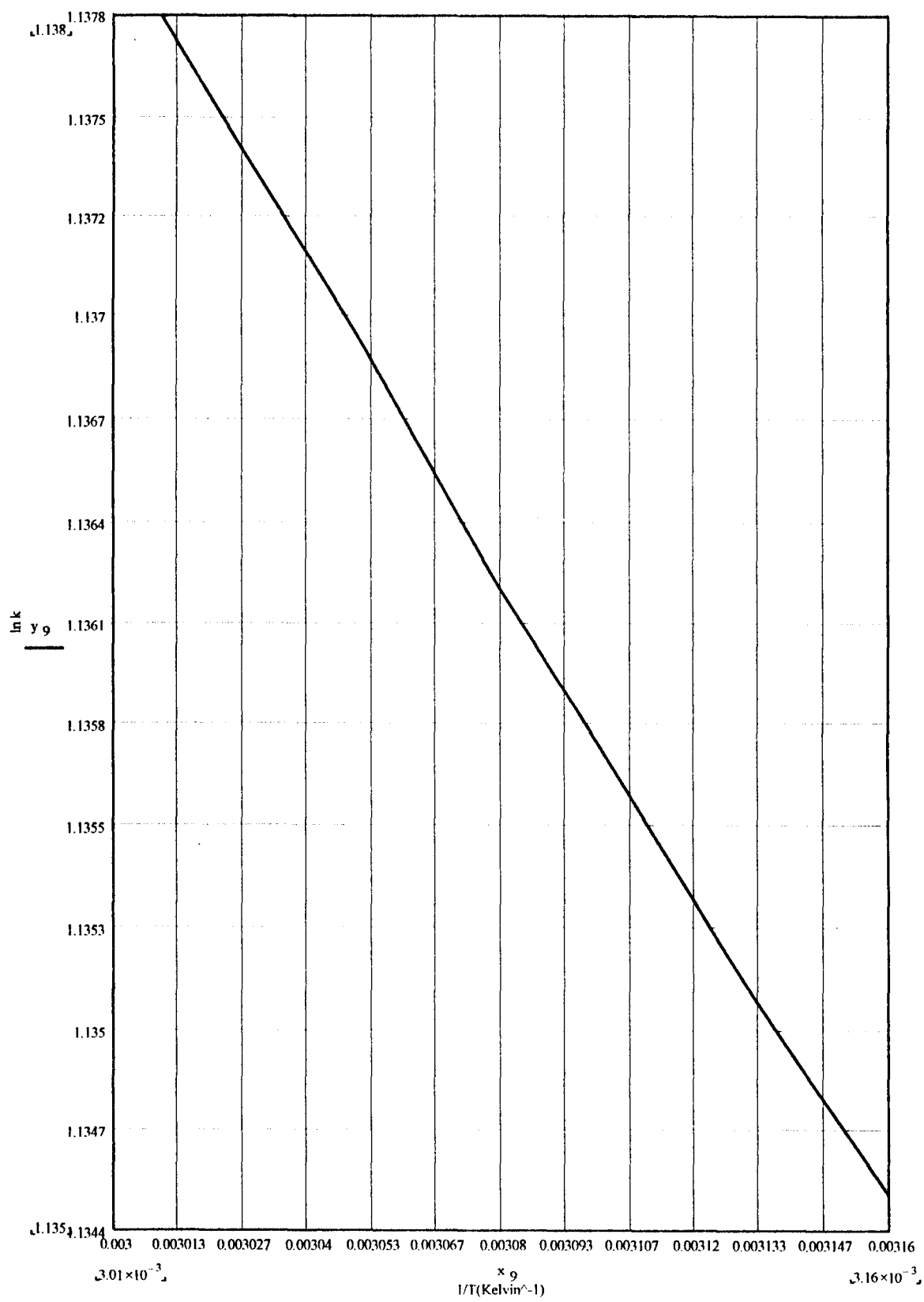


Graph of  $\ln k$  vs  $1/T$  (SIRI)

