MODEL DESCRIMINATION OF THE REACTION
CHANISM OF 3-METHYL HEXANE AROMATIZATION
ON PT/AL$_2$O$_3$ CATALYST

BY

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F.U.T MINNA

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DECLARATION

I hereby declare that this work was carried out by me and it is a record of my research work. It has not been presented in any previous application for a higher degree. All the sources of information are duly acknowledged by means of references.

……………………………………… 15/9/05 ………………
Ame Emmanuel Date

CERTIFICATION

This thesis titled “Model Descrimination of The Reaction Mechanism of 3-Methyl Hexane Aromatization on PT/AL_2O_3 Catalyst” by Ameh Emmanuel meets the regulations governing the award of the degree of Master of Engineering of Federal University of Technology, Minna and is approved for its contribution to scientific knowledge and literary presentation.

15/09/2005

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DATE

DEDICATION

This work is wholly dedicated to my God for he has shown me much love.

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ABSTRACT

Models for the Kinetics of the aromatization of 3-methythexane in N_2 and H_2 carrier gases over Pt/Al_2O_3 catalyst at temperature ranging from 330 - 500^{O}c and at flow rate of 40 – 120 mls/min were undertaken. Different schemes were used with every rate equation as possible rate controlling steps with different assumptions of hydrogen adsorption

The data were treated by the differential method to give rate of reactions. Using gauss Jordan iterative method and a computer programme written in Visual Basic the Kinetic rate and equilibrium constants were obtained for each model. Discrimination amongst the models was based on trends of rate and equilibrium constants over the temperature range. Nitrogen atmosphere, of all six reaction mechanism tested, mechanisms 4 and reaction step 5 in which demethylation of adsorbed toluene to adsorbed benzene and adsorbed methane was found to be the rate controlling step that described 3-methythexane aromatization on Pt/Al_2O_3 catalyst and the model rate equation is given as

$$r_5 = \frac{6.191*IO^{1}\,C_TC_{H2} - 5.539*10^{5}\,C_BC_{me}}{(1+8.487*10^{5}C_B+3.480*10^{6}C_T+5.476*10^{5}C_{me})^{2}}$$

The activation energies for forward and reverse reactions were determined to be 58.93 KJ/mol and 88.56 KJ/mol respectively.

In hydrogen atmosphere, the rate determining step is the reaction of 3-methylhexane to form adsorbed butane and adsorbed propane with hydrogen adsorbed dissociatively. It is Scheme 2, reaction step 3.

The model rate equation is given as

$$r_3 = \frac{1.150*10^{4}C_1 - 2.320*10^{4}\quad \dfrac{C_{bt}C_{me}}{C_{H2}}}{1+5.87*10^{4}C_1 + 9.430*10^{4}C_{me} + 1.990*10^{5}C_{Bt} + 9.23*10^{2}C_{H2}}$$

The activation energies for both forward and reverse reactions are 203.60 KJ/mol and 74.70 KJ/mol respectively.

The difference in activation energies in both carrier gases is due to a difference in reaction mechanism

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NOMENCLATURE

C_I = Concentration of 3 methyl hexane

C_T = Concentration of Toluene

C_B = Concentration of Benzene

C_H = Concentration of Hydrogen

C_{Me} = Concentration of Methane

C_{CP} = Concentration Cracked product

S = Active site of a Catalyst

C_{IS} = Concentration Of adsorbed 3 methyl hexane

C_{TS} = Concentration Of adsorbed Toluene

C_{BS} = Concentration Of adsorbed Benzene

C_{HS} = Concentration Of adsorbed Hydrogen

C_{Mes} = Concentration Of adsorbed Methane

C_{cps} = Concentration Of adsorbed Cracked product

C_{MCH} = Concentration of Methylcyclohexane

W/F = Contact time

F = Flow rate

X_{cp} = mole fraction of Cracked product

X_H = mole fraction of Hydrogen

X_T = mole fraction of Toluene

X_o = Overall Conversion

$K_2/K_1 = K_a$

$K_4/K_3 = K_b$

$K_6/K_5 = K_c$

$K_8/K_7 = K_d$

$K_{12}/K_{11} = K_f$

$K_{14}/K_{13} = K_g$

$K_{16}/K_{15} = K_h$

$K_{18}/K_{17} = K_i$

$K_{20}/K_{19} = K_j$

$K_{22}/K_{21} = K_k$

K_F = Forward rate constant

K_r = Reverse rate constant

K = Equilibrium constant

CHAPTER ONE

1.0 INTRODUCTION

Aromatization is the process of formation of aromatics with the given off of hydrogen from an organic compound. It is an important aspect of reforming reactions. The aromatics formed include toluene and benzene and could be used as chemicals in the petrochemical industry. It is worthy of note that some of these chemicals produced during aromatization are sold at higher prices than the base chemicals that produce them. These aromatics are used as component of gasoline to improve the octane rating.

Octane rating of these aromatics are higher than those of iso-alkanes. Therefore, they could replace tetra ethyl lead and tetra methyl lead antiknock chemicals. Tetra ethyl lead and tetra methyl lead as antiknock chemicals have negative effects on the environment (Sinfelt 1979) and on the machines/vehicles in which they are applied. Because of these negative effects, some Federal agencies such as that of United States of America are interested in its phase out. Without the present antiknock chemicals the aromatics produced could improve the octane rating of the available gasoline.

Several catalysts are available for aromatization reactions. They include: plantinum-alumina, combined halogen, nickel, cobalt or platinum supported on silica-alumina and oxides of molybdenum, tungsten oxide deposited on silica-alumina. Reforming using platinum or platinum-alloy catalysts have the widest current application and are bifunctional in nature.

While catalyst reforming is a complex process involving reactions of a large number of hydrocarbons, a reasonable understanding of the process chemistry and of the functioning of the reforming catalysts has evolved. In 1958, there was a publication on cyclization (Ciapeta, 1958), since then several other aspects of cyclization steps have been further discussed together with other hydrocarbon processes (Paal, 1960). The review papers by Kazansky provide excellent summaries mainly of the Soviet research done in this field (Graziani and Ramage, 1978) presented a work on kinetic studies of reforming reactions. The development of rate equations are essentially empirical and restricted to start – of – cycle activity of the catalyst.

Isomerization of hexane has been described using first order kinetics (Chevalier et al, 1976 and Christoffel 1979). The relative magnitude of the first order rate constant was consistent with the classical bifuntional mechanism proposed by Mills (Mills et al, 1953, De Pauw and Froment, 1975) investigated the kinetics of the isomerization and cracking of n-pentane coupled with coking. Dominic and Susu (1988) wrote on the reforming of n-octane on a $Pt/Al_2 O_3$ catalyst. They considered the product distribution and kinetic analysis. Susu and Adedeji (1997) analyzed the model discrimination of reaction mechanism of n-Heptane. Product distribution of the aromatization of 3-metlhyhexane was considered by Aberuagba (Aberuagba 2001).

The most recent work has been the model discrimination of n-hepane reforming (Auta, 2003). In all, focus has not been on the reaction mechanism and parameter estimation on branched alkane especially 3-methylhexane.

This work aims at analyzing the reaction mechanism obtaining kinetic and equilibrium parameters for the reaction of 3-methylhexane over Pt/AI$_2$ 0$_3$ catalyst.

$$I - C_7 H_{16} \xrightarrow[P_t/AI_2\ 0_3]{H_2} C_7H_8 + 4H_2 \longrightarrow C_6 H_6 + CH_4 + 3H_2 \ldots\ldots\ldots\ldots 1$$

The main reactions in the aromatization of 3–methylhexane involve deep fragmentation.,dehydrocylization, dehydrogenation and demethylation. Pines suggestion of a reaction scheme where all the reactions are reversible was used (Sinfelt, 1981).

1.1 Aims/Objectives

The work involves among other things the

(a) Kinetic analysis of 3 - methylhexane

(b) Development and solution of appropriate model equations.

(c) Determination of Kinetic parameters (rate and equilibrium constants) from the model using a numerical optimization technique (Gauss Jordan). It includes a computer programme (Visual Basic) to solve the numerical problem and

(d) To fit the best equation for the aromatization of 3 – methylhexane via the derived model equation.

(c) To use the equation to show the reaction Pattern of 3 – methyl hexane.

CHAPTER TWO

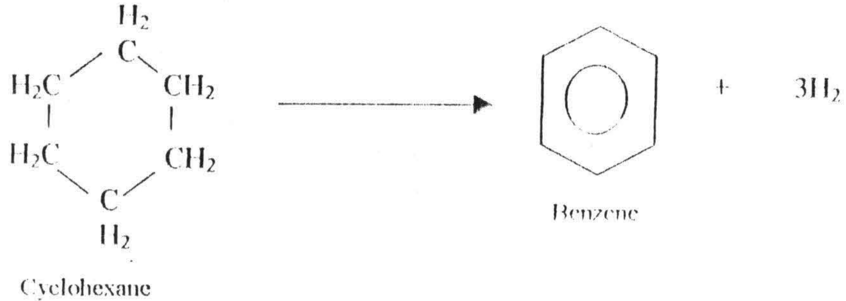
2.0 LITRATURE REVIEW

2.1 Aromatization

Aromatization is the conversion of Naphthas to obtain products of higher octane number. It could also be referred to as the process of dehydrogenation of organic compounds to aromatics. These aromatics have their parent material as benzene C_6H_6 Michael Faraday in 1825 was credited with the first isolation of the parent compound of aromatics. Early in the development of organic chemistry, the present of a distinct group of compound with pleasant odour was a source of concern until Micheal Faraday completed his work (Pines 1981)

A number of routes were used to obtain aromatic hydrocarbons from petroleum. Some crude oil contains a minor but significant percentage of aromatics which can be extracted directly. This is not common, and synthetic techniques usually have to be adopted.

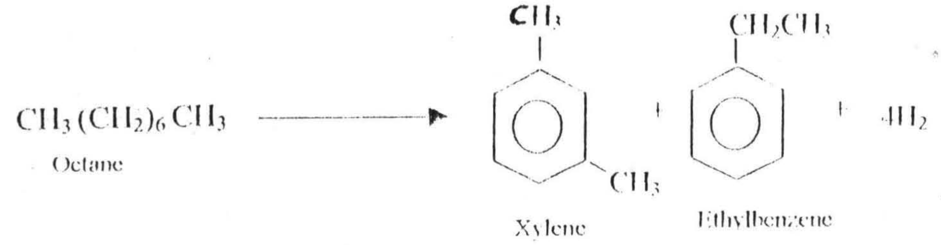
Aromatization of other hydrocarbon types can be applied most obviously to cycloalkanes, the cycloalkanes structure define the aromatic compound obtained.



Cyclohexane

Benzene

Conversion to aromatic structure is not confined to cycloalkanes, however. Alkanes can undergo cyclization and aromatization, the alkane structure again determine the aromatic compound or mixture.



The above operation, whether applied to cycloalkane or alkane is called hydroforming or platforming if platinum containing catalyst is used. The preferred feedstock is a light petroleum fraction rich in suitable cycloalkanes.

2.2 Reforming of Hydrocarbon

Catalytic reforming is one of the most important industrial applications of catalysis. The major reactions in the process involve the production of aromatic hydrocarbons from saturated hydrocarbon via dehydrogenation of cyclohexanes, dehydroisomerization of alkylcyclopentanes and dehydrocylization of alkanes. Isomerization, hydrogenolysis and hydrocracking reactions are also involved in the process. The objective of reforming is to obtain high production of aromatics as selectively as possible due to their anti-knock qualities as component of automotive fuels. The temperature range for reforming is from 770 K upwards and pressure between 10 – 35 atm.

Reforming is better done in the presence of catalyst. The catalyst employed are bifunctional in nature, in that they posses both acidic and metallic components. The metallic component i.e. platinum possesses high affinity for hydrogenation and dehydrogenation reactions. The acidic component which consists of the carrier on which the metallic component is dispersed is active for reactions which are commonly associated with acid catalysis i.e. isomerization and hydrocracking. The carrier is commonly alumina which contains a small amount of chlorine as a promoter. Between 1950s and 1960s,

Pt/Al_2O_3 was much in use for reforming in the industries, but during the past decade they have been replaced largely by catalysts containing platinum and a second metallic element such as rhenium or iridium. These new catalysts exhibit improved performance relative to. the original catalyst.

A typical catalytic reforming unit consists of a number of fixed bed reactions (four) in series. The naphtha feedstock is vaporized and heated to the desired reaction temperature prior to being admitted to the first reactor. The reaction is endothermic therefore the temperature of the vapour phase decrease continuously. The hydrocarbon stream passes through all the reactors while heating is continues. Effluent from the final reactor is cooled and separated to gaseous and liquid phases. The liquid product is known as the reformate, consisting of C_5 - C_{10} hydrocarbons. Aromatic product in the liquid phase is between 60 – 70wt %. Hydrogen is 60 – 90 % of the gaseous phase and when recycled it serves to retard fouling of the catalyst surface by hydrocarbon residue. Increased hydrogen pressure also decrease the yield of aromatic hydrocarbons. Therefore, choice of hydrogen pressure for a reformer is a matter of balancing product yields against deactivation rates.

Of all the reactions taking place in catalytic reforming, the dehydrogenation of cyclohexanes occurs by far the most readily. Isomerization reactions also occur readily but not nearly as fast as the dehydrogenation of cyclohexanes. The limiting reactions in most catalytic reforming operations are hydrocracking and dehydrocyclization, which generally occur at much lower rates.

The typical feedstocks to catalytic reformers are heavy straight – run (HSR) gasoline and Naphthas (180 to 350^0F). These are composed of the four major hydrocarbon groups, Paraffins, Olefins, Naphthenes and Aromatics (PONA). Typical feed stocks and reformer products have the following PONA analyses

Table 2.1: Feed stock for catalytic reformer (Sinfelt, 1979)

Component	Feed(Vol. %)	Product (Vol %)
Paraffins	45 – 55	30 – 50
Olefins	0 – 2	0
Naphthenes	30 – 40	5 – 10
Aromatics	5 – 10	45 – 60

The ease and probability of either of these occurring increases with the number of carbon atoms in the molecules and it is for this reason that only the HSR gasoline is used for reformer feed. The light straight – run gasoline (C_5, 180^0F) is largely composed of lower molecular weight paraffins that tend to crack to butane and lighter fractions and it is not economical to process the stream in a catalytic reformer. Hydrocarbons boiling above 400^0F are easily hydrocracked and cause an excessive carbon laydown on the catalyst.

2.2.1 Re forming reaction

There are two major reactions in reforming

(a) Reaction that produces desired product and (b) reaction that produces undesired product. While the desired reaction leads to the formation of aromatics and iso paraffins, the undesired hindered aromatic production.

Desired reaction occur in the following respect

(1) paraffins are isomerized and to some extent converted to naphthenes, the naphthenes are subsequently converted to aromatic

(2) olefins are saturated to form parafins which then react as in (1)

(3) Naphthenes are convertd to aromatics.

(4) Aromatics are left essentially unchanged.

Then the reactions that characterize the undesired products are

(1) Dealkylation of side chains on naphthens and aromatics to form butane and lighter paraffins.

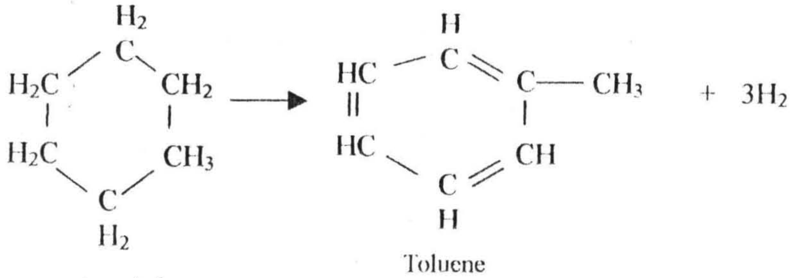
(2) Cracking of paraffins and naphthenes to form butane and lighter paraffins.

The major reactions of reforming generally are (a) dehydrogenation (b) dehydrocyclization (c) Isomerization and hydrocracking. The first two involves dehydrogenation.