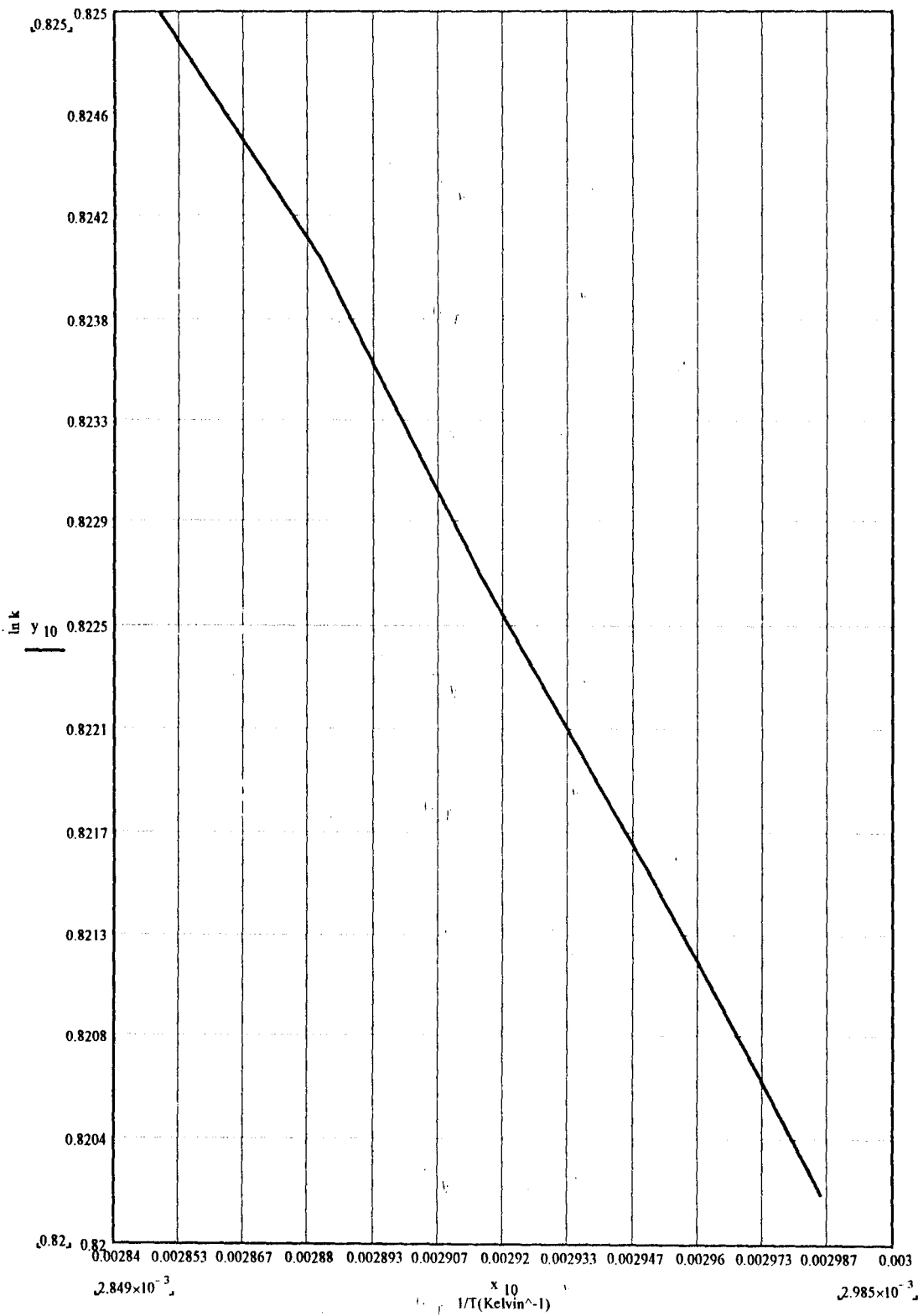




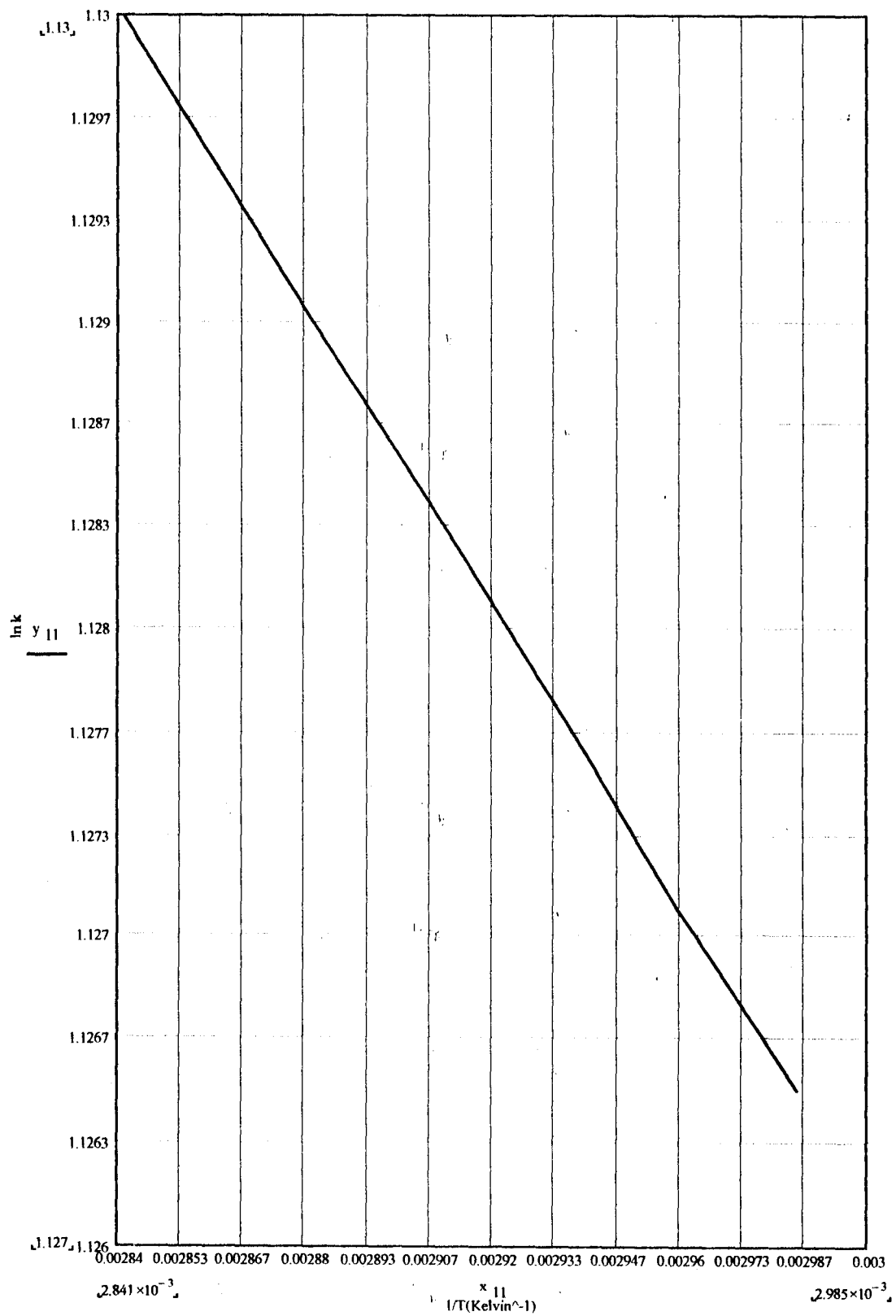
Graph of  $\ln k$  Vs  $1/T(\text{SIR2})$