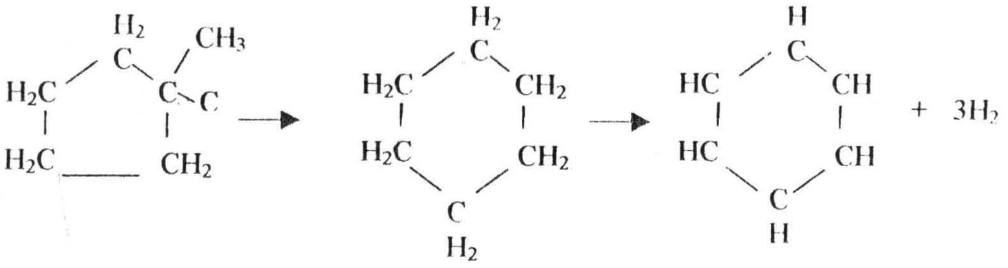
(a) Dehydrogenation

Dehydrogenation reaction are endothermic and have the highest reaction rates of the reforming reactions which necessitate the use of interheaters between catalyst beds to keep the mixture at sufficiently high temperatures for the reactions to proceed at practical rates. The major dehydrogenation reactions are:

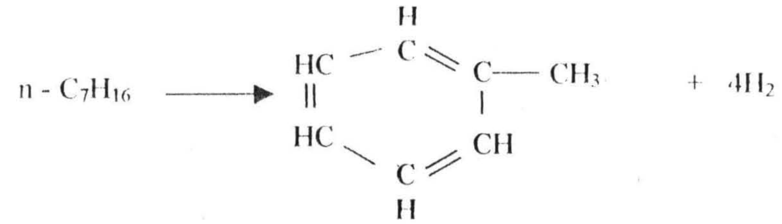
(i) Dehydrogenation of alkylcyclohexane to aromatics



(ii) Dehydro isomerization of alky cyclopentane to aromatics



(b) Dehydrocyclization of paraffins to aromatics



The following conditions favour the production of aromatics

(i) High temperature

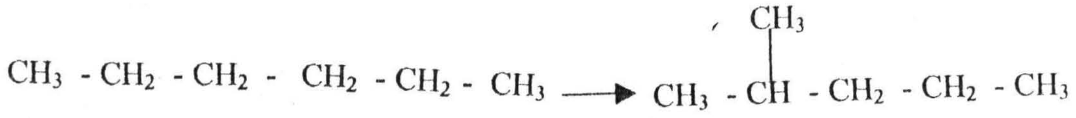
(ii) Low pressure

(iii) Low space velocity (promote approach to equilibrium)

(iv) Low hydrogen – to – hydrocarbon mole ratios (sufficient hydrogen partial pressure must be maintained to avoid excessive coke formation)

(c) Isomerization reactions

Isomerization of paraffins and cyclopentanes usually results in a lower octane product than those converted to aromatics. However, there is a substantial increase over that of the unisomerized materials. These are fairly rapid reactions with small heat effect an example here is the isomerization of normal paraffins to isoparaffins.



$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \longrightarrow CH_3 - \underset{}{\overset{CH_3}{\overset{|}{C}H}} - CH_2 - CH_2 - CH_3$$

n – Hexane   Iso hexane

Isomerization yield is favoured by the following:

(i) High temperature

(ii) Low space velocity

(iii) Low pressure

Isomerization effect due to hydrogen – to – hydrocarbon mole ratios is not present. High hydrogen – to – hydrocarbon ratios reduces the hydrocarbon partial pressure and thus favour the formation of aromatics.

(e) Hydrocracked reactions

The hydrocracking reactions are exothermic and result in the production of lighter liquid and gas products. They are relatively slow reactions and therefore most of the hydrocracking occurs in the last section of the reactor.

The major hydrocracking reactions involve the cracking and saturation of the paraffins.

$$C_{10}H_{22} + H_2 \longrightarrow CH_3\,CH_2\,CH(CH_3)\,CH_2\,CH_3 + CH_3\,CH_2\,CH_2\,CH_3$$

Decane Isohexane n - butane

The concentration of the paraffins in the charge stock determines the extent of the hydrocracking reaction but the relative fractions of isomers produced in any molecular weight group is independent of the charge stock.

In order to obtain high product quality and yield it is necessary to carefully control the hydrocracking and aromatization reactions. Reactor temperatures are carefully monitored to observe the extent of each of these reactions. The following favour increased yield :

(i) High temperature

(ii) High pressure

(iii) low space velocity

Table 2.2: Some basic relationships in catalytic reforming (Sinfelt, 1979)

	Reactions	**Reaction Rate**	**Heat Effect**	**High Pressure Effect**	**High temp. Effect**	**Effect on Hydrogen produced**
1	Hydro – Cracking	Slowest	Exothermic	Aids	Aids	Absorb
2	Isomeri – Zation	Rapid	Mildly exothermic	None	Aids	None
3	Cycliza – Tion	Slow	Mildly exothermic	Hinders	Aids	Evolves
4	Naphthene Isomerization	Rapid	Mildly exothermic	None	Aids	None
5	Naphthene Decyclization	Very Fast	Quite Endothermic	Hinders	Aids	Evolves

2.3 CATALYST FOR REFORMNG

Most chemical transformations of petroleum products are carried out in the presence of catalyst. Catalysts lower the activation energy of chemical reaction and thus appreciably increase their rate. The conducting of a reaction in the presence of a catalyst also reduces the temperature of the process.

Several catalysts are active for reforming reaction, they include the following: platinum-alumina, combined halogen, nickel, cobalt, platinum supported on silica-alumina and oxides such as molybdenum oxide and tungsten oxide deposited on silica-alumina. However, reforming processes using platinum or platinum alloy catalyst have the widest current application and are usually bifunctional in nature. It has been discovered that catalysts containing platinum in combination with certain metal like ruthenium, rhodium, rhenium, osmium and iridium, have marked advantages over catalysts consisting of platinum alone on alumina (Sinfelt, 1961, 1999).

2.3.1 Platinum-Alumina Catalysts

Platinum – alumina catalyst system was the first to be used widely in petroleum reforming. In commercial catalysts the amount of platinum present is commonly in the range of 0.3 – 0.6 wt %. The catalysts also contain chlorine in amounts typically in the range of 0.3 – 1.0 wt %.

One common method of preparing such catalysts involves impregnation of alumina with chloroplatinic acid. Its calcination is in air at temperatures in the range 820-870 K (Sinfelt, 1972). The alumina generally has a surface area in the range of 150 – 300 m^{2}g^{-1} The catalysts are commonly used in the form of pellets or extrudes in commercial reforming units with dimensions in the appropriate range of 1.5 – 4mm. The choice of size is based on considerations of pressure drop and diffusional limitations. For fundamental studies in small laboratory reactors, where pressure drop considerations are not a major issue. It may be preferable to use the catalyst in the form of small granules to minimize diffusional limitations.

Platinum – alumina catalyst is bifunctional in nature. They possess two different types of catalytic activity. They have the ability to catalyse hydrogenation and dehydrogenation reaction, which are characteristics of metallic catalysts. This function is associated with platinum portion of the catalyst. The catalysts are also effective for catalyzing hydrocarbon rearrangements which are typical of acid catalysts – this is associated with aluminaportion of the catalyst(Ciapetta and Hunter 1958). Chemisorption measurements have shown that freshly prepared platinum on alumina reforming catalysts are characterized by extremely high dispersion of platinum on the surface of the alumina carrier (Spenadel, 1960). In hydrogen chemisorption's studies on such catalysts, the amount of hydrogen taken up is frequently close to one hydrogen atom per atom of platinum. The presence of hydrogen influences its metallic quality (Sinfelt, 1979). Also demonstrated by the catalysts are the acidic properties shown by the affinity of the alumina surface for such basic molecules as ammonia, trimethylamine, n-butylamine, pyridine, and quinoline. The surface of alumina is characterized by the presence of

It is also about three times more active in terms of octane number enhancement than the latter (Pt-Re/Al_2O_3) for highly paraffinic feeds (Cecil et al, 1972). The greater activity appears to result from increased metal activity, particularly for dehydrocyclization; this is the slowest reforming reaction and occurs predominantly on the metal function, giving marked octane number enhancement.

2.5 Catalyst regeneration

Deactivated catalyst could be regenerated by burning off the accumulated coke which may be as much as 20% weight of the catalysts (Daniels et al,1972) under carefully controlled condition. This is done by purging the system with nitrogen and cooling, then burning off the carbon with gas stream containing 0.5 – 1% oxygen.

It is done for several days such that the temperature of the bed did not exceed 425°C. The temperature is designed to prevent sintering of Pt crystals and subsequent loss of surface area,selectivity and activity.

Nitrogen is used to purge the reactor after oxidation and hydrogen is used to reduce the oxidized Pt to its metallic state. The reactor is put in place by feeding it with several hundred ppm of sulphur compounds, after several days the feed is switched over to refinery stock.

This method of start up is similar to fresh catalyst, which may first be sulfided and brought on a stream with feed several hundred ppm of sulphur compounds. The procedure involves selective, controlled poisoning of Pt with sulphur to reduce its initial hydrogenation activity. Without such pre – treatment, a large fraction of the hydrocarbon undergo hydrogenolysis on the Pt to give gases with the liberation of much heat. The metal crystallites can be sintered to a useless state when the catalyst is overheated.

hydroxyl groups, which could be conceivably be a source of protonic acidity. However, it has been concluded that the hydroxyl groups do not contribute significantly as a source of protonic acid sites. The surface of alumina in a reforming catalyst normally contains chloride ions, which can interact with the hydroxyl groups to enhance their acidity.

2.4 Catalyst operation

The age of a catalyst affects its processing conditions. Its stability is determined by the operating temperature, pressure, and feed – pre – treatment to remove sulphur, nitrogen and oxygen compounds. Sulphur compounds poison the acidic component. Coke deposition is reduced by the application of high hydrogen partial pressure. At low pressures, deactivation may be so rapid that catalysts life may be only a few days; at high pressures catalyst life may approach a year.

Catalyst properties also affect deactivation rates. Platinum on promoted alumina has good stability. Separating the components result in more rapid deactivation because the deactivation-inhibiting platinum function is reduced (Cecil etal., 1972).

Stability of industrial reforming catalyst has undergone marked improvement in recent years, first with the introduction of multi-metallic catalysts (Kluksdah, 1968; Jacbson 1969).

The major advantage of Pt-Re/$Al_2 0_3$ is its enhanced resistance to deactivation by coking, which allows relatively long runs at relatively low pressures of operation. The improved deactivation resistance of Pt-Re/.$Al_2 0_3$ catalyst may be caused by a modification of the acidic support by the Re, at least a fraction of which is not reduced in the catalyst. Radium appears to stabilize the Pt component (Johnson, 1975; Webb, 1975), so that the metal surface area loss during regeneration is less than in Pt/Al_2O_3 catalysts. Both have the same initial activity. The multi metallic catalyst is even more stable because it accumulates coke at about half the rate characteristic of Pt-Re/Al_2O_3 (Cecil et al.,1972).

2.6 Steps to establish reaction mechanism

(1) Simple mechanism postulate with corresponding stoichiometry.

(2) When the stoichiometry appears to indicate the reaction to be one step and elementary the kinetic data was analysed according to integral method.

(3) For non-elementary reactions, it was assumed that the overall reaction consist of several elementary reaction steps with formation of intermediate compounds.

(4) A rate expression was formulated for each of the elementary steps and individual rate expression was summed up to describe the overall rate.

(5) When the resulting rate expression agrees with the experimental kinetic data, the assumed mechanism is accepted. Otherwise alternative mechanism will be assumed.

2.7 Rate equation for solid catalysed reaction

$A + B \rightleftharpoons R$ 2.1

An adsorption – surface reaction – desorption mechanism is assumed. s. represents a catalyst site.

(1) $A + s \rightleftharpoons As$

(2) $B + s \rightleftharpoons Bs$

Adsorption of A and B molecules 2.2

(3) $As + B \rightleftharpoons Rs$ —— Adsorbed A reacts with B in the fluid. This assumes that there is no reaction of A with B adsorbed. Adsorbed B serves only to block catalyst sites.

(4) $Rs \rightleftharpoons R + s$ 2.3

Desorption of product R

For the above reactions steps equation for both forward and backward reactions are formed

The concentration is related by equilibrium constant.

(1) $r_1 = k_{1f} C_A (1 - Q_A - Q_B - Q_R) - k_{1r} Q_A$

$$K_1 = \frac{Q_A}{C_A(1 - Q_A - Q_B - Q_R)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.4$$

(2) $r_2 = K_{2f} C_B (1 - Q_A - Q_B - Q_R) - K_{2r} Q_B$

$$K_2 = \frac{Q_2}{C_B(1 - Q_A - Q_B - Q_R)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.5$$

(3) $r_3 = K_{3f} (Q_A) C_B - K_{3r} Q_R$

$$K_3 = Q_R \big/ Q_A C_B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.6$$

(4) $r_4 = K_{4F} Q_R - K_{4R} C_R (1 - Q_A - Q_B - Q_R)$

$$K_4 = C_R(1 - Q_A - Q_B - Q_R) \big/ Q_R \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2.7$$

K1, K2, K3 and K4 are equilibrium constant for the individual steps. K4 is a desorption step and is reciprocal of the usual adsorption equilibrium constants. Q_A, Q_B and Q_R represent total catalyst sites occupied by A, B, and R respectively. Kf's are constants in the rate equation for adsorption, rf = KifCi (1 - ∑Qi). Also

$$Rr = K_{ir} Q_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.8$$

Assuming step 1, 2, and 4 to occur at near equilibrium allows the determination of Q_A and QR in terms of known quantities.

$$Q_A = K_1 C_A (1 - Q_A - Q_B - Q_R)$$

$$Q_R = \frac{C_R(1 - Q_A - Q_B\ Q_R)}{K_1} \qquad \ldots\ldots 2.8$$

$$and\ K_3 = \frac{K_{3f}}{K_{3r}} \text{ or } K_{3r} = \frac{K_{3f}}{K_3}$$

Thus

$$r_3\ \ k_{3f}(1\ \ Q_A\ \ Q_B\ \ Q_R)(K_1 C_A C_B\ \ \frac{C_R}{K_3 K_4}) \qquad \ldots\ldots 2.9$$

The fraction of totalcatalyst site vacant has been defined as

$$1 - K_1 C_A Q_V - K_2 C_B Q_V - (\frac{C_R}{K_4})Q_V = Q_V \qquad \ldots\ldots 2.10$$

since $Q_V = 1 - Q_A - Q_B - Q_R$.

when this is substituted into Eq.2.9, we have

$$r_3 = \frac{K_{3f} K_1 (C_A C_B - C_R / K_3 K_4 K_1)}{K_1 C_A + K_2 C_B + C_R / K_4 + 1} \qquad \ldots\ldots 2.11$$

The product $K_1 K_2 K_4$ equivalent to overall equivalent constant for all the productive steps in the assumed mechanism

$$r_3 = \frac{k((C_A C_B - C_R / K)}{K_A C_A + K_B C_B + K_R C_R + 1} \qquad \ldots\ldots 2.12$$

where $K = K_1 K_2 K_4$, $k = K_{3f} K_1$, $K_A = K_1$, $K_B = K_2$ and $K_R = 1/K_4$

Table 2.3: Industrial Catalytic (Heterogenous) Processes (Sinfelt, 1981)

	Major reaction Step	Product	Catalytic Type	Catalyst Poisons
1	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	Ammoina	FeO/Fe_2O_3 Promoted Al_2O_3 K_2O	Moisture, CO, CO_2, O_2
2	$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$	Ethanol	H_3PO_4 on Kisselgul	Compounds of S
3	$4NH_3 + 5\ H_2O \rightarrow NO + H_2O$ $2NO + O_2 \rightarrow 2NO_2$ $3NO_2 + H_2O \quad 2HNO_3 + NO$	Nitric acid	Pt on Rh	Compounds As and Cl_2
4	Acid catalyst reactions	Cracking alkylation and isomerization	Synthetic Aluminoslicate, $AlCl_3$, H_3PO_4	Organo metallic compounds, organic bases

Chemical equation	Catalytic steps	Rate equations
$A \rightleftharpoons R$	$A + s \rightleftharpoons As$	$r = \frac{K(C_A - C_R/K)}{1 + K_R C_R}$
	$As \rightleftharpoons Rs$	$r = \frac{K(C_A - C_R/K)}{1 + K_A C_A + K_R C_R}$
	$Rs \rightleftharpoons R + s$	$r = \frac{K(C_A - C_R/K)}{1 + K_A C_A}$
$A \rightleftharpoons R$	$2A + s \rightleftharpoons A_2s$	$r = \frac{K(C_A^2 - C_R^2/K^2)}{1 + K_p C_p + K_R^1 C_p^2}$
	$A_2s + s \rightleftharpoons 2As$	$r = \frac{K(C_A^2 - C_R^2/K^2)}{(1 + K_R C_R + K_R^1 C_A^2)^2}$
	$As \rightleftharpoons Rs$	$r = \frac{K(C_A - C_R/K)}{1 + K_A C_R^2 + K_A^1 C_A + K_R C_R}$
	$Rs \rightleftharpoons R + s$	$r = \frac{K(C_A - C_R/K)}{1 + K_A C_A}$

2.8 Modelling Studies

The knowledge of rates of chemical reaction, the maximum conversion obtainable, the nature of physical process interacting with the chemical reactions and the parameters which influence the proceeding is very important in analyses of a process. Chemical process rate data for most industrially important reactions cannot be estimated reliably from theories and must be determined experimentally.

In modeling an equation for the reforming of n-octane on a Pt/Al_2O_3 catalyst (Onukwuli and Susu, 1988) showed that the products are cracked products, ethylbenzene, o-p-m-xylene and toluene, the rate determining step is the

Conversion of adsorbed isooctane to adsorbed $_0$ – xylene. The activation energies were 21 2 and 14.3 Kca/gmol for forward and backward reactions respectively. For he reaction of n-heptane reforming on Pt/AI $_2$ O $_{b3}$ catalyst the products are hydrocracked product, toluene and benzene. The activation energies are 27 and 39 KJ/mol for forward and backward reactions. The rate controlling step is the dehydrocyclization of iso-heptanes to methylcyclohexane (SUSU et al 1997). The rate equation is

$$r_4 = \frac{K_{4r}K_1K_3C_N - K_{4r}\dfrac{K^2CH^2{}_2C_i}{K_4K_3K_{12}}}{K_4K_1C_N(I + K_3) + K_2C_{H2}\left(1 + \dfrac{C_1}{K_5K_{13}}\right) + \dfrac{C_H}{K_{12}} + \dfrac{C_b}{K_{10}} + \dfrac{C_{cp}}{K_{10}} + \dfrac{C_m}{K_{14}}} \quad \ldots\ldots 2.13$$

The aromatizatin of 3-methylhexane under H_2 and N_2 atmospheres on Pt/AI_2O_3 catalysts showed that reaction products under nitrogen atmosphere are, cracked products, toluene and benzene while under hydrogen atmosphere only cracked produces are formed. This is due to high partial pressure of hydrogen which hindered the formation to aromatics as was observed by Aberuagba (2000). The activation energies are 107 KJ/mol in N_2 and 202.03 KJ/mol in H_2

Physical processes involved in kinetic reaction are mass and heat transfer. This could be estimated adequately from the properties of substances participating in the reaction, the flow characteristics, the configuration of the reaction vessel and so forth, which is in contrast with the chemical process rate data for most industrially important reactions.

2.9.1. Model Development

In mechanistic modeling of heterogeneous reaction problems such as identification of an adequate model for the reaction and the estimation of parameters within the chosen model are often encountered. Some of the ways of solving these problems are:

Mathematical representation of the system, based on certain fundamental laws governing the entire systems, mathematical expressions are formulated which include algebra, calculus, etc. this is successfully done through assumptions.

Model constructions: the derived mathematical expressions are changed to standard equations which can be solved mathematically, with the knowledge of computer, such equations are written as algorithms which are later coded to a computer language (e.g. Fortran Pascal, Visual Basic C ++, Java etc). an alternative to computer programmes, the equations can be simplified or linearized for solutions with software like Mathematica, Polymath, Mat Lab etc.

Standard rate equations are as written below where concentration are know from experiments.

$$r = \frac{K_f K_i C^a - K_i K_3 C^b{}_j}{1 + k_m C^y{}_m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 2.14$$

Model discrimination: the empirical data is substituted into the computer programme for results which are later compared with experimental data. The results are the values of the unknown parameters in the equation

2.10 Techniques for parameters estimation

statistical techniques are required to obtain the best fit of the equations to the kinetic data or experimental data. Minimizing the deviations between the observed rate and the predicted rate from he equation is straight forward as ling as the constants are linearly related in the rate equation. When non-linearity exist the analysis is more complex, but the general procedure is the same and consists of the following steps (Himmelblau 1970).

1. Assuming various mechanisms and controlling steps for each mechanism. Develop a rate equation for each combination of mechanism and controlling step.

2. Determine the numerical values of the constants which give the best fit of each equation to the observed rate data.
3. Choose the equation which best fits the data and agrees with the available independent information about the reaction.

The optimization routine is an automatic method of minimizing an object function subject to other functional constraints placed on it. The routines try different values for the parameters until no other values are found with smaller error. The objective function in an estimation problem is such that it describes how well the model being tested fits the available data. The smaller the value of this objective function the better the model fits the available data. Consequently, the model with the smallest value of the objective function is the one which best fits the data. Such an objective function is called a method of estimation. Several methods of estimation are used, amongst which are the unweighted least squares estimates (Aoki,1971) .The unweighted least squares method is one of the widely used methods. It can be applied directly to the deterministic model, without cognizance being taken of the probability distribution of the observations. While it is sometimes the best form of estimates to use, estimates obtained from it may be quite unsatisfactory. The weighted least square method offers advantages of preventing certain quantities from dominating other measure on different scales (e.g. temperature values dominating mole fractions) are reducing the influence on the parameter of less reliable data.

Non-linear model occurs when the parameters (coefficients) to be estimated are not linear. Because of the complexity of the non-linear model equations, we rely on approximate rather than exact methods.

Five of the more effective optimization techniques commonly used are:

1. Derived – free method.

    (i) Simplex method (ii) Direct search method

2. Derivative method

    (i) Gauss – Siedel (ii) Gradient methods (iii) Marquardt's method

All the effective procedures are iterative ones which are best executed on a digital or hybrid computer.

2.11 Estimation with the parameter and/or variables subject to constraints.

The idea of imposing constraints on the parameters and the variables in a process model comes about quite naturally especially for chemical kinetics empirical models such as

$$\gamma = \frac{kK_A C_A C_B}{1 + K_A + K_B C_B} \text{ .... } 2.15$$

Where γ is a rate of reaction, k and K are constants, and C is the concentration. Arguments on physical grounds lead to the conclusion that k, K_A, and K_B must be non-negative. Consequently, fitting the model estimates will lead to unreasonable, often negative Values(Himmeblau, 1970)

2.12 Computer programme

In this project a computer programming language called Visual Basic was used. This program was employed because it is user friendly. Also in the world today, it is the most popular programming language (Visual Basic 6.0 from Ground UP). It is very fast, powerful and very easy to use. It is fully an Object Oriented Program (OOP) and has the ability to create true executable files and even the ability to make Controls. Last but not the least Its internet power and powerful database features which can not be over emphasized.

In this program, nine (9) forms (files) and two (2) modules were used. Each form was used to compute and store the parameters peculiar to it. On the other hand, module 1 contains the Concentration, Contact time, rate, and the given formulas. Modules 2 contains the code for Gauss Jordan's iterative method. To run this program, one supply a temperature (valid temperature) and rate (valid rate) and click the computer button after indicating the desired scheme. The computer automatically goes to the formular in the previously indicated scheme and via them generates simultaneous equations (6 equations with 6 unknown). From there, the second module (Modules 2) is activated. Here, the six equation s are converted to 6x6 matrices. Then a function called "Gauss function" is called and the coefficient of the simultaneous equation is computed. The result is the display on the screen.

CHAPTER THREE

3.0 METHODOLOGY

3.1 Data

Experimental data used for this project were obtained from Aberuagba (1995). These data were for N_2 and H_2 atmosphere (i.e Table B1 and B2 respectively in Appendix B)

3.2 Development of reaction mechanisms under nitrogen

Six reaction mechanisms were developed from the following reaction network under N_2

3.2.1 Scheme 1

In this scheme hydrogen was not adsorbed on the catalyst surface. Hydrogen participation is by Eley – Rideal mechanism

ADSORPTION:

$$I + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} IS \quad \ldots\ldots 3.1a$$

REACTION

$$IS \underset{K_4}{\overset{K_3}{\rightleftharpoons}} CPS \quad \ldots\ldots 3.2a$$

$$CPS \underset{K_6}{\overset{K_5}{\rightleftharpoons}} CP + S \quad \ldots\ldots 3.3a$$

$$IS \underset{K_8}{\overset{K_7}{\rightleftharpoons}} M1S + H_2 \quad \ldots\ldots 3.4a$$

$$M1S \underset{K_{10}}{\overset{K_9}{\rightleftharpoons}} M2S + H_2. \quad \ldots\ldots 3.5a$$

$$M2S \underset{K_{12}}{\overset{K_{11}}{\rightleftharpoons}} TS + 2H_2 \quad \ldots\ldots 3.6a$$

$$TS + H2 \underset{K_{14}}{\overset{K_{13}}{\rightleftharpoons}} BS + Me \quad \ldots\ldots 3.7a$$

DESORPTION

$$BS \underset{K_{16}}{\overset{K_{15}}{\rightleftharpoons}} B + S \quad \ldots\ldots 3.8a$$

$$TS \underset{K_{18}}{\overset{K_{17}}{\rightleftharpoons}} T + S \quad \ldots\ldots 3.9a$$

RATE EXPRESSION

At equilibrium the rate of reaction, r = 0. Using step 1 as the rate controlling step

$$r_1 \quad k_1 C_i C_s - k_2 C_{is} \qquad \text{.............................} \; 3.11a$$

at equilibrium other rates equal zero

$$r_2 \quad K_3 C_{is} - K_4 C_{cps} \qquad = 0$$

$$C_{IS} = \frac{C_{cps}}{K_b} \quad \text{..} \; 3.12$$

$$r_3 = K_5 C_{CPS} - K_6 C_{CP} S = 0$$

$$C_{CPS} = \frac{C_{CP} S}{K_C} \quad \text{..} \; 3.13$$

$$r_4 = K_7 C_{IS} - K_8 C_{M_1S} C_{H_2} = 0$$

$$C_{IS} = \frac{C_{MIS} C_{H_2}}{K_d} \quad \text{..} \; 3.14$$

$$r_5 = K_9 C_{MIS} - K_{10} C_{M_2S} C_{H_2} = 0$$

$$C_{MIS} = \frac{C_{M2S} C_{H_2}}{K_E} \quad \text{..} \; 3.15$$

$$r_6 = K_{11} C_{M2S} - K_{12} C_{TS} C_{H_2^2}$$

$$C_{M2S} = \frac{C_{TS} C_{H_2^2}}{K_f} \quad \text{..} \; 3.16$$

$$r_7 = K_{13} C_{TS} C_{H_2} - K_{14} C_{BS} C_{me} = 0$$

$$C_{TS} = \frac{C_{BS} C_{Me}}{k_g C_{H2}} \quad \text{..} \; 3.17$$

$$r_8 = K_{15} C_{BS} - K_{16} C_B S = 0$$

$$C_{BS} = \frac{C_{BS}}{K_h} \quad \text{..} \; 3.18$$

$$r_9 = K_{17} C_{TS} - K_{18} C_T S = 0$$

$$C_{TS} = \frac{C_T S}{K_i} \quad \text{..} \; 3.19$$

Substituting Equation3.19 and3.18 in3.17

$$C_{H2} = \frac{C_B C_{me} K_i}{C_T K_g k_h} \quad \text{..} \; 3.20$$

substituting equation 20 in 6

$$C_{m2s} = \frac{C_{B^2} C_{Me^2} K_1 S}{C_T K_f K_h^2 K_g^2} \ldots\ldots 3.21a$$

$$C_{MIS} = \frac{C_B^3 C_{Me}^3 K_1^2 S}{C_T^2 K_e K_f K_h^3 K_g^3} \ldots\ldots 3.22a$$

substitute equation 22 and 20 in 14

$$\mathrm{C}_{\mathrm{IS}} = \frac{C_{me}^4 C_B^4 K_i^3 S}{C_T^3 K_d K_e K_f K_h^4 K_g^4} \ldots\ldots 3.23a$$

equating equation 12 and 23

$$C_{CPS} = \frac{C_B^4 C_{me}^4 K_i^3 K_b S}{C_T^3 K_d K_e K_f K_h^4 K_g^4} \ldots\ldots 3.24a$$

Site balance

$$1 = S + IS + C_P S + M_I S + M_2 S + TS + BS$$

$$= S + \frac{C_B^4 C_{me}^2 K_i S}{\mathrm{K_d} K_e K_f K_g^4 K_h^4 C_T^3} + \frac{\mathrm{C_B^4} C_{me}^4 K_i^3 K_b S}{K_d K_e K_f K_g^4 K_h^4 C_T^3} + \frac{\mathrm{C_B^3} C_{me}^3 K_k S}{K_e K_f K_g^3 K_h^4 C_T^2}$$

$$+ \frac{C_B^2 C_{me}^2 K_i S}{K_f K_g^2 K_h^2 C_T} + \frac{C_T S}{K_i} + \frac{C_B S}{K_h} \ldots\ldots 3.25a$$

$$S = \frac{1}{1 + \frac{C_B^4 C_{me}^4 K_i}{K_d K_e K_f K_g^4 K_h^4 C_T^3} + \frac{C_B^4 C_{me}^4 K_i K_b}{K_d K_e K_f K_g^4 K_h^4 C_T^3} + \frac{C_B^3 C_{me}^3 K_i}{K_e K_f K_g^3 K_h^4 C_T^2} +}$$

$$\frac{1}{\frac{C_B^2 C_{me}^2 K_i}{K_f K_g^2 K_h^2 G} + \frac{G}{K_i} + \frac{C_B}{K_h}} \ldots\ldots 3.26a$$

when r_1 is the rate controlling

$$r_1 = K_I C_I S - K_2 C_{IS} \ldots\ldots 3.27a$$

$$\left[K_1 C_I - \frac{K_2 C_B^4 C_{me}^4 K_i^3}{K_d K_e K_f K_g^4 K_h^4 C_T^3} \right] [S] \ldots\ldots 3.28a$$

$$r_1 = \frac{K_1 C_I - \frac{K_2 C_B^4 C_{me}^4 K_i^3}{K_d K_e K_f K_g^4 K_h^4 C_T^3}}{1 + \frac{C_B^4 C_{me}^4 K_i^3}{K_d K_e K_f K_g^4 K_h^4 C_T^3} + \frac{C_B^4 C_{me}^4 K_i K_b}{K_d K_e K_f K_g^4 K_h^4 C_T^3} + \frac{C_B^3 C_{me}^3 K_i^2}{K_e K_f K_g^3 K_h^3 C_T^2} +}$$

$$\frac{1}{\frac{C_B^2 C_{me}^2 K_i}{K_f K_g^2 K_h^2 C_T} + \frac{C_T}{K_i} + \frac{C_B}{K_h}} \quad \ldots\ldots 3.29a$$

When r2 is rate controlling

$$r_2 = K_3[IS] - K_4 C_P S \quad \ldots\ldots 3.30a$$

$$r_2 = B\frac{K_3 K_a C_I - \frac{K_4 C_P}{K_C}}{1 + K_a C_I + \frac{C_P}{K_C} + \frac{K_1^2 C_B^3 C_{me}^3}{K_e K_f K_h^3 K_g^3 C_T^2} + \frac{K_I C_B^2 C_{me}^2}{K_f K_h^2 K_g^2 C_T} + \frac{C_T}{K_i} + \frac{C_B}{K_h}} \quad \ldots\ldots 3.31a$$

r_3 as rate controlling

$$r_3 = K_5 C_{CPS} - K_6 C_{CP} S \quad \ldots\ldots 3.32a$$

$$r_3 = \frac{K_5 K_a K_b I - K_6 C_P}{1 + K_a C_I + K_a K_b C_I + \frac{K_i^2 C_B^3 C_{me}^3}{K_f K_e K_h^3 k_g^3 C_T^2} + \frac{K_i C_B^2 C_{me}^2}{K_f K_h^2 K_g^2 C_T} + \frac{C_B}{K_h} + \frac{C_T}{K_i}} \quad \ldots\ldots 3.33a$$

r_4 as rate controlling

$$r_4 = K_7 C_{IS} - K_8 C_{MIS} C_{H2} \quad \ldots\ldots 3.34a$$

$$r_4 = \frac{K_7 K_a C_I - \frac{K_8 C_B^4 C_{me}^4 K_i^3}{K_e K_f K_g^4 K_h^4 C_T^3}}{1 + K_a C_I + \frac{C_{CP}}{K_c} + \frac{K_i^2 C_B^3 C_{me}^3}{K_e K_f K_g^3 K_h^3 C_T^2} + \frac{K_i C_B^3 C_{me}^3}{K_e K_f K_g^3 K_h^3 C_T^2} + \frac{C_B}{K_h} + \frac{C_T}{K_i}} \quad \ldots\ldots 3.35a$$

r_5 as rate controlling

$$r_5 = K_9 C_{MIS} - K_{10} C_{M2S} C_{H2} \quad \ldots\ldots 3.36a$$

$$r_5 = \frac{[K_9 - K_{10} K_e]\frac{K_I^2 C_B^3 C_{me}^3}{K_e K_f K_h^3 K_g^3 C_T^2}}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{K_I^2 C_B^3 C_{me}^3}{K_f K_e K_h^3 K_g^3 C_T^2} + \frac{C_B^2 C_{me}^2 K_i}{K_f K_h^2 K_g^2 C_T} + \frac{C_B}{K_h} + \frac{C_T}{K_i}} \quad \ldots\ldots 3.37a$$