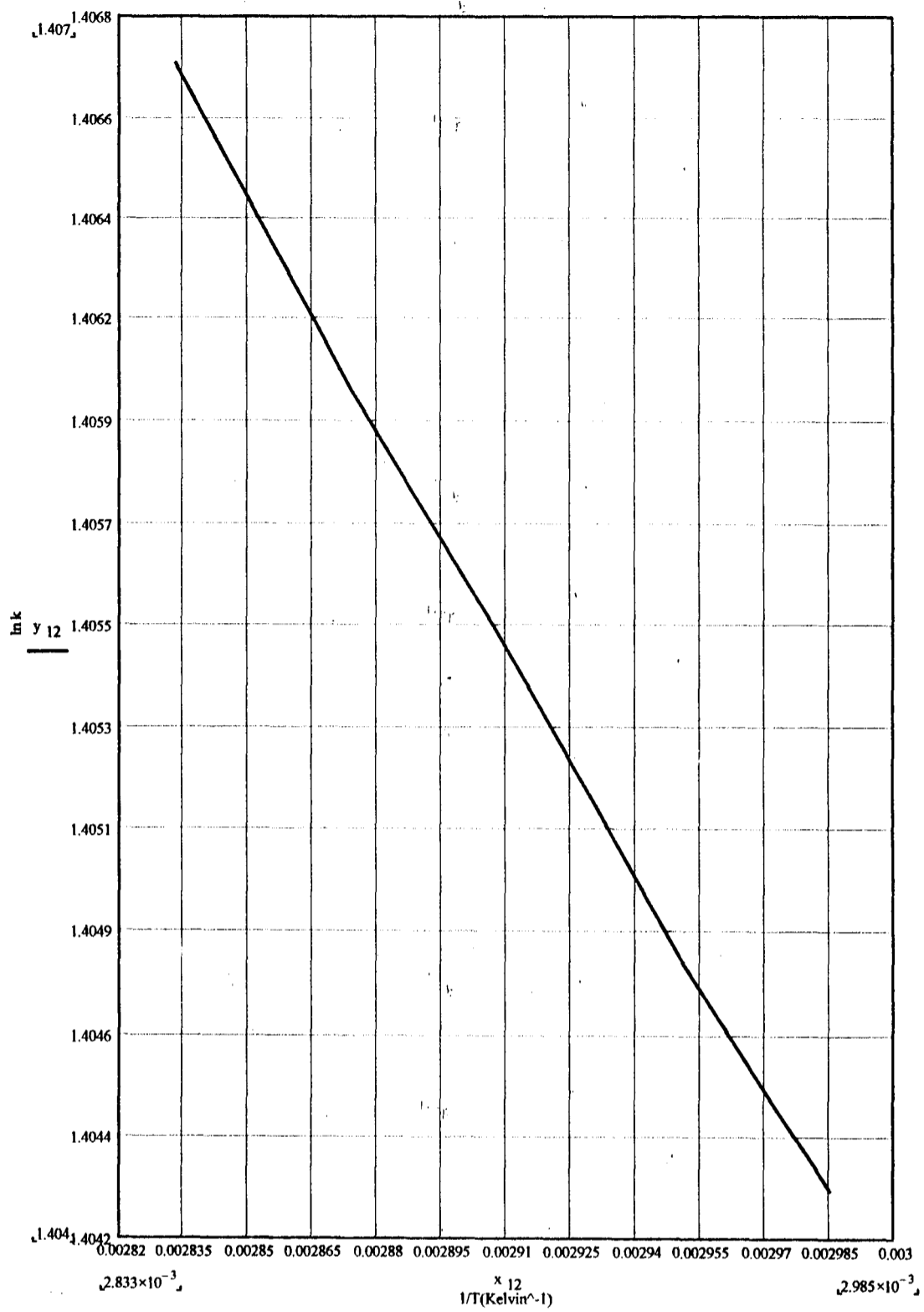
Graph of  $\ln k$  Vs  $1/T(\text{SIR3})$



Graph of  $\ln k$  Vs  $1/T$  (S2R1)



Graph of  $\ln k$  Vs  $1/T$  (S2R2)



Graph of  $\ln k$  Vs  $1/T$  (S2R3)

From the graphs, the values for the rate constant were obtained as shown in Appendix A2. The rate equations for the disappearance of butane for the experimental runs are:

For S1R1:  $-R_b = (1.971 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$

S1R3:  $-R_b = (2.557 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$

S1R3:  $-R_b = (3.13 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$

S2R1:  $-R_b = (2.25 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$

S2R2:  $-R_b = (3.10 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$

S2R3:  $-R_b = (4.08 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$

And the average rate expression for the experimental runs is

$$-R_{b,ave} = (2.85 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$$

The corresponding activation energies are

For S1R1  $E = 341.43 \text{ KJ/kmol} = 81.6 \text{ kcal/gmol}$

S1R2  $E = 238.83 \text{ KJ/kmol} = 57.08 \text{ kcal/gmol}$

S1R3  $E = 190.93 \text{ KJ/kmol} = 45.63 \text{ kcal/gmol}$

S2R1  $E = 290.83 \text{ KJ/kmol} = 69.51 \text{ kcal/gmol}$

S2R2  $E = 182.07 \text{ KJ/kmol} = 43.51 \text{ kcal/gmol}$

S2R3  $E = 134.13 \text{ KJ/kmol} = 32.06 \text{ kcal/gmol}$

Also, from the appendix. The following values were obtained:

Heat of reaction,  $\Delta H_r = 167.35 \text{ KJ/mol}$

Heat transfer coefficient,  $h = 63.74 \text{ KJ/hr.m}^2\text{K}$

Mass transfer coefficient,  $k_m = 0.0018 \text{ m/hr}$

$$\frac{\text{Observed rate}}{\text{Rate if film resistance controls}} = 19.66$$

$$\frac{-(\bar{R}_{b,obs})L^2}{D_e C_{bg}} = 0.022$$

$$\Delta T_{\text{particle}} = -0.0001 \text{ }^\circ\text{C}$$

$$\Delta T_{\text{film}} = -0.006 \text{ }^\circ\text{C}$$

Average activation energy,  $E_{ave} = 229.7 \text{ KJ/kmol} = 54.9 \text{ kcal/gmol}$

## 5.2 DISCUSSION OF RESULTS

The gas was assumed to behave ideally and the inlet concentrations were obtained for the different runs from the ideal gas equation  $P = CRT$ . The differential analysis technique was used to interpret the kinetic data obtained.

With increasing weight of catalyst, it was observed that the conversions for each 5-minute reaction time increased. With the 40-60°C petroleum ether, the conversion for SIR1, SIR2 and SIR3 obtained were 53.5%, 60.75 and 67.95 respectively. With the petroleum ether of 60-80°C range, the conversions for S2R1, S2R2, S2R3 obtained were 54.6%, 64.9% and 74.7% respectively. It was also observed as the temperature range increase for the same catalyst weight and molar rate, that there was an increase in conversion. The high value of conversions obtained is primarily due to the effectiveness and high activity of the zeolite catalyst and its high yield ability. The fact that domestic gas which was the source of butane used originally contained little mixture of the lighter fractions obtained as products also brought about high conversion values.

The rate expression was determined by measuring the concentration of the unreacted butane in the product collected in the petroleum ether. To obtain the rate of disappearance of butane, a guess of first order was made and the plots of  $(-R_b)$  versus concentration was obtained for the experimental runs. The plots obtained were linear passing through the origin indicating that a first order reaction satisfactorily fits the kinetic data. The first order reaction obtained also satisfied the three-step mechanism proposed in **chapter three** for the cracking of butane over zeolite catalyst.

With the order of reaction established, the slope of the graphs gave different values of the rate constants, confirming theory that a rate of reaction is a function of the temperature dependent term  $k$  and function of composition.

With increase in the catalyst weight, it was observed that the rate constant  $k$  increased. For experimental run SIR1, SIR2, SIR3 the rate constants obtained were 1.971, 2.557, 3.13  $m^3/hr.kg$  respectively. For S2R1, S2R2, S2R3 the rate constants obtained were 2.25, 3.10 and 4.08  $m^3/hr.kg$  respectively. The increase in temperature also resulted in increase in the value of the rate constants. With the values of the rate constants, the corresponding rate expressions were obtained also showing an increase in the rate as both the catalyst weight and temperature range were increased.

The Arrhenius plots were used to obtain the activation energy, and as the catalyst weight increased the activation energy of the experimental runs decreased. This is attributed

to the fact that more catalyst weight provides more surface area for the catalytic reaction to proceed faster with the bonds in the butane gas easily broken to give the products. The activation energy of the catalytic cracking of butane obtained in this experiment was 32.06kcal/gmol (minimum) and 81.6kcal/gmol (maximum) when compared with 219.7kcal (minimum) and 278.7kcal/gmol (maximum) for thermal cracking as given in literature, it was observed that the zeolite catalyst effectively reduced the activation energy for the catalytic cracking of butane, confirming the theory behind the use of catalysts. The zeolite catalysts reduced the activation to above 70%.

The heat of reaction, heat transfer coefficient and mass transfer coefficient calculated from experimental values as shown in the appendix were used with the values of effective thermal diffusivity and effective thermal conductivity given in literature to determine the resistance

that controls the catalytic reaction. The value  $\frac{k_{obs} V_p}{k_m S_{ex}} = 19.66$  indicates that gas film

resistance affects the rate and this shows that the movement of gas molecules through the film is the lowest and the rate-limiting step of the catalytic reaction. In agreement, the value

$$\frac{-(\bar{R}_{b,obs})L^2}{D_c C_{bg}} = 0.022$$

indicates that there is no strong pore diffusion resistance.

The value of  $\Delta T_{particle} = -0.0001^\circ\text{C}$ , indicates that the pellet is close to uniform temperature and that non-isothermal effects do not influence the catalytic reaction.

The value of  $\Delta T_{film} = -0.006^\circ\text{C}$ , indicates that the catalyst pellet and the surrounding fluid are at the same temperature agreeing that non-isothermal effects do not influence the catalytic reaction, also conforming with theory in literature which states that a fluidized bed reactor operates isothermally.

The values of  $\Delta H_r$  obtained as 167.35kJ/mol (a positive value) also conforms with theory that endothermic reactions take place in a fluidized bed reactor.



## CHAPTER SIX

### 6.0 CONCLUSION AND RECOMMENDATIONS

#### 6.1 CONCLUSION

The results showed that a conversion of up to 0.75 was obtained using zeolite catalyst in the cracking of butane in the laboratory prototype fluidized bed reactor. An average rate constant  $k = 2.85 \text{ m}^3/\text{hr.kg}$  with a corresponding first order reaction rate with respect to disappearance of butane obtained as

$$- R_{h,ave} = (2.85 \text{ m}^3/\text{hr.kg}) (C_b, \text{ kmol/m}^3)$$

Also the average activation energy obtained,  $E = 229.7 \text{ kJ/kmol} = 54.9 \text{ kcal/gmol}$

This study also showed that the reaction mechanism with respect to disappearance of butane obeyed a first order kinetics with mass transfer through the gas film controlling the catalytic reaction.