r_6 *as* rate controlling

$$r_6 = K_{11} C_{M2S} - K_{12} C_{TS} C_{H2}^2 \quad \ldots\ldots 3.38a$$

$$r_6 = \frac{K_{11}\left[\frac{K_g K_h C_T}{K_i C_B C_{me}}\right]^2 K_a K_d - \frac{K_{12} K_i}{C_T}\left[\frac{C_B C_{me}}{K_g K_h}\right]^2}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{K_a K_d K_g K_h C_I C_T}{K_i C_B C_{me}} + \left[\frac{K_g K_h C_T}{K_i C_B C_{me}}\right]^2 K_a K_d + \frac{C_B}{K_h} + \frac{C_T}{K_i}} \text{..........} 3.39a$$

r7 as rate controlling

$$r_7 = K_{13} C_{TS} C_{H2} - K_{14} C_{BS} C_{me} \text{....................................} 3.40a$$

$$r_7 = \frac{K_{13}\left[\frac{C_T}{K_i}\right]^{\frac{3}{4}}\left[K_a K_d K_e K_f C_I\right]^{\frac{1}{4}} - K_{14}\frac{C_B C_{me}}{K_h}}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{\left[K_a K_d C_I\right]^{\frac{3}{4}} C_T^{\frac{1}{4}}}{\left[K_e K_f K_i\right]^{\frac{1}{4}}} + \left[\frac{K_a K_d K_e C_I}{K_I K_f}\right]^{\frac{1}{2}} + \frac{C_B}{K_h} + \frac{C_T}{K_i}} \text{......................} 3.41a$$

r_8 as rate controlling

$$r_8 = K_{15} C_{BS} - K_{16} C_B C_S \text{...} 3.42a$$

$$r_8 = \frac{\frac{K_{15} K_g \left[K_a K_d K_e K_f C_I\right]^{\frac{1}{4}} C_T^{\frac{3}{4}} - K_{16} C_B}{K_i^{\frac{3}{4}} C_{me}}}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{\left[K_a K_d C_I\right]^{\frac{3}{4}} C_T^{\frac{1}{4}}}{\left[K_i K_e K_f\right]^{\frac{1}{4}}} + \left[\frac{K_a K_d K_f C_T}{K_f K_i}\right]^{\frac{1}{2}} + \frac{\left[K_a K_d K_e K_f C_I\right]^{\frac{1}{4}}}{K_i^{\frac{3}{4}} C_{me}}}$$

$$\frac{1}{K_g T^{\frac{3}{4}} + \frac{C_T}{K_1}} \text{..} 3.43a$$

where r_9 is the rate controlling

$$r_9 = \frac{K_{17}\left[\frac{C_B C_{me}}{K_g K_h}\right]^{\frac{4}{3}} - K_{18} C_T}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \left[\frac{C_B C_{me}}{K_e K_f K_g K_h}\right]^{\frac{1}{3}}\left[K_a K_I C_I\right]^{\frac{2}{3}} + \left[\frac{C_B C_{me}}{K_f K_g K_h}\right]^{\frac{2}{3}}\left[K_a K_d K_e I\right]^{\frac{1}{3}} +}$$

$$\frac{1}{\frac{C_B}{K_h}} \text{..} 3.44a$$

Table 3.1: Reaction rate model for scheme 1

$$r_1 = \frac{K_1 C_I - K_2 K_i^3 C_B^4 C_{me}^4 / K_L}{1 + \frac{C_B^4 C_{me}^4 K_i^3}{K_L} + \frac{C_B^4 C_{me}^4 K_i K_h}{K_L} + \frac{C_B^3 C_{me}^3 K_i^2}{K_L} + \frac{C_T}{K_i} + \frac{C_B}{K_h}}$$

where $K_L = K_d K_e K_f K_g^4 K_h^4 C_T^3$

$$r_2 = \frac{K_3 K_a C_I - K_4 C_P / K_C}{1 + K_a C_I + \frac{C_P}{K_C} + \frac{K_1^2 C_B^3 C_{me}^3}{K_e K_f K_h^3 K_g^3 C_I^2} + \frac{K_I C_B^2 C_{me}^2}{K_f K_h^2 K_g^2 C_I} + \frac{C_T}{K_i} + \frac{C_B}{K_h}}$$

$$r_3 = \frac{K_5 K_a K_b C_I - K_6 C_P}{1 + K_a C_I + K_a K_b C_I + \frac{K_i^2 C_B^3 C_{me}^3}{K_f K_e K_h^3 K_g^3 C_T^2} + \frac{K_i C_B^2 C_{me}^2}{K_f K_h^2 K_g^2 C_T} + \frac{C_B}{K_i}}$$

$$r_4 = \frac{K_7 K_a C_I - K_i^3 K_8 C_B^4 C_{me}^4 / K_e K_f K_g^4 K_h^4 C_T^3}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{K_i C_B^3 C_{me}^3}{K_e K_f K_g^3 K_h^3 C_T^2} + \frac{K_i C_B^2 C_{me}^2}{K_f K_g^2 K_h^2 C_T} + \frac{C_B}{K_h} + \frac{C_T}{K_i}}$$

$$r_5 = \frac{\frac{K_9 K_i C_B^3 C_m^3}{K_e K_f K_g^3} - \frac{K_{10} K_e C_B^3 C_m^3}{K_e K_f K_g^3 C_T^2}}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{K_a K_d k_g K_h C_I C_T}{K_i C_B C_{me}} + \left[\frac{K_g K_h C_T}{K_i C_B C_{me}}\right]^2 K_a K_d + \frac{C_B}{K_h} + \frac{C_T}{K_i}}$$

$$r_6 = \frac{K_{11}\left[\frac{K_g K_{11} C_T}{K_i C_B C_{me}}\right]^2 K_a K_d - \frac{K_{12} K_i}{C_T}\left[\frac{C_B C_{me}}{K_g K_h}\right]^2}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{K_a K_d K_g K_h C_I C_T}{K_1 C_B C_{me}} + \left[\frac{K_g K_h C_T}{K_1 C_B C_{me}}\right]^2 K_a K_d + \frac{C_B}{K_h} + \frac{C_T}{K_2}}$$

$$r_7 = \frac{K_{13}\left[\frac{C_T}{K_i}\right]^{\frac{1}{4}}\left[K_a K_d K_e K_f C_I\right]^{\frac{1}{4}} - K_{14} C_B C_{me} / K_h}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{[K_a K_d C_I] C_T^{\frac{1}{4}}}{[K_e K_f K_i]^{\frac{1}{4}}} + \left[\frac{K_a K_d K_e C_I}{K_i k_f}\right]^{\frac{1}{2}} + \frac{C_B}{K_h} + \frac{C_T}{K_i}}$$

$$r_8 = \frac{\frac{K_{15} K_g [K_a K_d K_e K_f C_I]^{\frac{1}{4}} C_T^{\frac{3}{4}}}{K_i^{\frac{3}{4}} C_{me}} - K_{16} C_B}{1 + K_a C_i + \frac{C_{CP}}{K_C} + \frac{[K_a K_d C_I]^{\frac{3}{4}} C_T^{\frac{1}{4}}}{[K_i K_e K_f]^{\frac{1}{4}}} + \frac{[K_a K_d K_f C_I]^{\frac{1}{4}} K_g}{K_i^{\frac{3}{4}} C_{me}} + \frac{C_T}{K_i}}$$

$$r_9 = \frac{K_{17}\left[\frac{C_B C_{me}}{K_g K_h}\right]^{\frac{4}{3}} - K_{18}C_T}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \left[\frac{C_B C_{me}}{K_e K_f K_g K_h}\right]^{\frac{1}{3}}\left[K_a K_I C_I\right]^{\frac{2}{3}} + \left[\frac{C_B C_{me}}{K_f K_g K_h}\right]^{\frac{2}{3}}\left[K_a K_d K_e C_I\right]^{\frac{1}{3}} + \frac{C_B}{K_h}}$$

3.2.2 Scheme two

Hydrogen is not absorbed and there is no production of intermediates product like methyl cyclohexane.

$I + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} IS$ ……………………………3.01b

$IS \underset{K_4}{\overset{K_3}{\rightleftharpoons}} TS + 4H_2$ ……………………3.02b

$TS + H2 \underset{K_6}{\overset{K_5}{\rightleftharpoons}} BS + Me$……………………3.03b

$IS \underset{K_8}{\overset{K_7}{\rightleftharpoons}} CPS$ …………………………3.04b

$BS \underset{K_{10}}{\overset{K_9}{\rightleftharpoons}} B + S$ ………………………3.05b

$CPS \underset{K_{12}}{\overset{K_{11}}{\rightleftharpoons}} CP + S$ ……………………3.06b

$TS \underset{K_{14}}{\overset{K_{13}}{\rightleftharpoons}} T + S$ ……………………….3.07b

Using equation 1 as the rate controlling step all other steps are at equilibrium

$r_1 = K_1 C_I C_S - K_2 C_{IS}$……………………………………………3.08b

$r_2 = K_3 C_{IS} - K_4 C_{IS} C^4_{H2} = 0$

$C_{IS} = \frac{C_{TS} C^4_{H2}}{K_b}$……………………………………………3.09b

$r_3 = K_5 C_{TS} C_{H2} - K_6 C_{BS} C_{me} = 0$

$C_{H2} = \frac{C_{BS} C_{me}}{K_C C_{TS}}$……………………………………………3.10b

$K_7 C_{IS} - K_8 C_{PS} = 0$

$C_{IS} = \frac{C_{CPS}}{K_d}$……………………………………………3.11b

$$K_9C_{BS}-K_{10}C_BC_S=0$$

$$C_{BS}=\frac{C_BC_S}{K_e}\ldots\ldots\ldots\ldots 3.12b$$

$$K_{11}C_{CPS}-K_{12}C_{CP}C_C=0$$

$$C_{CPS}=\frac{C_{CP}C_S}{K_f}\ldots\ldots\ldots\ldots 3.13b$$

$$K_{13}C_{TS}-K_{14}C_TC_S=0$$

$$C_{TS}=\frac{C_TC_S}{K_g}\ldots\ldots\ldots\ldots 3.14b$$

when equation (13) is substituted into equation (11) we have

$$C_{IS}=\frac{C_{CP}C_S}{K_dK_f}\ldots\ldots\ldots\ldots 3.15b$$

for site balance

$$1=S+IS+BS+TS+CPS$$

$$1=C_S+\frac{C_{CP}C_S}{K_dK_f}+\frac{C_BC_S}{K_e}+\frac{C_TC_S}{K_g}+\frac{C_{CP}C_S}{K_f}\ldots\ldots\ldots\ldots 3.16b$$

$$S=\frac{1}{1+\frac{C_{CP}}{K_dK_f}+\frac{C_B}{K_e}+\frac{C_T}{K_g}+\frac{C_{CP}}{K_f}}\ldots\ldots\ldots\ldots 3.17b$$

$$r_1=\left[K_1C_I-\frac{K_2C_{CP}}{K_dK_f}\right]C_S\ldots\ldots\ldots\ldots 3.18b$$

$$r_1=\frac{K_1C_I-\frac{K_2C_{CP}}{K_dK_f}}{1+\frac{C_{CP}}{K_dK_f}+\frac{C_B}{K_e}+\frac{C_T}{K_g}+\frac{C_{CP}}{K_f}}\ldots\ldots\ldots\ldots 3.19b$$

when r_2 is the rate controlling

$$r_2=\left[K_3K_aC_I-\frac{K_4K_g^4C_B^4C_{me}^4}{K_C^4K_e^4C_T^3}\right]C_S\ldots\ldots\ldots\ldots 3.20b$$

$$r_2=\frac{K_3K_aC_I-\frac{K_4K_g^4C_B^4C_{me}^4}{K_C^4K_e^4C_T^3}}{1+K_aC_I+\frac{C_B}{K_e}+\frac{C_{CP}}{K_f}+\frac{C_T}{K_g}}\ldots\ldots\ldots\ldots 3.21b$$

r_3 as rate controlling

$$r_3=\left[K_5C_T^{\frac{3}{4}}\left[K_aK_bK_gC_I\right]^{\frac{1}{4}}-\frac{K_6C_BC_{me}}{K_e}\right]C_S\ldots\ldots\ldots\ldots 3.22b$$

$$r_3 = \frac{K_5 C_T^{\frac{3}{4}}\left[K_a K_b K_g C_I\right]^{\frac{1}{4}} - \frac{K_C C_B C_{me}}{K_e}}{1 + K_a C_I + \frac{C_B}{K_e} + \frac{C_{CP}}{K_f} + \frac{C_T}{K_g}} \ldots\ldots\ldots\ldots 3.23b$$

r_4 as rate controlling

$$\mathrm{r}_4 = \left[K_7 K_a C_I - \frac{K_8 C_{CP}}{K_f}\right] C_S \ldots\ldots\ldots\ldots 3.24b$$

$$r_4 = \frac{\left[K_7 K_a C_I - K_8 \frac{C_{CP}}{K_f}\right]}{1 + K_a C_I + \frac{C_B}{K_e} + \frac{C_{CP}}{K_f} + \frac{C_T}{K_g}} \ldots\ldots\ldots\ldots 3.25b$$

r_5 as rate controlling

$$\mathrm{r}_5 = \left[\frac{K_9\left[K_a K_b\right]^{\frac{1}{4}} K_C C_T^{\frac{3}{4}}}{K_g^{\frac{3}{4}} C_{me}} - K_{10} C_B\right] C_S \ldots\ldots\ldots\ldots 3.26b$$

$$r_5 = \frac{\frac{K_a\left[K_a K_b\right]^{\frac{1}{4}} K_C C_T^{\frac{3}{4}}}{K_g^{\frac{3}{4}} C_{me}} - K_{10} C_B}{1 + K_a C_I + \frac{\left[K_a\right]^{\frac{1}{4}} K_C C_T^{\frac{3}{4}}}{K_g^{\frac{3}{4}} C_{me}} + \frac{C_{CP}}{K_f} + \frac{C_T}{K_g}} \ldots\ldots\ldots\ldots 3.27b$$

r_6 as rate controlling

$$\mathrm{r}_6 = \left[K_{11} K_a K_d C_I - K_{12} C_{CP}\right] C_S \ldots\ldots\ldots\ldots 3.28b$$

$$r_6 = \frac{K_{11} K_a K_d C_I - K_{12} C_{CP}}{1 + K_a C_I + \frac{C_B}{K_e} + K_a K_d C_I + \frac{C_T}{K_g}} \ldots\ldots\ldots\ldots 3.29b$$

when r_7 is the rate controlling

$$r_7 = \left[\frac{K_{13}\left[C_B C_{me}\right]^{\frac{4}{3}} - K_{14} C_T}{K_C^{\frac{4}{3}}\left[K_d C_I\right]^{\frac{1}{3}}}\right] C_S \ldots\ldots\ldots\ldots 3.30b$$

$$r_7 = \frac{\frac{K_{13}\left[C_B C_{me}\right]^{\frac{4}{3}}}{K_C^{\frac{4}{3}}\left[K_d C_I\right]^{\frac{1}{3}}} - K_{14} C_T}{1 + K_a C_I + \frac{C_B}{K_C} + \frac{C_{CP}}{K_f} + \frac{\left[C_B C_{me}\right]^{\frac{4}{3}}}{K_C^{\frac{4}{3}}\left[K_d C_I\right]^{\frac{1}{3}}}} \ldots\ldots\ldots\ldots 3.31b$$

Table 3.2: Reaction rate model for scheme 2

$$r_1 = \frac{K_1 C_I - \dfrac{K_2 C_{CP}}{K_d K_f}}{1 + \dfrac{C_{CP}}{K_d K_f} + \dfrac{C_B}{K_e} + \dfrac{C_T}{K_g} + \dfrac{C_{CP}}{K_f}}$$

$$r_2 = \frac{K_3 K_a C_I - \dfrac{K_4 K_g^{1} C_B^{1} C_{me}^{1}}{K_C^{4} K_e^{4}}}{1 + K_a C_I + \dfrac{C_B}{K_e} + \dfrac{C_{CP}}{K_f} + \dfrac{C_T}{K_g}}$$

$$r_3 = \frac{K_5 C_T^{\frac{3}{4}} \left(K_a K_b K_g\right)^{\frac{1}{4}} - \dfrac{K_6 C_B C_{me}}{K_e}}{1 + K_a C_I + \dfrac{C_B}{K_e} + \dfrac{C_{CP}}{K_f} + \dfrac{C_T}{K_g}}$$

$$r_4 = \frac{K_7 K_a C_I - K_8 \dfrac{C_{CP}}{K_f}}{1 + K_a C_I + \dfrac{C_B}{K_e} + \dfrac{C_{CP}}{K_f} + \dfrac{C_T}{K_g}}$$

$$r_5 = \frac{\dfrac{K_a K_b^{\frac{1}{4}} K_C C_T^{\frac{3}{4}}}{K_g^{\frac{3}{4}} C_{me}} - K_{10} C_B}{1 + K_a C_I + \dfrac{K_a K_b^{\frac{1}{4}} K_C C_T^{\frac{3}{4}}}{K_g^{\frac{3}{4}} C_{me}} + \dfrac{C_{CP}}{Kf} + \dfrac{C_T}{K_g}}$$

$$r_6 = \frac{K_{11} K_a K_d C_I - K_{12} C_p}{1 + K_a C_I + \dfrac{C_B}{K_e} + K_a K_d C_I + \dfrac{C_T}{K_g}}$$

$$r_7 = \frac{K_{13} \left(C_B C_{me}\right)^{\frac{4}{3}} \Big/ K_C^{\frac{4}{3}} \left(K_d C\right)^{\frac{1}{3}} - K_{14} C_T}{1 + K_a C_I + C_B \big/ K_C + C_{CP} \big/ K_f + \left(C_B C_{me}\right)^{\frac{4}{3}} \Big/ K_C^{\frac{4}{3}} \left(K_d C_I\right)^{\frac{1}{3}}}$$

3.2.3 Scheme three

In this scheme hydrogen is adsorbed on the catalyst surface as a modular species.

ADSORPTION

$I + S \rightleftharpoons I,S$ 3.01c

$H_2 + S \rightleftharpoons H_2S$ 3.02c

REACTION

$IS + S \rightleftharpoons MCHS + H_2S$ 3.03c

$MCHS + 3S \rightleftharpoons TS + 3H_2S$ 3.04c

$TS + H_2S \rightleftharpoons BS + MeS$ 3.05c

$IS \rightleftharpoons CPS$ 3.06c

DESORPTION

$BS \rightleftharpoons B + S$ 3.07c

$CPS \rightleftharpoons CP + S$ 3.08c

$TS \rightleftharpoons T + S$ 3.09c

$H_2S \rightleftharpoons H_2 + S$ 3.10c

$MeS \rightleftharpoons Me + S$ 3.11c

RATE EXPRESSION

At equilibrium the rate of reaction, r = 0

$$r_1 = K_1 C_I C_S - K_2 C_{IS} \quad \text{..........} 3.12c$$

$$r_2 = K_3 C_{H2} C_S - K_4 C_{H2S} = 0$$

$$C_{H2} = \frac{C_{H2S}}{K_b C_S} \quad \text{..........} 3.13c$$

$$r_3 = K_5 C_{IS} C_S - K_6 C_{MCHS} C_{H2S} = 0$$

$$IS = \frac{C_{MCHS} C_{H2S}}{K_C C_S} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.14c$$

$$r_4 = K_7 C_{MCHS} C_S^3 - K_8 C_{TS} C_{H2S}^3 = 0$$

$$C_{MCHS} = \frac{C_{TS} C_{H2S}^3}{K_d C_S^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.15c$$

$$r_5 = K_9 C_{TS} C_{H2S} - K_{10} C_{BS} C_{mes}$$

$$C_{TS} = \frac{C_{BS} C_{mes}}{K_e C_{H2S}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.16c$$

$$r_6 = K_{11} C_{IS} - K_{12} C_{PS} = 0$$

$$C_{IS} = \frac{C_{CPS}}{K_f} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.17c$$

$$r_7 = K_{13} C_{BS} - K_{14} C_B C_S = 0$$

$$C_{BS} = \frac{C_B C_S}{K_g} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.18c$$

$$r_8 = K_{15} C_{CPS} - K_{16} C_{CP} C_S = 0$$

$$C_{CPS} = \frac{C_{CP} C_S}{K_h} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.19c$$

$$r_9 = K_{17} C_{TS} - K_{18} C_T C_S$$

$$C_{TS} = \frac{C_T C_S}{K_i} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.20c$$

$$r_{10} = K_{19} C_{H2S} - K_{20} C_{H2} C_S$$

$$C_{H2S} = \frac{C_{H2} C_S}{K_j} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.21c$$

$$r_{11} = K_{21}C_{Mes} - K_{22}C_{Me}C_S$$

$$C_{Mes} = \frac{C_{ME}C_S}{K_K} \text{..} 3.22c$$

substitute 20c and 21c in 15c, then

$$C_{MCHS} = \frac{C_T C_{H2}^3 C_S}{K_d K_i K_j^3} \text{..} 3.23c$$

Site balance

$1 = S + IS + H_2S + MCHS + TS + BS + MeS + C_{PS}$

$$1 = C_S + \frac{C_{CPS}C_S}{K_f K_h} + \frac{C_{H2}C_S}{K_j} + \frac{C_T C_{H2}^3 C_S}{K_d K_i K_J^3} + \frac{C_T C_S}{K_i} + \frac{C_B C_S}{K_g} + \frac{C_{Me}C_S}{K_K} + \frac{C_{CP}C_S}{K_h} \text{......} 3.24c$$

$$C_S = \frac{1}{1 + \frac{C_{CP}}{K_f K_h} + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_d K_i K_j^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}} \text{..............................} 3.25c$$

From equation 12c

$$r_1 = \left[KC_I - \frac{K_2 C_{CP}}{K_f K_h} \right] C(S) \text{..} 3.26c$$

$$r_1 = \frac{K_1 C_1 - \frac{K_2 C_{CP}}{K_f K_h}}{1 + \frac{C_{cp}}{K_f K_h} + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_d K_i K_J^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}} \text{..............................} 3.27c$$

when r_2 is the rate controlling

$$r_2 = \left[K_3 C_{H2} - K_4 \frac{C_{H2}}{K_j} \right] C_S \text{..} 3.28c$$

$$r_2 = \frac{K_3 C_{H2} - \dfrac{K_4 C_{H2}}{K_j}}{1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_i K_d K_J^3} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.29c$$

r_3 as rate *controlling*

$$r_3 = \left[K_5 \frac{C_{CP}}{K_f K_h} - \frac{K_6 C_T C_{H2}^4}{K_d K_i K_J^4} \right] S^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.30c$$

$$r_3 = \frac{K_5 \dfrac{C_{CP}}{K_f K_h} - \dfrac{K_6 C_T C_{H2}^4}{K_d K_i K_j^4}}{1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_d K_i K_j^3} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.31c$$

r_4 as rate controlling

$$\mathrm{r}_4 = \frac{\dfrac{K_7 K_C K_j C_{CP}}{K_f K_h C_{H2}} - \dfrac{K_8 C_T C_{H2}^3}{K_i K_j^3}}{\left[1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}}{K_j} + \dfrac{K_a K_c K_J C_I}{C_{H2}} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h} \right]^4} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.32c$$

r_5 as rate *controlling*

$$r_5 = \left[\frac{K_9 C_I C_{H2}}{K_i K_j} - \frac{K_{10} C_B C_{me}}{K_g K_k} \right] S^2$$

$$r = \frac{\dfrac{K_9 C_I C_{H2}}{K_i K_j} - \dfrac{K_{10} C_B C_{me}}{K_g K_K}}{\left[1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_d K_i K_j^3} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h} \right]^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.33c$$

r_6 as the rate controlling

$$r_6 = \frac{K_{11}\left[\frac{K_g K_h C_T}{K_i C_B C_{me}}\right]^2 K_a K_d - \frac{K_{12} K_i}{C_T}\left[\frac{C_B C_{me}}{K_g K_h}\right]^2}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{K_a K_d K_g K_h C_I C_T}{K_i C_B C_{me}} + \left[\frac{K_g K_h C_T}{K_i C_B C_{me}}\right]^2 K_a K_d + \frac{C_B}{K_h} + \frac{C_T}{K_i}} \quad \text{.........} 3.39a$$

r7 as rate controlling

$$r_7 = K_{13} C_{TS} C_{H2} - K_{14} C_{BS} C_{me} \quad \text{..................................} 3.40a$$

$$r_7 = \frac{K_{13}\left[\frac{C_T}{K_i}\right]^{\frac{3}{4}} \left[K_a K_d K_e K_f C_I\right]^{\frac{1}{4}} - K_{14}\frac{C_B C_{me}}{K_h}}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{\left[K_a K_d C_I\right]^{\frac{3}{4}} C_T^{\frac{1}{4}}}{\left[K_e K_f K_i\right]^{\frac{1}{4}}} + \left[\frac{K_a K_d K_e C_I}{K_I K_f}\right]^{\frac{1}{2}} + \frac{C_B}{K_h} + \frac{C_T}{K_i}} \quad \text{.....................} 3.41a$$

r_8 as rate controlling

$$r_8 = K_{15} C_{BS} - K_{16} C_B C_S \quad \text{...} 3.42a$$

$$r_8 = \frac{\dfrac{K_{15} K_g \left[K_a K_d K_e K_f C_I\right]^{\frac{1}{4}} C_T^{\frac{3}{4}} - K_{16} C_B}{K_i^{\frac{3}{4}} C_{me}}}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \frac{\left[K_a K_d C_I\right]^{\frac{3}{4}} C_T^{\frac{1}{4}}}{\left[K_i K_e K_f\right]^{\frac{1}{4}}} + \left[\frac{K_a K_d K_f C_T}{K_f K_i}\right]^{\frac{1}{2}} + \frac{\left[K_a K_d K_e K_f C_I\right]^{\frac{1}{4}}}{K_i^{\frac{3}{4}} C_{me}}}$$

$$\frac{1}{K_g T^{\frac{3}{4}} + \frac{C_T}{K_1}} \quad \text{..} 3.43a$$

where r_9 is the rate controlling

$$r_9 = \frac{K_{17}\left[\frac{C_B C_{me}}{K_g K_h}\right]^{\frac{4}{3}} - K_{18} C_T}{1 + K_a C_I + \frac{C_{CP}}{K_C} + \left[\frac{C_B C_{me}}{K_e K_f K_g K_h}\right]^{\frac{1}{3}} \left[K_a K_I C_I\right]^{\frac{2}{3}} + \left[\frac{C_B C_{me}}{K_f K_g K_h}\right]^{\frac{2}{3}} \left[K_a K_d K_e I\right]^{\frac{1}{3}} +}$$

$$\frac{1}{\frac{C_B}{K_h}} \quad \text{..} 3.44a$$

$$r_6 = \left[K_{11}K_aC_I - \frac{K_{12}C_{CP}}{K_h}\right]C_S \ldots\ldots\ldots 3.34c$$

$$r_6 = \frac{K_{11}K_aC_I - \frac{K_{12}C_{CP}}{K_h}}{1 + K_aC_I + \frac{C_{H2}}{K_J} + \frac{C_T C_{H2}^3}{K_dK_iK_j^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}} \ldots\ldots\ldots 3.35c$$

r_7 as rate controlling

$$r_7 = \left[\frac{K_{13}K_eK_KC_TC_{H2}}{K_iK_jC_{me}} - K_{14}C_B\right]C_S \ldots\ldots\ldots 3.36c$$

$$r_7 = \frac{\frac{K_{13}K_eK_KC_TC_{H2}}{K_iK_jC_{me}} - K_{14}C_B}{1 + K_aC_I + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_dK_iK_j^3} + \frac{C_T}{K_i} + \frac{K_eK_kC_TC_{H2}}{K_iK_jC_{me}} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}} \ldots\ldots\ldots 3.37c$$

r_8 as rate controlling

$$r_8 = \left[K_{15}K_fK_aC_I - K_{16}C_{CP}\right]C_S \ldots\ldots\ldots 3.38c$$

r_9 as rate controlling

$$r_9 = \left[\frac{K_{17}K_jC_BC_{me}}{K_eK_gK_kC_{H2}} - K_{18}C_T\right]C_S \ldots\ldots\ldots 3.40c$$

$$r_9 = \frac{\frac{K_{17}K_jC_BC_{me}}{K_eK_gK_KC_{H2}} - K_{18}C_T}{1 + K_aC_I + \frac{C_{H2}}{K_j} + \frac{K_aK_cK_jC_I}{C_{H2}} + \frac{K_jC_BC_{me}}{K_eK_gK_KC_{H2}} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}} \ldots\ldots\ldots 3.41c$$

r_{10} as rate contrlling

$$r_{10} = \left[K_{19}K_bC_{H2} - K_{20}C_{H2}\right]C_S \ldots\ldots\ldots 3.42c$$

$$r_{10} = \frac{K_{19}K_bC_{H2} - K_{20}C_{H2}}{1 + K_aC_I + \frac{C_{H2}}{K_j} + \frac{K_aK_cC_I}{K_bC_{H2}} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{CP}}{K_h} + \frac{C_{me}}{K_K}} \quad \text{..............................3.43c}$$

r_{11} as rate controlling

$$\mathrm{r}_{11} = \left[\frac{K_{21}K_eK_gC_{H2}C_Y}{K_iK_jC_B} - K_{22}C_{me}\right]C_S \quad \text{..............................3.44c}$$

$$r_{11} = \frac{\frac{K_{21}K_eK_gC_{H2}C_T}{K_iK_j} - K_{22}C_{me}}{1 + K_aC_I + \frac{C_{H2}}{K_j} + \frac{K_aK_cK_jC_I}{C_{H2}} + \frac{C_B}{K_g} + \frac{C_T}{K_i} + \frac{K_eK_gC_HC_T}{K_iK_jC_B} + \frac{C_{CP}}{K_h}} \quad \text{............3.45c}$$

Table 8: Reaction rate model for scheme 3

$$r_1 = \frac{K_1 C_I - \frac{K_2 C_{CP}}{K_f K_h}}{1 + \frac{C_{CP}}{K_f K_h} + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_d K_i K_j^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}}$$

$$r_2 = \frac{K_3 C_{H2} - \frac{K_4 C_{H2}}{K_j}}{1 + \frac{C_{CP}}{K_f K_h} + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_i K_d K_j^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}}$$

$$r_3 = \frac{\frac{K_5 C_{CP}}{K_f K_h} - \frac{K_6 C_T C_{H2}^4}{K_d K_i K_j^4}}{1 + \frac{C_{CP}}{K_f K_h} + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_d K_i K_j^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}}$$

$$r_4 = \frac{\frac{K_7 K_c K_j C_{CP}}{K_f K_h C_{H2}} \quad \frac{K_8 C_T C_{H2}^3}{K_i K_j^3}}{\left[1 + \frac{C_{CP}}{K_f K_h} + \frac{C_{H2}}{K_j} + \frac{K_a K_c K_j C_I}{C_{H2}} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}\right]^4}$$

$$r_5 = \frac{\frac{K_9 C_I C_{H2}}{K_i K_j} - \frac{K_{10} C_B C_{me}}{K_g K_K}}{1 + \frac{C_{CP}}{K_f K_h} + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_d K_i K_j^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}}$$

$$r_6 = \frac{K_{11} K_a C_I - \frac{K_{12} C_{CP}}{K_h}}{1 + K_a C_I + \frac{C_{H2}}{K_j} + \frac{C_T C_{H2}^3}{K_d K_i K_j^3} + \frac{C_T}{K_i} + \frac{C_B}{K_g} + \frac{C_{me}}{K_K} + \frac{C_{CP}}{K_h}}$$

$$r_7 = \frac{\dfrac{K_{13}K_eK_KC_TC_{H2}}{K_iK_jC_{me}} - K_{14}C_B}{1 + K_aC_I + \dfrac{C_{H2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_dK_i K_j^3} + \dfrac{C_T}{K_i} + \dfrac{K_eK_KC_TC_{H2}}{K_iK_jC_{me}} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}}$$

$$r_8 = \frac{K_{15}K_fK_aC_i - K_{16}C_{CP}}{1 + K_aC_i + \dfrac{C_{H2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_iK_d K_j^3} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + K_fK_aC_I}$$

$$r_9 = \frac{\dfrac{K_{17}K_jC_BC_{me}}{K_eK_gK_KC_{H2}} - K_{18}C_T}{1 + K_aC_I + \dfrac{C_{H2}}{K_j} + \dfrac{K_jC_BC_{me}}{K_iK_d K_j^3} + \dfrac{C_{CP}}{K_h} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{K_aK_CK_jC_I}{C_{H2}}}$$

$$r_{10} = \frac{K_{19}K_bC_{H2} - K_{20}C_{H2}}{1 + K_aC_I + \dfrac{C_{H2}}{K_j} + \dfrac{K_aK_CC_I}{K_bC_{H2}} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_K}}$$

$$r_{11} = \frac{\dfrac{K_{21}K_eK_gC_{H2}C_T}{K_iK_jC_B} - K_{22}C_{me}}{1 + K_aC_I + \dfrac{C_{H2}}{K_j} + \dfrac{K_aK_CK_jC_I}{C_{H2}} + \dfrac{C_B}{K_g} + \dfrac{C_T}{K_i} + \dfrac{K_eK_gC_HC_T}{K_iK_jC_B} + \dfrac{C_{CP}}{K_h}}$$

3.2.4 Scheme four (4)

In this scheme hydrogen is absorbed dissociatively on the catalyst surface.