#### 6.2 RECOMMENDATION

1. For subsequent study in the determination of the kinetics of hydrocarbon cracking, an automatic concentration-measuring device other than the gas chromatograph should be installed alongside the experimental set-up. This will go a long way to enable the conducting of the experiment as a continuous operation instead of the batch operation used here-in.
2. Further studies should incorporate a wide variety of catalyst types, whereby the effects of the activity of catalyst on the reaction rate is determined.
3. Better and improved fluidized bed reactors should be implored in subsequent study, to minimize the sources of error in the experimental runs. In addition, with the improved reactors, the kinetics and conversion of butane can be ascertained at a high temperature and high-pressure range.
4. Cracking gases such as hydrogen should be introduced. This aids in obtaining rate equations characterized by the langmuir isotherm which will produce further explanation on the phenomena of adsorption o catalyst surface.
5. Economic analysis of the cracking of butane to lighter products should be used to prepare feasibility reports on the advantages of producing lighter paraffinic hydrocarbons over their direct production from heavy hydrocarbon distillates of petroleum.
6. Modeling of the experiment above will be useful in providing a basis for the scale up of future plants with fluidized bed cracking of butane or hydrocarbons as their major operations.

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## APPENDIX

### A1: NOTATIONS

$a_m$	Exterior area per unit mass of catalyst
$\Lambda$	Reactor area
$C_{bed}$	Specific heat of catalyst bed
$C_{bin}$	Inlet concentration of butane gas
$C_{bo}$	Initial concentration of butane gas
$C_{b,out}$	Outlet concentration of butane gas
$\Delta C$	Change in concentration
$C_f$	Specific heat of fluid i.e. butane
$C_p$	Specific heat of zeolite particle
$D_c$	Effective thermal diffusivity of zeolite
$d_p$	Diameter of catalyst particle
$E$	Activation energy
$\varepsilon_f$	Void fraction
$\varepsilon_{mf}$	Void fraction at minimum fluidization velocity
$F_{Bo}$	Molar rate of butane gas
$h$	Heat transfer coefficient
$\Delta H_r$	Heat of reaction
$k_m$	Mass transfer coefficient
$K_{eff}$	Effective thermal conductivity of zeolite
$k_o$	Pre-exponential factor
$k$	Rate Constant
$L$	Characteristic length of catalyst
LMTD	Logarithmic mean temperature difference
$M_h$	Mass flow rate per unit length
$M_v$	Mass flow rate per unit volume
$\rho_p$	Density of catalyst
$P$	Pressure
$Q$	Heat rate
$-R_b$	Rate of disappearance of butane based on weight of catalyst
$-R_{b,obs}$	Observed rate based on catalyst volume
$S_{ex}$	Exterior surface area of catalyst

## APPENDIX

$T$	Temperature
$T_w$	Temperature at reactor walls
$T_B$	Temperature of catalyst bed
$g$	Flow rate of butane gas
$V_f$	Fluidization velocity
$V_{mf}$	Minimum fluidization velocity
$W$	Catalyst weight
$X_{b,in}$	Conversion of butane at inlet
$X_{b,out}$	Conversion of butane at outlet
$\Delta X_b$	Change in conversion.

## APPENDIX

### A.2: MANIPULATION OF DATA

#### A.2.1 MANIPULATIONS FOR RATE VS CONCENTRATION PLOTS

##### Assumptions:

1. The butane behaves ideally and obeys the ideal gas law.
2. The cracking system is a constant density system; therefore expansion the factor is zero.

Thus,  $C_b = P/RT$

$$\text{And } X_b = 1 - [C_b/C_{b0}]$$

For table 5.1 for S1R1

$$P = 1.6\text{bar} \quad w = 0.05\text{kg}$$

$$Q = 2000\text{cm}^3/\text{min}$$

$$Q = (2000\text{cm}^3/\text{min})(1\text{m}^3/100^3\text{cm}^3)(60\text{min}/1\text{hr})$$

$$Q = 0.12\text{m}^3/\text{hr}$$

At initial temperature i.e  $25^\circ\text{C}$

$$C_{b0} = \frac{1.6 \times 10^5}{8314 \times (25 + 273)}$$

$$C_{b0} = 0.0646 \text{ kmol}/\text{m}^3$$

$$F_{b0} = C_{b0} \cdot Q = (0.0646 \text{ kmol}/\text{m}^3 \times 0.12 \text{ (m}^3/\text{hr)})$$

$$F_{b0} = 0.007752 \text{ (kmol/hr)}$$

$$\frac{W}{F_{b0}} = \frac{0.05 \text{ (kg)}}{0.007752 \text{ (kmol/hr)}}$$

$$\frac{W}{F_{b0}} = 6.4495 \text{ hr.kg/kmol}$$

With an assumption of a first order reaction rate with respect to butane, the rate of disappearance  $-R_b = \Delta X_b/(W/F_{b0})$  at temperature of  $42^\circ\text{C}$ .

$$C_{b,in} = \frac{1.6 \times 10^5}{8314 \times (42+273)}$$

$$C_{b,in} = 0.0611 \text{ kmol}/\text{m}^3$$

$$X_{b,in} = 1 - (0.0611/0.0646)$$

$$X_{b,in} = 0.0542$$

Result from chromatogram showed that  $C_{b,out} = 0.0247 \text{ kmol/m}^3$

$$X_{b,out} = 1 - (0.0247/0.0646)$$

$$X_{b,out} = 0.6176$$

$$C_{b,ave} = \frac{C_{b,in} + C_{b,out}}{2} = \frac{0.0611 + 0.0247}{2}$$

$$C_{b,ave} = 0.0429 \text{ kmol/m}^3$$

$$\Delta X_b = X_{b,out} - X_{b,in} = 0.6176 - 0.0542$$

$$\Delta X_b = 0.5630$$

$$\therefore R_b = \Delta X_b / (W/F_{b0}) = 0.5630/6.44995$$

$$-R_b = 0.0847 \text{ kmol/hr.kg}$$

This trend of calculation was used to tabulate the results of the experimental runs for S1R2, S1R3, S2R1 S2R2 and S2R3 in order to obtain the plots of rate Vs concentration.