ADSORPTION

$I + S \rightleftharpoons IS$ ……………………….3.01d

$\frac{1}{2} H_2 + S \rightleftharpoons HS$ ……………………….3.02d

REACTION

$IS + 2S \rightleftharpoons 2HS + MCHS$ ……………….3.03d

$MCHS + 6S \rightleftharpoons TS + 6HS$ …………………..3.04d

$TS + 2HS \rightleftharpoons BS + MeS$ …………………..3.05d

IS $\rightleftharpoons$ CS ……………………………3.06d

DESORPTION

BS $\rightleftharpoons$ B + S …………………………3.07d

CPS $\rightleftharpoons$ CP + S ………………………3.08d

TS $\rightleftharpoons$ T + S …………………………3.09d

HS $\rightleftharpoons$ 1/2H2 + S ……………………3.10d

MeS $\rightleftharpoons$ Me + S ………………………3.11d

RATE EXPRESSION

Using rate one (r1) as rate controlling step, other steps are at equilibrium.

$$r_1 = K_1 C_I C_S - K_2 C_{IS} \quad\ldots\ldots\ldots 3.12d$$

$$r_2 = K_3 C_{H2}^{\frac{1}{2}} C_S - K_4 C_{HS} = 0$$

$$C_{HS} = K_b C_{H2}^{1/2} C_S \quad\ldots\ldots\ldots 3.13d$$

$$r_3 = K_5 C_{IS} C_S{}^2 - K_6 C_{HS}^2 C_{MCHS} = 0$$

$$C_{IS} = \frac{C_{HS}^2 C_{MCHS}}{K_C C_S^2} \quad\ldots\ldots\ldots 3.14d$$

$$r_4 = K_7 C_{MCHS} C_S^6 - K_8 C_{TS} C_{HS}^6 = 0$$

$$MCHS = \frac{C_{TS} C_{HS}^6}{K_d C_S^6} \quad\ldots\ldots\ldots 3.15d$$

$$r_5 = K_9 C_{TS} C_{HS}^2 - K_{10} C_{BS} C_{mes} = 0$$

$$C_{TS} = \frac{C_{BS} C_{mes}}{K_e C_{HS}^2} \quad\ldots\ldots\ldots 3.16d$$

$$r_6 = K_{11}C_{IS} - K_{12}C_{CPS} = 0$$

$$C_{IS} = \frac{C_{CPS}}{K_f} \tag{3.17d}$$

$$r_7 = K_{13}C_{BS} - K_{14}C_B C_S = 0$$

$$C_{BS} = \frac{C_B C_S}{K_g} \tag{3.18d}$$

$$r_8 = K_{15}C_{PS} - K_{16}C_{CP}C_S = 0$$

$$C_{CPS} = \frac{C_{CP}C_S}{K_h} \tag{3.19d}$$

$$r_9 = K_{17}C_{TS} - K_{18}C_T C_S = 0$$

$$C_{TS} = \frac{C_T C_S}{K_i} \tag{3.20d}$$

$$r_{10} = K_{19}C_{HS} - K_{20}\,C_{H2}^{1/2}C_S = 0$$

$$C_{HS} = \frac{C_{H2}^{1/2}C_S}{K_j} \tag{3.21d}$$

$$r_{11} = K_{21}C_{Mes} - K_{22}C_{me}C_S = 0$$

$$C_{mes} = \frac{C_{me}C_S}{K_K} \tag{3.22d}$$

Substituting equations 3.20d and 3.21d in 3.15d, we have

$$C_{MCHS} = \frac{C_T\,C_{H2}^{3}C_S}{K_d K_i\,K_j^{6}} \tag{3.23d}$$

also substituting equation 3.19d in 3.17d, we have

$$C_{IS} = \frac{C_{CP}C_S}{K_f K_h} \dots\dots\dots 3.24d$$

Site balance

$$1 = \mathrm{S} + \mathrm{IS} + \mathrm{HS} + \mathrm{MCHS} + \mathrm{BS} + \mathrm{TS} + \mathrm{M_e}S + CpS$$

$$1 = C_S + \frac{C_{CP}C_S}{K_f K_h} + \frac{C_{H2}^{1/2}C_S}{K_j} + \frac{C_T C_{H2}^{3} C_S}{K_d K_i K_j^{6}} + \frac{C_B C_S}{K_g} + \frac{C_T C_S}{K_i} + \frac{C_{me}C_S}{K_K} + \frac{C_{CP}C_S}{K_h} \dots 3.25d$$

From 1d

$$\mathrm{r}_1 = K_1 C_1 C_S - K_2 C_{IS}$$

$$r_1 = \left[K_1 C_I - \frac{K_2 C_{CP}}{K_f K_h} \right] C_S \dots\dots\dots 3.26d$$

$$r_1 = \frac{K_1 C_I - \dfrac{K_2 C_{CP}}{K_f K_h}}{1 + \dfrac{C_{CP}}{K_h K_f} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_T C_{H2}^{3}}{K_d K_i K_j^{6}} + \dfrac{C_B}{K_g} + \dfrac{C_T}{K_i} + \dfrac{C_{Me}}{K_K} + \dfrac{C_{CP}}{K_h}} \dots\dots\dots 3.27d$$

r_2 as rate controlling

$$\mathrm{r}_2 = \frac{K_3 C_{H2}^{1/2} - \dfrac{K_4 C_{H2}^{1/2}}{K_j}}{1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_T C_{H2}^{3}}{K_d K_i K_j^{6}} + \dfrac{C_B}{K_g} + \dfrac{C_T}{K_i} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}} \dots\dots\dots 3.28d$$

when r_3 *is the* rate cntrolling step

$$r_3 = \left[K_5 K_a C_I - \frac{K_6 C_{H2}^{4} C_T}{K_d K_i K_j^{8}} \right] C_S^{3} \dots\dots\dots 3.29d$$

$$r_3 = \frac{K_5 K_a C_I - \dfrac{K_6 C_{H2}^4 C_T}{K_d K_i K_j^8}}{\left[1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_d K_i K_j^6} + \dfrac{C_B}{K_g} + \dfrac{C_T}{K_i} + \dfrac{C_{me}}{K_K} + \dfrac{C_P}{K_h}\right]^3} \ldots\ldots\ldots\ldots 3.30d$$

using r_4 as the rate contrlling

$$r_4 = \frac{\dfrac{K_7 K_C K_j^2 C_{CP}}{K_f K_h C_{H2}} - \dfrac{K_8 C_T C_{H2}^3}{K_i K_j^6}}{\left[1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{K_C K_j^2 C_{CP}}{K_f K_h C_{H2}} + \dfrac{C_B}{K_g} + \dfrac{C_T}{K_i} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}\right]^7} \ldots\ldots\ldots\ldots 3.32d$$

When r_5 is used as the rate controlling step

$$r_5 = \left[\frac{K_9 C_T \quad C_{H2}}{K_i K_j^2} - \frac{K_{10} C_B C_{me}}{K_g K_K}\right] CS^2 \ldots\ldots\ldots\ldots 3.33d$$

$$r_5 = \frac{\dfrac{K_9 C_T C_{H2}}{K_i K_j^2} - \dfrac{K_{10} C_B C_{me}}{K_g K_K}}{\left[1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{K_C K_j^2 C_{CP}}{K_f K_h C_{H2}} + \dfrac{C_B}{K_g} + \dfrac{C_T}{K_i} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}\right]^2} \ldots\ldots\ldots\ldots 3.34d$$

when r_6 is used as the rate controlling

$$r_6 = \left[\frac{K_{11} C_{H2}^4 C_T}{K_C K_d K_i K_j^8} - \frac{K_{12} C_{CP}}{K_h}\right] C_S \ldots\ldots\ldots\ldots 3.35d$$

$$r_6 = \frac{\dfrac{K_{11} C_{H2}^4 C_T}{K_C K_d K_i K_j^8} - \dfrac{K_{12} C_{CP}}{K_h}}{1 + \dfrac{C_{H2}^4 C_T}{K_C K_d K_i K_j^8} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_{H2}^3 C_T}{K_d K_i K_j^6} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}} \ldots\ldots\ldots\ldots 3.36d$$

r_7 as rate controlling

$$r_7 = \left[\frac{K_{13}K_e K_K C_{H2} C_T}{K_i K_j^2 C_{me}} - K_{14} C_B\right] C_S \qquad \text{.......... } 3.37d$$

$$r_7 = \frac{\dfrac{K_{13}K_e K_K C_{H2} C_T}{K_i K_j^2 C_{me}} - K_{14} C_B}{1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_d K_i K_j^6} + \dfrac{C_T}{K_i} + \dfrac{K_e K_K C_{H2} C_T}{K_i K_j^2 C_{me}} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}} \qquad \text{.......... } 3.38d$$

r_8 as the rate controlling

$$r_8 = \left[\frac{K_{15}K_f C_T C_{H2}^4}{K_C K_d K_i K_j^8} - K_{16} C_{CP}\right] C_S \qquad \text{.......... } 3.39d$$

$$r_8 = \frac{\dfrac{K_{15}K_f C_T C_{H2}^4}{K_C K_d K_i K_j^8} - K_{16} C_{CP}}{1 + \dfrac{C_T C_{H2}^4}{K_C K_d K_i K_j^8} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_d K_i K_j^6} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{K_f C_T C_{H2}^4}{K_C K_d K_i K_j^8}} \qquad \text{.......... } 3.40d$$

when r_9 is the rate cntrolling step

$$r_9 = \frac{\dfrac{K_{17}K_j C_B C_{me}}{K_e K_g K_K C_{H2}} - K_{18} C_T}{1 + K_a C_I + \dfrac{C_{H2}}{K_j} + \dfrac{K_a K_C K_j C_I}{C_{H2}} + \dfrac{K_j C_B C_{me}}{K_e K_g K_K C_{H2}} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}} \qquad \text{.......... } 3.41d$$

when r_{10} *is* the rate controlling step,

$$r_{10} = \left[K_{19} K_b C_{H2} - K_{20} H2 C_{H2}\right] C_S \qquad \text{.......... } 3.42d$$

$$r_{10} = \frac{K_{19} K_b C_{H2} - K_{20} C_{H2}}{1 + K_a C_I + \dfrac{C_{H2}}{K_j} + \dfrac{K_a K_C C_I}{K_b C_{H2}} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_K}} \qquad \text{.......... } 3.43d$$

when r_{11} is the rate controlling step,

$$r_{11} = \left[\frac{K_{21}K_e K_g C_{H2} C_T}{K_j K_i C_B} - K_{22} C_{me}\right] C_S \qquad \text{.......... } 3.44d$$

$$r_{11}=\frac{\dfrac{K_{21}K_eK_gC_{H2}C_T}{K_jK_iC_B}-K_{22}C_{me}}{1+K_aC_I+\dfrac{C_{H2}}{K_j}+\dfrac{K_aK_CK_jC_I}{C_{H2}}+\dfrac{C_B}{K_g}+\dfrac{C_T}{K_i}+\dfrac{K_eK_gC_HC_T}{K_iK_jC_B}+\dfrac{C_{CP}}{K_h}}\quad\ldots\ldots\ldots\ldots\ldots\ldots 3.45d$$

Table 9: Reaction rate models for scheme 4

$$r_1=\frac{K_1C_I-\dfrac{K_2C_{CP}}{K_fK_h}}{1+\dfrac{C_{CP}}{K_hK_f}+\dfrac{C_{H2}^{1/2}}{K_j}+\dfrac{C_TC_{H2}^3}{K_dK_iK_j^6}+\dfrac{C_B}{K_g}+\dfrac{C_T}{K_i}+\dfrac{C_{me}}{K_K}+\dfrac{C_{CP}}{K_h}}$$

$$r_2=\frac{K_3C_{H2}^{1/2}-\dfrac{K_4C_{H2}^{1/2}}{K_j}}{1+\dfrac{C_{CP}}{K_fK_h}+\dfrac{C_{H2}^{1/2}}{K_j}+\dfrac{C_TC_{H2}^3}{K_dK_iK_j}+\dfrac{C_B}{K_g}+\dfrac{C_T}{K_i}+\dfrac{C_{Me}}{K_K}}$$

$$r_3=\frac{K_5K_aC_I-\dfrac{K_6C_{H2}^4C_T}{K_dK_iK_j^8}}{\left[1+\dfrac{C_{CP}}{K_fK_h}+\dfrac{C_{H2}^{1/2}}{K_j}+\dfrac{C_TC_{H2}^3}{K_dK_iK_j^6}+\dfrac{C_B}{K_g}+\dfrac{C_T}{K_i}+\dfrac{C_{me}}{K_K}\right]^3}$$

$$r_4=\frac{\dfrac{K_7K_CK_j^2C_{CP}}{K_fK_hC_{H2}}-\dfrac{K_8C_TC_{H2}^3}{K_iK_j^6}}{\left[1+\dfrac{C_{CP}}{K_fK_h}+\dfrac{C_{H2}^{1/2}}{K_j}+\dfrac{K_CK_j^2C_{CP}}{K_fK_hC_{H2}}+\dfrac{C_B}{K_g}+\dfrac{C_T}{K_i}+\dfrac{C_{me}}{K_k}\right]^7}$$

$$r_5=\frac{\dfrac{K_9C_TC_{H2}}{K_iK_j^2}-\dfrac{K_{10}C_BC_{me}}{K_gK_K}}{\left[1+\dfrac{C_{CP}}{K_fK_h}+\dfrac{C_{H2}^{1/2}}{K_j}+\dfrac{K_CK_j^2C_{CP}}{K_fK_hC_{H2}}+\dfrac{C_B}{K_g}+\dfrac{C_T}{K_i}+\dfrac{C_{me}}{K_K}\right]^2}$$

$$r_6 = \frac{\dfrac{K_{11}C_{H2}^4 C_T}{K_C K_d K_i K_j^8} - \dfrac{K_{12}C_{CP}}{K_h}}{1 + \dfrac{C_{H2}^4 C_T}{K_C K_d K_i K_j^8} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_{H2}^3 C_T}{K_d K_i K_j^6} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K}}$$

$$r_7 = \frac{\dfrac{K_{13}K_e K_K C_{H2} C_T}{K_i K_j^2 C_{me}} - K_{14}C_B}{1 + \dfrac{C_{CP}}{K_f K_h} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_d K_i K_j^6} + \dfrac{C_T}{K_i} + \dfrac{K_e K_k C_{H2} C_T}{K_i K_j^2 C_{me}} + \dfrac{C_{me}}{K_K}}$$

$$r_8 = \frac{\dfrac{K_{15}K_f C_T C_{H2}^4}{K_C K_d K_i K_j^8} - K_{16}C_{CP}}{1 + \dfrac{C_T C_{H2}^4}{K_C K_d K_i K_j^8} + \dfrac{C_{H2}^{1/2}}{K_j} + \dfrac{C_T C_{H2}^3}{K_d K_i K_j^6} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K}}$$

$$r_9 = \frac{\dfrac{K_{17}K_j C_B C_{me}}{K_e K_g K_k C_{H2}} - K_{18}C_T}{1 + K_a C_I + \dfrac{C_{H2}}{K_j} + \dfrac{K_a K_c K_j C_I}{C_{H2}} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_K} + \dfrac{C_{CP}}{K_h}}$$

$$r_{10} = \frac{K_{19}C_b C_{H2} - K_{20}C_{H2}}{1 + K_a C_I + \dfrac{C_{H2}}{K_j} + \dfrac{C_T}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_k}}$$

$$r_{11} = \frac{\dfrac{K_{21}K_e K_g C_{H2} C_I}{K_j K_i C_B} - K_{22}C_{me}}{1 + K_a C_I + \dfrac{C_{H2}}{K_j} + \dfrac{C_B}{K_i} + \dfrac{K_e K_g C_{H2} C_T}{K_i K_j C_B} + \dfrac{C_{CP}}{K_h}}$$

3.2.5 Scheme 5

In this scheme hydrogen was not absorbed but there was no production Methyl cyclohexane (MCH).

ADSORPTION

$$I + S \rightleftharpoons IS \quad \text{.................................} 3.01e$$

REACTION

IS $\rightleftharpoons$ CPS ……………………………3.02e

IS $\rightleftharpoons$ TS + 4H2 ………………………3.03e

TS + H2 $\rightleftharpoons$ BS + Me ………………………3.04e

DESORPTION

TS $\rightleftharpoons$ T + S …………………………….3.05e

BS $\rightleftharpoons$ B + S ……………………………3.06e

CPS $\rightleftharpoons$ CP + S …………………………3.07e

RATE EXPRESSION

When r1 is the rate controlling step other rates are at equilibrium.

$r_1 = K_1 C_I C_S - K_2 C_{IS}$ ……………………………………………………………3.08e

$r_2 = K_3 C_{IS} - K_4 C_{CPS} = 0$ ……………………………………………………3.09e

$$C_{IS} = \frac{C_{CPS}}{K_b}$$

$r_3 = K_5 C_{IS} - K_6 C_{TS} C_{H2}^4 = 0$ ……………………………………………3.10e

$$C_{IS} = \frac{C_{TS} C_{H2}^2}{K_C}$$

$$r_4 = K_7 C_{TS} C_{H2} - K_8 C_{BS} C_{me} = 0$$

$T_S = \dfrac{C_{BS} C_{me}}{K_d C_{H2}}$ ……………………………………………………3.11e

$$r_5 = K_9 C_{TS} - K_{10} C_T C_S = 0$$

$C_{TS} = \dfrac{C_T C_S}{K_e}$ ……………………………………………………………3.12e

$$r_6 = K_{11} C_{BS} - K_{12} C_B C_S = 0$$

$$C_{BS} = \frac{C_B C_S}{K_f} \ldots\ldots\ldots\ldots 3.13e$$

$$r_7 = K_{13} C_{CPS} - K_{14} C_{CP} C_S = 0$$

$$C_{CPS} = \frac{C_{CP} C_S}{K_g} \ldots\ldots\ldots\ldots 3.14e$$

substituting equation 3.14e in 3.09e, we have

$$\mathrm{C_{IS}} = \frac{C_{CP} C_S}{K_b K_g} \ldots\ldots\ldots\ldots 3.15e$$

SITE BALANCE

$$1 = \mathrm{S + IS + TS + BS + CPS}$$

$$1 = CS + \frac{C_{CP} C_S}{K_b K_g} + \frac{C_T C_S}{K_b K_g} + \frac{C_T C_S}{K_e} + \frac{C_B C_S}{K_f} + \frac{C_{CP} C_S}{K_g} \ldots\ldots\ldots\ldots 3.16e$$

$$C_S = \frac{1}{1 + \frac{C_{CP}}{K_b K_g} + \frac{C_T}{K_e} + \frac{C_B}{K_f} + \frac{C_{CP}}{K_g}} \ldots\ldots\ldots\ldots 3.17e$$

From 8e,

$$\mathrm{r}_1 = K_1 C_I C_S - K_2 C_{IS} \ldots\ldots\ldots\ldots 3.18e$$

$$r_1 = \left[K_1 C_I - \frac{K_2 C_{CP}}{K_b K_g} \right] C_S \ldots\ldots\ldots\ldots 3.19e$$

$$r_1 = \frac{K_1 C_I - K_2 \frac{C_{CP}}{K_b K_g}}{1 + \frac{C_P}{K_b K_g} + \frac{C_T}{K_e} + \frac{C_B}{K_f} + \frac{C_{CP}}{K_g}} \ldots\ldots\ldots\ldots 3.20e$$

When r_2 is the rate controlling

$$r_2 = \frac{\dfrac{K_3 C_T C_{H2}^4}{K_C K_e} - \dfrac{K_4 C_{CP}}{K_g}}{1 + \dfrac{C_T C_{H2}^4}{K_C K_e} + \dfrac{C_T}{K_e} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}} \qquad \text{3.21e}$$

when r_3 is the rate controlling

$$r_3 = \left[K_5 C_{IS} - K_6 C_{TS} C_{H2}^4\right] C_S \qquad \text{3.22e}$$

$$r_3 = \frac{\dfrac{K_5 C_{CP}}{K_b K_g} - K_6 \dfrac{C_T C_{H2}^4}{K_e}}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_T}{K_e} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}} \qquad \text{3.23e}$$

when r_4 is the rate controlling

$$r_4 = \frac{\dfrac{K_7 C_T C_{H2}}{K_e} - \dfrac{K_8 C_B C_{me}}{K_f}}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_T}{K_e} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}} \qquad \text{3.24e}$$

when r_5 is the rate controlling

$$r_5 = \frac{\dfrac{K_9 C_B C_{me}}{K_d K_f C_{H2}} - K_{10} C_T}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_B C_{me}}{K_d K_f C_{H2}} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}} \qquad \text{3.25e}$$

r_6 *as* the rate controlling step

$$r_6 = \frac{\dfrac{K_{11} K_d C_{H2} C_T}{K_e C_{me}} - K_{12} C_B}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_T}{K_e} + \dfrac{K_d C_{H2} C_T}{K_e C_{me}} + \dfrac{C_{CP}}{K_g}} \qquad \text{3.26e}$$

when r_7 acts as the rate controlling, then

$$r_7 = \frac{\dfrac{K_{13}C_B C_T C_{H2}}{K_C K_e} - K_{14}C_{CP}}{1 + \dfrac{C_T C_{H2}^4}{K_C K_e} + \dfrac{C_T}{K_e} + \dfrac{C_B}{K_g} + \dfrac{K_6 C_T C_{H2}^4}{K_C K_e}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.27e$$

Table 3.5: Reaction rate models for scheme 5

$$r_1 = \frac{K_1 C_T - \dfrac{K_2 C_{CP}}{K_b K_g}}{1 + \dfrac{C_P}{K_b K_g} + \dfrac{C_T}{K_e} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}}$$

$$r_2 = \frac{\dfrac{K_3 C_T C_{H2}^4}{K_C K_e} - \dfrac{K_4 C_C}{K_g}}{1 + \dfrac{C_T C_{H2}^4}{K_C K_e} + \dfrac{C_T}{K_e} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}}$$

$$r_3 = \frac{\dfrac{K_5 C_{CP}}{K_b K_g} - \dfrac{K_6 C_T C_{H2}^4}{K_c}}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_T}{K_c} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}}$$

$$r_4 = \frac{\dfrac{K_7 C_T C_{H2}}{K_e} - \dfrac{K_8 C_B C_{me}}{K_f}}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_T}{K_e} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}}$$

$$r_5 = \frac{\dfrac{K_9 C_B C_{me}}{K_d K_f C_{H2}} - K_{10} C_T}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_B C_{me}}{K_d K_f C_{H2}} + \dfrac{C_B}{K_f} + \dfrac{C_{CP}}{K_g}}$$

$$r_6 = \frac{\dfrac{K_{11} K_d C_{H2}}{K_e C_{me}} - K_{12} C_B}{1 + \dfrac{C_{CP}}{K_b K_g} + \dfrac{C_T}{K_e} + \dfrac{K_d C_{H2} C_T}{K_e C_{me}} + \dfrac{C_{CP}}{K_g}}$$

$$r_7 = \frac{\frac{K_{13}K_6C_TC_{H2}}{K_CK_e} - K_{14}C_{CP}}{1 + \frac{C_TC_{H2}^4}{K_CK_e} + \frac{C_T}{K_e} + \frac{C_B}{K_g} + \frac{K_6C_TC_{H2}^4}{K_CK_F}}$$

3.2.6 Scheme 6

In this scheme, hydrogen was absorbed as a molecular species but there was no production of methyl cyclohexane (MCH).

ADSORPTION

$I + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} IS$ 3.01f

$H2 + S \underset{K_4}{\overset{K_3}{\rightleftharpoons}} H2S$ 3.02f

REACTION

$IS + 4S \underset{K_6}{\overset{K_5}{\rightleftharpoons}} TS + 4H2S$ 3.03f

$TS + H2S \underset{K_8}{\overset{K_7}{\rightleftharpoons}} BS + MeS$ 3.04f

$IS \underset{K_{10}}{\overset{K_9}{\rightleftharpoons}} CPS$ 3.05f

DESORPTION

$TS \underset{K_{12}}{\overset{K_{11}}{\rightleftharpoons}} T + S$ 3.06f

$BS \underset{K_{14}}{\overset{K_{13}}{\rightleftharpoons}} B + S$ 3.07f

$CPS \underset{K_{16}}{\overset{K_{15}}{\rightleftharpoons}} CP + S$ 3.08f

$H2S \underset{K_{18}}{\overset{K_{17}}{\rightleftharpoons}} H2 + S$ 3.09f

$MeS \underset{K_{20}}{\overset{K_{19}}{\rightleftharpoons}} Me + S$ 3.10f

RATE EXPRESSION

When r1 is the rate controlling step, other rates are at equilibrium.

$r1 = K1CICS - K_2CIS$ 3.11f

$r_2 = K_3C_{H2}C_S - K_4C_{H2}S = 0$

$$C_{H2S} = K_b C_{H2} C_S \ldots\ldots\ldots\ldots 3.12f$$

$$r_3 = K_5 C_{IS} C_S^4 - K_6 C_{H2S}^4 C_{TS} = 0$$

$$C_{TS} = \frac{C_{H2S}^4 C_{TS}}{K_C C_S^4} \ldots\ldots\ldots\ldots 3.13f$$

$$r_4 = K_7 C_{TS} C_{H2S} - K_8 C_{BS} C_{mes} = 0$$

$$H_2S = \frac{C_{BS} C_{mes}}{K_d C_{TS}} \ldots\ldots\ldots\ldots 3.14f$$

$$r_5 = K_9 C_{IS} - K_{10} C_{CPS} = 0$$

$$C_{IS} = \frac{C_{CPS}}{K_E} \ldots\ldots\ldots\ldots 3.15f$$

$$r_6 = K_{11} C_{TS} - K_{12} C_T C_S = 0$$

$$C_{TS} = \frac{C_T C_S}{K_f} \ldots\ldots\ldots\ldots 3.16f$$

$$r_7 = K_{13} C_{BS} - K_{14} C_B C_S = 0$$

$$C_{BS} = \frac{C_B C_S}{K_g} \ldots\ldots\ldots\ldots 3.17f$$

$$r_8 = K_{15} C_{CPS} - K_{16} C_{CP} C_S = 0$$

$$C_{CPS} = \frac{C_{CP} C_S}{K_h} \ldots\ldots\ldots\ldots 3.18f$$

$$r_9 = K_{17} C_{H2S} - K_{18} C_{H2} C_S = 0$$

$$C_{H2S} = \frac{C_{H2} C_S}{K_i} \ldots\ldots\ldots\ldots 3.19f$$

$$r_{10} = K_{19} C_{mes} - K_{20} C_{me} C_S$$

$$C_{mes} = \frac{C_{me} C_S}{K_j} \ldots\ldots\ldots 3.20f$$

substituting 19f *in* 15f we have

$$C_{IS} = \frac{C_{CP} C_S}{K_e K_h} \ldots\ldots\ldots 3.21f$$

Site balance
$1 = S + IS + H_2S + TS + BS + CPS + MeS$

$$1 = C_S + \frac{C_{CP} C_S}{K_e K_h} + \frac{C_{H2} C_S}{K_i} + \frac{C_T C_S}{K_f} + \frac{C_B C_S}{K_g} + \frac{C_{CP} C_S}{K_h} + \frac{C_{me} C_S}{K_j}$$

From 11f, $r_1 = K_1 C_I C_S - K_2 C_S$

$$r_1 = \left[K_1 C_I - \frac{K_2 C_{CP}}{K_e K_h} \right] C_S \ldots\ldots\ldots 3.22f$$

$$r_1 = \frac{K_1 C_I - \dfrac{K_2 C_{CP}}{K_e K_h}}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}} \ldots\ldots\ldots 3.23f$$

when r_2 is the rate controlling

$$r_2 = \left[K_3 C_{H2} - K_4 \frac{C_{H2}}{K_i} \right] C_S \ldots\ldots\ldots 3.24f$$

$$r_2 = \frac{K_3 C_{H2} - \dfrac{K_4 C_{H2}}{K_i}}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}} \ldots\ldots\ldots 3.25f$$

When r3 is the rate controlling

$$r_3 = \left[\frac{K_5 C_{CP}}{K_e K_h} - \frac{K_6 C_{H2} C_T}{K_i K_f}\right] C_S^5 \quad \ldots\ldots 3.26f$$

$$r_3 = \frac{\dfrac{K_5 C_{CP}}{K_e K_h} - \dfrac{K_6 C_{H2} C_T}{K_i K_f}}{\left[1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}\right]^5} \quad \ldots\ldots 3.27f$$

r4 as the rate controlling, then

$$r_4 = \left[\frac{K_7 C_T C_{H2}}{K_f K_i} - \frac{K_8 C_B C_{me}}{K_g K_i}\right] C_S^2 \quad \ldots\ldots 3.28f$$

$$r_4 = \frac{\dfrac{K_7 C_T C_{H2}}{K_f K_i} - \dfrac{K_8 C_B C_{me}}{K_g K_i}}{\left[1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}\right]^2} \quad \ldots\ldots 3.29f$$

when r_5 is the rate contrlling, then

$$r_5 = \left[\frac{K_9 C_{H2}^4 C_T}{K_C K_i^4 K_f} - K_{10} \frac{C_{CP}}{K_h}\right] C_S \quad \ldots\ldots 3.30f$$

$$r_5 = \frac{\dfrac{K_9 C_{H2}^4 C_T}{K_C K_i^4 K_f} - K_{10} \dfrac{C_{CP}}{K_h}}{1 + \dfrac{C_{H2}^4 C_T}{K_C K_f K_i^4} + \dfrac{C_{H2}}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j} + \dfrac{C_T}{K_f}} \quad \ldots\ldots 3.31f$$

when r_6 is the rate controlling step, then

$$r_6 = \left[\frac{K_{11} K_i C_{me} C_B}{K_d K_g K_j C_{H2}} - K_{12} C_T\right] C_S \quad \ldots\ldots 3.32f$$

$$r_6 = \frac{\dfrac{K_{11}K_iC_{me}C_B}{K_dK_gK_jC_{H2}} - K_{12}C_T}{1 + \dfrac{C_{CP}}{K_eK_h} + \dfrac{C_{H2}}{K_i} + \dfrac{K_iC_{me}C_B}{K_dK_gK_jC_{H2}} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}} \cdots\cdots\cdots 3.33f$$

when r_7 is the rate controlling step

$$r_7 = \frac{\dfrac{K_{13}K_dK_JC_{H2}C_T}{K_iK_fC_{me}} - K_{14}C_B}{1 + \dfrac{C_{CP}}{K_eK_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{K_dK_jC_{H2}C_T}{K_iK_fC_{me}} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}} \cdots\cdots\cdots 3.34f$$

r_8 as the rate controlling step

$$r_8 = \left[\frac{K_{15}K_eC_{H2}^4C_T}{K_fK_i^4K_C} - K_{16}C_{CP}\right]C_S \cdots\cdots\cdots 3.35f$$

$$r_8 = \frac{\dfrac{K_{15}K_eC_{H2}^4C_T}{K_fK_i^4K_c} - K_{16}C_{CP}}{1 + \dfrac{C_{H2}^4C_T}{K_fK_i^4K_C} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{K_eC_{H2}^4C_T}{K_fK_i^4K_C} + \dfrac{C_{me}}{K_j}} \cdots\cdots\cdots 3.36f$$

When r_9 is the rate controlling

$$r_9 = \frac{\dfrac{K_{17}K_fC_BC_{me}}{K_dK_gK_jC_T} - K_{18}C_{H2}}{1 + \dfrac{C_{CP}}{K_eK_h} + \dfrac{K_fC_BC_{me}}{K_dK_gK_jC_T} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_P}{K_h} + \dfrac{C_{me}}{K_j}} \cdots\cdots\cdots 3.37f$$

when r_{10} is the rate controlling step, then

$$r_{10} = \frac{\dfrac{K_{19}K_dC_{H2}C_T}{K_iK_fC_B} - K_{20}C_{me}}{1 + \dfrac{C_{CP}}{K_eK_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{K_dC_TC_{H2}}{K_iK_fC_B}} \cdots\cdots\cdots 3.38f$$

Table 3.6: Reaction rate models for scheme 6

$$r_1 = \frac{K_1 C_T - \dfrac{K_2 C_{CP}}{K_e K_h}}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}}$$

$$r_2 = \frac{K_3 C_{H2} - \dfrac{K_4 C_{H2}}{K_i}}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{Me}}{K_j}}$$

$$r_3 = \frac{\dfrac{K_5 C_{CP}}{K_e K_h} - \dfrac{K_6 C_{H2} C_T}{K_i K_f}}{\left[1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{me}}{K_j}\right]^5}$$

$$r_4 = \frac{\dfrac{K_7 C_T C_{H2}}{K_f K_i} - \dfrac{K_8 C_B C_{me}}{K_g K_j}}{\left[1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{Me}}{K_j}\right]^2}$$

$$r_5 = \frac{\dfrac{K_{11} K_i C_{me} C_B}{K_d K_g K_j C_{H2}} - K_{12} C_T}{1 + \dfrac{C_{H2}^4 C_T}{K_C K_f K_i^4} + \dfrac{C_{H2}}{K_i} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j} + \dfrac{C_T}{K_f}}$$

$$r_6 = \frac{\dfrac{K_{11} K_i C_{me} C_B}{K_d K_g K_j C_{H2}} - K_{12} C_T}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{K_i C_{me} C_B}{K_d K_g K_j C_{H2}} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}}$$

$$r_7 = \frac{\dfrac{K_{13} K_d K_j C_{H2} C_T}{K_i K_f C_{me}} - K_{14} C_B}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{K_d K_j C_{H2} C_T}{K_i K_f C_{me}} + \dfrac{C_{CP}}{K_h} + \dfrac{C_{me}}{K_j}}$$

$$r_8 = \frac{\dfrac{K_{15}K_e C_{H2}^{4} C_T}{K_f K_i^{4} K_C} - K_{16}C_{CP}}{1 + \dfrac{C_{H2}^{4} C_T}{K_f K_i^{4} K_C} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_j} + \dfrac{C_{me}}{K_j}}$$

$$r_9 = \frac{\dfrac{K_{17}K_f C_B C_{me}}{K_d K_g K_j C_T} - K_{18}C_{H2}}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{K_f C_B C_{me}}{K_d K_g K_j C_T} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_P}{K_h} + \dfrac{C_{me}}{K_j}}$$

$$r_{10} = \frac{\dfrac{K_{19}K_d C_{H2} C_T}{K_i K_f C_B} - K_{20}C_{me}}{1 + \dfrac{C_{CP}}{K_e K_h} + \dfrac{C_{H2}}{K_i} + \dfrac{C_T}{K_f} + \dfrac{C_B}{K_g} + \dfrac{C_{CP}}{K_h} + \dfrac{K_d C_T C_{H2}}{K_i K_f C_B}}$$