## A.2.2 MANIPULATION FOR ARRHENIUS PLOT

For table 5.7 (for S1R1)

From Arrhenius equation

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

$$\ln k = \ln k_o - \left(\frac{E}{R}\right) \frac{1}{T}$$

$$T = 42^{\circ}C = 42 + 273 = 315 \text{ K}$$

$$\frac{1}{T} = \frac{1}{315} = 0.00317 \text{ (K}^{-1}\text{)}$$

$$k = \frac{R_b}{C_{b,arc}} = \frac{\left(\frac{\Delta X_b}{w/F_{bo}}\right)}{C_{b,arc}}$$

$$k = \frac{0.0847}{0.0429}$$

$$k = 1.974 \text{ m}^3/\text{hr.kg}$$

$$\ln k = 0.6801$$

this method was used to tabulate the results of the experiental runs in order to plot of graphs of  $\ln k$  versus  $1/T$

### A2:3 OBTAINING RATE CONSTANTS FROM GRAPHS OF RATE VERSUS CONCENTRATION

$$\text{For S1 R1: } k = \frac{0.04435 - 0}{0.0225 - 0}$$

$$k = 1.971 \text{ m}^3/\text{hr.kg}$$

$$\text{S1 R2: } k = \frac{0.063 - 0}{0.025 - 0}$$

$$k = 2.557 \text{ m}^3/\text{hr.kg}$$

$$\text{S1 R3: } k = \frac{0.0651 - 0}{0.0208 - 0}$$

$$k = 3.13 \text{ m}^3/\text{hr.kg}$$



$$\text{For S2R1: } k = \frac{0.0225 - 0}{0.01 - 0}$$

$$k = 2.25 \text{ m}^3/\text{hr.kg}$$

$$\text{S2R2 } k = \frac{0.0413 - 0}{0.0133 - 0}$$

$$k = 3.10 \text{ m}^3/\text{hr.kg}$$

$$\text{S2R3 } k = \frac{0.0613 - 0}{0.015 - 0}$$

$$k = 4.08 \text{ m}^3/\text{hr.kg}$$

Therefore the rate expression is given as

$$\text{For S1R1 } -R_b = (1.971 \text{ m}^3/\text{hr.kg}) (C_b \text{ kmol/m}^3)$$

With the equation  $-R_b = k C_b$  used to write the subsequent rate equations with cognizance to their individual rate constant values.

#### A. 2. 4. CALCULATION OF ACTIVATION ENERGY FROM ARRENIUS' PLOTS.

From the graph of  $\ln k$  versus  $1/T$ , the value of the slope is equal to  $-E/R$

$$\text{for S1R1: } \frac{-E}{R} = \left( \frac{0.6836 - 0.6808}{0.00306 - 0.003128} \right)$$

$$\frac{-E}{R} = -41.067 \text{ K}$$

$$E = 41.067 \times R = 41.067 \times 8314$$

$$E = 341.43 \text{ kJ/kmol}$$

$$E = 341.43 \left( \frac{\text{kJ}}{\text{kmol}} \right) \left( \frac{1987 \text{ kcal/gmol}}{8314 \text{ kJ/kmol}} \right)$$

$$E = 81.6 \text{ kcal/g mol} = 341.43 \text{ kJ/kmol}$$

$$\text{S1R2: } \frac{-E}{R} = \frac{0.9364 - 0.9348}{0.00306 - 0.003116}$$

$$\frac{-E}{R} = -28.727 \text{ K}$$

$$E = 238.83 \text{ kJ/kmol} = 57.08 \text{ kcal/gmol}$$

$$\text{S1R3: } \frac{-E}{R} = \frac{1.1365 - 1.1355}{0.003067 - 0.0031105}$$

$$\frac{-E}{R} = -22.96 \text{ K}$$

$$E = 190.93 \text{ kJ/kmol} = 45.63 \text{ Kcal /gmol}$$

$$\text{S2R1: } \frac{-E}{R} = \frac{0.8244 - 0.8221}{0.002867 - 0.002933}$$

$$\frac{-E}{R} = -34.98 \text{ K}$$

$$E = 290.83 \text{ kJ/kmol} = 69.51 \text{ kcal /gmol}$$

$$\text{S2R2: } \frac{-E}{R} = \frac{1.1289 - 1.1276}{0.00288 - 0.2939}$$

$$\frac{-E}{R} = -21.9 \text{ K}$$

$$E = 182.07 \text{ kJ/kmol} = 43.51 \text{ kcal /gmol}$$

$$\text{S2R3: } \frac{-E}{R} = \frac{1.4062 - 1.4051}{0.002865 - 0.002933}$$

$$\frac{-E}{R} = -16.13 \text{ K}$$

$$E = 134.13 \text{ kJ/kmol} = 32.06 \text{ kcal /gmol}$$

## A.2.5 CALCULATION OF HEAT TRANSFER COEFFICIENT

$$h = \frac{Q}{A \text{ LMTD}}$$

$$A = \pi d_i^2$$

$$A = \frac{\pi d_i^2}{4} = \frac{\pi \times 0.0853^2}{4} = 0.00571 \text{ m}^2$$

For a fluidized bed,  $Q = m_n C_{\text{bed}} (T_w - T_{\text{bed}})$

$$C_{\text{bed}} = C_p (1 - \epsilon_f) + C_r \epsilon_f$$

**For zeolite**  $C_p = \int_{298}^{333} (24.1 + 0.0495T) dT$  in  $\text{kJ/mol K}$

(Himmelblau, 1996)

Assumption  $T_w$  is 50% greater than  $T_{bed}$  due to heating element wound round the walls of the reactor.

For SIRI at  $T_{bed} = 60^\circ\text{C}$   $T_w = 90^\circ\text{C}$

$$C_p = \int_{298}^{333} (24.1 + 0.0495T) dT$$

$$C_p = 24.1 (333 - 298) + \frac{0.095}{2} (333^2 - 298^2)$$

$$C_p = 1390 \text{ kJ/kmol}$$

also  $\epsilon_r = \epsilon_{mf} \left( \frac{V_r}{V_{mf}} \right)^{0.085}$  (Vermesan et al, 1990)

$$v_r = \frac{Q}{A} = \left( 2000 \frac{\text{cm}^3}{\text{min}} \right) \left( \frac{1}{0.00571 \text{ m}^2} \right) \left( \frac{1 \text{ min}}{60 \text{ Sec}} \right) \left( \frac{1 \text{ m}^3}{100^3 \text{ cm}^3} \right)$$

$$V_r = 0.00584 \text{ m/s}$$

But from Geldart Classification of particle sizes and minimum fluidization velocities, for

$$d_p = 250 \times 10^{-6} \text{ m} \quad \epsilon_{mf} = 0.509 \text{ and } V_{mf} = 0.05 \text{ m/s}$$

$$\therefore \epsilon_r = 0.509 \left( \frac{0.00584}{0.05} \right)^{0.085}$$

$$\epsilon_r = 0.424$$

$$C_f = 25.2518 \text{ kJ/mol K} \quad (\text{Perry et al, 1997})$$

$$C_{bed} = 1390 (1 - 0.424) + 25.2518 \times 0.424$$

$$C_{bed} = 811.35 \text{ kJ/k mol K}$$

$$M_h = Q \cdot \rho_b$$

$$\rho_b = 2.519 \frac{\text{kg}}{\text{m}^3}$$

$$M_h = \left( 2000 \frac{\text{cm}^3}{\text{min}} \right) \left( \frac{60 \text{ min}}{1 \text{ hr}} \right) \left( \frac{1 \text{ m}^3}{100^3 \text{ cm}^3} \right) \left( 2.519 \frac{\text{kg}}{\text{m}^3} \right)$$

$$h = 0.30228 \text{ kg/hr.}$$

$$Q = 0.30228 \times 811.35 \quad (363-333)$$

$$Q = 126.6 \text{ kJ/hr.}$$

$$h = \frac{Q}{A \text{ LMFD}} = \frac{126.6}{0.00571 \left[ \frac{363-333}{\ln \left( \frac{363}{333} \right)} \right]}$$

$$h = 63.74 \text{ kJ/hr m}^2 \text{ K.}$$

## A.2.6 CALCULATION OF MASS TRANSFER COEFFICIENT

For a fluidized bed,  $M_{v.} = \rho_p (1 - \epsilon_f) k_m a_m \Delta C$  (Smith 1981)

$$a_m = \frac{6}{d_p \rho_p}, \quad M_{v.} = \frac{M_h}{A}$$

$$\Rightarrow \frac{M_h}{A} = \rho_p (1 - \epsilon_f) k_m \frac{6}{d_p \rho_p \Delta C}$$

$$k_m = \frac{M_h \times d_p}{A (1 - \epsilon_f) 6 \Delta C}$$

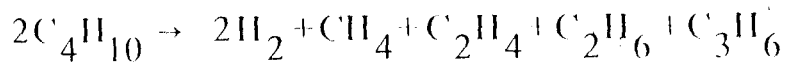
for S1R1;  $\epsilon_f = 0.424$ ,  $\Delta C = 0.011 - 0.0235 = 0.0376 \text{ kmol/m}^3$

$$\therefore k_m = \frac{0.30228 \times 250 \times 10^{-6}}{0.00571 (1 - 0.424) \times 6 \times 0.0376}$$

$$k_m = 0.0018 \text{ m/hr.}$$

## A.2.7. CALCULATION OF HEAT OF REACTION

With reference to equation in literature review, the heat of reaction of the catalytic cracking of butane is calculated. The equation for the reaction is:



$$\Delta H_r = H_f + R \int_{T_0}^T (A + BT + CT^2 + DT^{-2}) dT \quad (JM \text{ Smith, } 1996)$$

Table below gives the value of that Heat of formation and constants.

	$H_f$ (J/mol)	A	$B \times 10^3$	$C \times 10^6$	$D \times 10^5$
$C_4H_{10}$	-125,790	1.935	36.915	-11.402	—
$H_2$	—	3.249	0.422	—	0.083
$CH_4$	-74,520	1.702	9.081	-2.164	—
$C_2H_4$	-52,510	1.424	14.394	-4.392	—
$C_2H_6$	-83,820	1.131	19.225	-5.561	—
$C_3H_6$	19,710	1.637	22.706	-6.915	—

With the constants, the enthalpy for each species is calculated at  $60^\circ C = 333 \text{ K}$ .

For  $CH_4$ :

$$\Delta H = 125,790 + 8.314 \int_{298}^{333} (1.935 + 36.915 \times 10^{-3} T - 11.402 \times 10^{-6}) dT$$

$$\Delta H = 125,790 + 8.314 \left[ 1.935 (333 - 298) + \frac{36.915 \times 10^{-3}}{2} (333^2 - 298^2) - \frac{11.402 \times 10^{-6}}{3} (333^3 - 298^3) \right]$$

$$\Delta H = -125,790 + 8.314[67.725 + 407.634 - 39.764]$$

$$\Delta H = -122,168.4 \text{ J/mol.}$$

for  $H_2$ :

$$\Delta H = 0 + 8.314 \int_{298}^{333} (3.249 + 0.422 \times 10^{-3} T + 0.083 \times 10^{-5} T^{-1}) dT$$

$$\Delta H = 984.170 \text{ J/mol.}$$

for  $CH_4$ :

$$\Delta H = -74,520 + 8.314 \int_{298}^{333} (1.702 + 9.081 \times 10^{-3} T - 2.164 \times 10^{-6} T^{-2}) dT$$

$$\Delta H = -73253.778 \text{ J/mol}$$

for  $C_2H_4$ :

$$\Delta H = 52510 + 8.314 \int_{298}^{333} (1.424 + 14.394 \times 10^{-3} T - 4.392 \times 10^{-6} T^{-2}) dT$$

$$\Delta H = 54118.50 \text{ J/mol.}$$

for  $C_2H_6$ :

$$\Delta H = -83820 + 8.314 \int_{298}^{333} (1.131 + 19.225 \times 10^{-3} T - 5.561 \times 10^{-6} T^{-2}) dT$$

$$\Delta H = -81887.136 \text{ J/mol.}$$

for  $C_3H_6$ :

$$\Delta H = 19170 + 8.314 \int_{298}^{333} (1.637 + 22.706 \times 10^{-3} T - 6.915 \times 10^{-6} T^{-2}) dT$$

$$\Delta H = 22070.427 \text{ J/mol.}$$

The heat of reaction  $\Delta H_r = \sum \Delta H_{\text{Product}} - \sum \Delta H_{\text{reactants}}$

$$\begin{aligned} \Delta H_r &= 2(984.170) + (-73253.778) + (54118.501) \\ &\quad + (-81887.136) + (22070.42) - 2(-122168.46) \\ \Delta H_r &= 167.35 \text{ kJ/mol} \end{aligned}$$

### A.2.8 DETERMINATION OF THE RATE CONTROLLING MECHANISM

(a) Film mass transfer

$$\frac{\text{observed rate}}{\text{rate if film resistance controls}} = \frac{\left(-R_{b,obs}/C_{bg}\right) \frac{\pi}{3} \left(\frac{dp}{2}\right)^3}{k_m \pi \left(\frac{dp}{2}\right)^3} = \frac{k_{obs} Vp}{k_m S_{cv}}$$

$$\text{but } -\bar{R}_{b,obs} Vp = -R_b W$$

$$-\bar{R}_{b,obs} Vp = -R_b \frac{W}{Vp} = -R_b \rho_p$$

$$R_{b,obs} = 1.971 C_b \times 1120 \quad (\text{i.e. for S1R1})$$

$$\text{Using } C_b = 0.0235 \text{ kmol/m}^3$$

$$R_{b,obs} = 1.971 \times 0.0235 \times 1120$$

$$R_{b,obs} = 51.88 \text{ kmol/hr.m}^3$$

$$\text{at } C_{bg} = 0.0611 \text{ kmol/m}^3; \quad k_m = 0.0018 \text{ m/hr}$$

$$\frac{\text{observed rate}}{\text{rate if film resistance controls}} = \frac{(-\bar{R}_{b,obs}) dp}{k_m C_{bg}^6}$$

$$\frac{\text{observed rate}}{\text{rate if film resistance controls}} = \frac{51.88 \times 250 \times 10^{-6}}{0.0018 \times 0.0611 \times 6} = 19.660$$

(b) for strong pore diffusion;

$$\frac{(-\bar{R}_{b,obs})L^2}{De C_{bg}} > 1$$

$$De = 1.88 \times 10^{-4} \text{ cm}^2/\text{s} \quad (\text{perry et al 1997})$$

$$De = \left( 1.88 \times 10^{-4} \left( \frac{\text{cm}^2}{\text{s}} \right) \right) \left( \frac{1 \text{ m}^2}{100^2 \text{ cm}^2} \right) \left( \frac{3600 \text{ S}}{1 \text{ hr}} \right)$$

$$De = 6.768 \times 10^{-5} \text{ m}^2/\text{hr}$$

for a sphere  $L = \frac{R}{3} = \frac{dp}{6}$

$$\frac{(-\bar{R}_{b,obs})L^2}{De C_{bg}} = \frac{51.88 \times (250 \times 10^{-6})^2}{6.768 \times 10^{-5} \times 0.0611} = 0.022$$

(c) Temperature effects

$$\Delta T_{particle} = \frac{De (C_{bg} - O) (-\Delta H_r)}{K_{eff}}$$

at 350K,  $K_{eff} = 2 \text{ W / mK} \dots \dots \dots (\text{www.google.com, 1991})$

$$(1) \quad K_{eff} = \left[ 2 \frac{\text{W}}{\text{mK}} \right] \frac{\text{J / S}}{\text{IW}} \frac{3600 \text{ S}}{1 \text{ hr.}}$$

$$K_{eff} = 7.2 \text{ kJ / hr. m.K}$$

$$\therefore \Delta T_{particle} = \frac{6.768 \times 10^{-5} \times 0.0611 \times (-167.3)}{7.2}$$

$$\Delta T_{particle} = -0.0001 \text{ } ^\circ\text{C}$$

$$(2) \quad \Delta T_{film} = \frac{L(-\bar{R}_{b,obs}) (-\Delta H_r)}{h}$$



$$\Delta T_{film} = \frac{250 \times 10^{-6} \times 51.88 \times (-167.3)}{6 \times 63.74}$$

$$\Delta T_{film} = 0.006 \text{ } ^\circ\text{C}$$