3.30 Development of reaction mechanisms under Hydrogen

Two reaction mechanisms based on the following reaction network were considered under H2

3.3.1 Hydrogen is adsorbed as a molecular spices

ADSORPTION

$$I + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} IS$$

$$H2 + S \underset{K_4}{\overset{K_3}{\rightleftharpoons}} H2S$$

REACTION

$$IS \underset{K_6}{\overset{K_5}{\rightleftharpoons}} Me + HxS$$

$$HxS \underset{K_8}{\overset{K_7}{\rightleftharpoons}} Me + PtS$$

$$PtS + H2S \underset{K_{10}}{\overset{K_9}{\rightleftharpoons}} MeS + BtS$$

DESORPTION

$$\mathrm{MeS} \underset{K_{12}}{\overset{K_{11}}{\rightleftharpoons}} \mathrm{Me + S}$$

$$\mathrm{BtS} \underset{K_{14}}{\overset{K_{13}}{\rightleftharpoons}} \mathrm{Bt + S}$$

$$r_1 = K_1 C_I C_S - K_2 C_{IS}$$

$$r_2 = K_3 C_{H2} C_S - K_3 C_{H2S} = 0$$
$$C_{H2S} = K_b C_{H2} C_S$$

$$r_3 = K_5 C_{IS} - K_6 C_{me} C_{HXS} = 0$$

$$C_{IS} = \frac{C_{me} C_{HXS}}{K_C}$$

$$r_4 = K_7 C_{HXS} - K_8 C_{me} C_{PTS} = 0$$

$$C_{HXS} = \frac{C_{me} C_{pts}}{K_d}$$

$$r_5 = K_9 C_{pts} C_{H2S} - K_{10} C_{mes} C_{Bts} = 0$$

$$C_{PTS} = \frac{C_{mes} C_{Bts}}{K_e C_{H2S}}$$

$$r_6 = K_{11} C_{me} S - K_{12} C_{me} C_S = 0$$

$$C_{mes} = \frac{C_{me} C_S}{K_f}$$

$$r_7 = K_{13} C_{Bts} - K_{14} C_{Bt} C_S = 0$$

$$C_{Bts} = \frac{C_{Bt} C_S}{K_g}$$

$$r_8 = K_{15} C_{H2S} - K_{16} C_{H2} C_S = 0$$

$$C_{H2S} = \frac{C_{H2}C_S}{K_h}$$

substituting for C_{BtS}, H_2S and C_{mes} *in* r_5

$$C_{Pts} = \frac{C_{me}C_S}{K_f K_g K_e K_b}\frac{C_{Bt}C_S}{C_{H2}C_S} = \frac{C_{me}C_{Bt}C_S}{K_b K_e K_f K_g C_{H2}}.$$ substitute this into r_4

$$C_{HXS} = \frac{C_{me}C_{me}C_{Bt}C_S}{K_b K_d K_e K_f K_g C_{H2}} = \frac{C_{me}^2 C_{Bt}C_S}{K_b K_d K_e K_f K_g C_{H2}}$$

when H_{XS} is substituted in r_3

$$C_{IS} = \frac{C_{me}C_{me}^2 C_{Bt}C_S}{K_b K_d K_C K_f K_g C_{H2}} = \frac{C_{me}^3 C_{Bt}C_S}{K_b K_d K_c K_f K_g C_{H2}}$$

From r_1, we have that

$$r_1 = K_1 C_I C_S - K_2 C_{IS}$$

$$r_1 = K_1 C_I C_S - \frac{K_2 C_{me}^3 C_{Bt}C_S}{K_b K_d K_c K_f K_g C_{H2}}$$

site balance

$$1 = S + IS + M_eS + BtS + H_2S + P_tS + HxS$$

$$= C_S + \frac{C_{Me}C_S}{K_f} + \frac{C_{Bt}C_S}{K_g} + K_b C_{H2}C_S + \frac{C_{me}C_{Bt}C_S}{K_b K_e K_f K_g C_{H2}} + \frac{C_{me}^2 C_{Bt}C_S}{K_b K_d K_e K_f K_g C_{H2}} + \frac{C_{me}^3 C_{Bt}C_S}{K_b K_d K_c K_f K_g C_{H2}}$$

$$C_S = \frac{1}{1 + \frac{C_{me}}{K_f} + \frac{C_{Bt}}{K_g} + K_b C_{H2} + K_N C_N}$$

Table 3.7: Reaction rate models for scheme 1 (Hydrogen atmosphere)

$$r_1 = \frac{K_1 C_I - \dfrac{K_2 C_{me}^3 C_{Bt}}{K_b K_d K_c K_f K_g C_{H2}}}{1 + \dfrac{C_{me}}{K_f} + \dfrac{C_{Bt}}{K_g} + K_b C_{H2} + K_N C_N}$$

other rates follow the same pattern

$$r_2 = \frac{K_3 C_{H2} - \dfrac{K_4 C_{H2}}{K_h}}{1 + K_a C_I + \dfrac{C_{me}}{K_f} + \dfrac{C_{Bt}}{K_g} + \dfrac{C_{H2}}{K_h} + K_N C_N}$$

$$r_3 = \frac{K_5 K_a C_I - \dfrac{K_6 C_{me}^3 C_{Bt}}{K_b K_C K_e K_g K_f C_{H2}}}{1 + K_a C_I + \dfrac{C_{me}}{K_f} + \dfrac{C_{Bt}}{K_g} + K_b C_{H2} + K_N C_N}$$

$$r_4 = \frac{\dfrac{K_7 K_C K_a C_I}{C_{me}} - \dfrac{K_8 K_d K_C K_a C_I}{C_{me}}}{1 + K_a C_I + \dfrac{C_{me}}{K_f} + \dfrac{C_{Bt}}{K_g} + K_b C_{H2} + K_N C_N}$$

$$r_5 = \frac{\dfrac{K_9 K_d K_C K_a K_b C_I C_{H2}}{C_{me}} - \dfrac{K_{10} C_{me} C_{Bt}}{K_g K_f}}{\left[1 + K_a C_I + \dfrac{C_{me}}{K_f} + \dfrac{C_{Bt}}{K_g} + K_b C_{H2} + K_N C_N\right]^2}$$

$$r_6 = \frac{\dfrac{K_{11} K_{a-g} C_{H2} C_I}{C_{Bt} C_{me}^2} - K_{12} C_{me}}{1 + K_a C_I + \dfrac{K_{a-g} C_{H2} C_I}{C_{Bt} C_{me}^2} + \dfrac{C_{Bt}}{K_g} + K_b C_{H2} + K_N C_N}$$

$$r_s = \frac{\dfrac{K_{13}K_{(a-f)}C_I C_{H2}}{C_{me}^3} - K_{14}C_{Bt}}{1 + K_a C_I + \dfrac{C_{me}}{K_f} + \dfrac{K_{(a-f)}C_I C_{H2}}{C_{me}^3} + K_b C_{H2} + K_N C_N}$$

3.3.2 Scheme 2

HYDROGEN ATMOSPHERE

Hydrogen is adsorbed dissociatively

ADSORPTION

$I + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} IS$

$½ H2 + S \underset{K_4}{\overset{K_3}{\rightleftharpoons}} HS$

REACTION

$IS + S \underset{K_6}{\overset{K_5}{\rightleftharpoons}} Bts + Prs$

$Prs + 2HS \underset{K_8}{\overset{K_7}{\rightleftharpoons}} 3Mes$

DESORPTION

$Mes \underset{K_{10}}{\overset{K_9}{\rightleftharpoons}} Me + S$

$Bts \underset{K_{12}}{\overset{K_{11}}{\rightleftharpoons}} Bt + S$

$HS \underset{K_{14}}{\overset{K_{13}}{\rightleftharpoons}} ½ H2 + S$

$$r_1 = K_1 C_I C_S - K_2 C_{IS}$$

$$r_2 = K_3 C_{H2}^{1/2} C_S - K_4 C_{HS}$$

$$C_{HS} = K_b C_{H2}^{1/2} C_S$$

$$r_3 = K_5 C_{IS} C_S - K_6 C_{Bts} C_{prs} = 0$$

$$C_{IS} = \frac{C_{Bts} C_{prs}}{K_C C_S}$$

$$r_4 = K_7 C_{prs} C_{HS}^2 - K_8 C_{mes}^3 = 0$$

$$C_{prs} = \frac{C_{mes}^3}{K_d C_{HS}^2}$$

$$r_5 = K_9 C_{mes} - K_{10} C_{me} C_S = 0$$

$$C_{mes} = \frac{C_{me} C_S}{K_e}$$

$$r_6 = K_{11} C_{Bts} - K_{12} C_{Bt} C_S = 0$$

$$C_{Bts} = \frac{C_{Bt} C_S}{K_f}$$

$$r_7 = K_{13} C_{HS} - K_{14} C_{H2}^{1/2} C_S = 0$$

$$C_{HS} = \frac{C_{H2}^{1/2} C_S}{K_g}$$

substituting C_{mes} and C_{HS} in r_4

$$C_{prs} = \frac{C_{me}^3 C_S^3 K_g}{K_e^3 K_d C_{H2} C_S^2} = \frac{K_g C_{me} C_S}{K_e^3 K_d C_{H2}}$$

from r_3,

$$C_{IS} = \frac{C_{Bts}C_{prs}}{K_C C_S} = \frac{C_{Bt}C_S K_g C_{me} C_S}{K_C K_f C_S K_e^3 K_d C_{H2}} = \frac{C_{Bt}K_g C_{me} C_S}{K_C K_f K_e^3 K_d C_{H2}}$$

$$r_1 = K_1 C_I C_S - \frac{K_2 C_{Bt} K_g C_{me} C_S}{K_C K_f K_e^3 K_d C_{H2}}$$

site balance

1 = S + IS + MeS + Bts + Prs + HS

$$1 = \mathrm{C_S} + \frac{C_{Bt}K_g C_{me} C_S}{K_C K_f K_e^3 K_d C_{H2}} + \frac{C_{me}C_S}{K_e} + \frac{C_{Bt}C_S}{K_f} + \frac{K_g C_{me} C_S}{K_e^3 K_d C_{H2}} + \frac{C_{H2}^{1/2} C_S}{K_g}$$

$$C_S = \frac{1}{1 + \frac{C_{Bt}K_g C_{me}}{K_C K_f K_e^3 K_d C_{H2}} + \frac{C_{me}}{K_e} + \frac{C_{Bt}}{K_f} + \frac{K_g C_{me}}{K_e^3 K_d C_{H2}} + \frac{C_{H2}^{1/2}}{K_g}}$$

Table 3.8: Reaction rate models for scheme 2

$$r_1 = \frac{K_1 C_I - \dfrac{K_2 K_g C_{Bt} C_{me}}{K_C K_d K_e^3 K_f C_{H2}}}{\dfrac{C_{Bt} K_g C_{me}}{K_C K_f K_e^3 K_d C_{H2}} + \dfrac{C_{me}}{K_e} + \dfrac{C_{Bt}}{K_f} + \dfrac{K_g C_{me}}{K_e^3 K_d C_{H2}} + \dfrac{C_{H2}^{1/2}}{K_g}}$$

other rates follow suit

$$r_2 = \frac{K_3 C_{H2}^{1/2} - \dfrac{K_4 C_{H2}^{1/2}}{K_g}}{1 + K_a C_I + \dfrac{C_{me}}{K_e} + \dfrac{C_{Bt}}{K_f} + \dfrac{K_g C_{me}}{K_e^3 K_d C_{H2}} + \dfrac{C_{H2}^{1/2}}{K_g}}$$

$$r_3 = \frac{K_5 K_a C_I - \dfrac{K_C K_g C_{Bt} C_{me}}{K_f K_e^3 K_d C_{H2}}}{1 + K_a C_I + \dfrac{C_{me}}{K_e} + \dfrac{C_{Bt}}{K_f} + \dfrac{K_g C_{me}}{K_e^3 K_d C_{H2}} + \dfrac{C_{H2}^{1/2}}{K_g}}$$

$$r_4 = \frac{\dfrac{K_9 K_C K_f K_a C_I C_{H2}}{K_g^2 C_{Bt}} - \dfrac{K_g C_{me}^3}{K_e^3}}{1 + K_a C_I + \dfrac{C_{me}}{K_e} + \dfrac{C_{Bt}}{K_f} + \dfrac{K_a K_c K_f C_I}{C_{Bt}} + \dfrac{C_{H2}^{1/2}}{K_g}}$$

$$r_5 = \frac{K_9 \left(\dfrac{K_d K_C K_a K_f C_I}{K_g C_{Bt}} \right)^{\frac{1}{3}} - K_{10} C_{me}}{1 + K_a C_I + \left[\dfrac{K_d K_C K_a K_f C_{H2}}{K_g C_{Bt}} \right]^{\frac{1}{3}} + \dfrac{C_{Bt}}{K_f} + \dfrac{C_{H2}^{1/2}}{K_g} + \dfrac{K_C K_a K_f C_I}{C_{Bt}}}$$

$$r_6 = \frac{\dfrac{K_{11} K_a K_c K_d K_e^3 C_{H2}}{K_g C_{me}} - K_{12} C_{Bt}}{1 + K_a C_I + \dfrac{C_{me}}{K_e} + \dfrac{C_{H2}^{1/2}}{K_g} + \dfrac{K_a K_c K_d K_e^3 C_{H2}}{K_g C_{me}} + \dfrac{K_g C_{me}}{K_e^3 K_d C_{H2}}}$$

$$r_7 = \frac{K_{13}K_bC_{H2}^{1/2} - K_{14}C_{H2}^{1/2}}{1 + K_aC_I + \frac{C_{me}}{K_e} + \frac{C_{Bt}}{K_f} + \frac{K_gC_{me}}{K_e^3K_dC_{H2}} + K_bC_{H2}^{1/2}}$$

3.3 Parameter estimation techniques

The models equations obtained were linearized before the use of Gauss *Jordan* numerical method via a computer programming language (Visual Basic) to estimate the rate and equilibrium constant.

3.4 Linearization of kinetic equation

Given $R = \dfrac{K_FC_N - K_rC_B}{1 + \frac{C_B}{K_B} + \frac{C_m}{K_M} + \frac{C_{CP}}{K_{CP}} + \frac{C_T}{K_T} + K_NC_N}$ 3.01g

Where K(f, r) = rate constants

K (m, B, Cp, T, N) = equilibrium constants

R = Rate

According to Himmelblau, (1970) ; the kinetic equation can be linearized as follows for regression analysis.

$$\frac{K_fC_N - K_rC_B}{R} = 1 + \frac{C_B}{K_B} + \frac{C_m}{K_m} + \frac{C_T}{K_T} + \frac{C_{CP}}{K_{CP}} + K_NC_N \text{................3.02g}$$

Further multiplication and collection of like terms gives

$$R = K_fC_N - K_rC_B - \frac{C_BR}{K_B} - \frac{C_mR}{K_m} - \frac{C_TR}{K_T} - \frac{C_{CP}}{K_{CP}} - K_NC_NR. \text{ ....3.03g}$$

For kinetic equation with squared denominator i.e.

$$R = \frac{K_f C_N - K_r C_{CP}}{\left[1 + \frac{C_m}{K_m} + \frac{C_B}{K_B} + \frac{C_{CP}}{K_{CP}} + K_N C_N\right]^2} \quad \text{...3.04g}$$

$$R^{\frac{1}{2}}\left[1 + \frac{C_m}{K_m} + \frac{C_B}{K_B} + \frac{C_T}{K_T} + \frac{C_{CP}}{K_{CP}} + K_N C_N\right] = \left[K_f C_N - K_r C_B\right]^{\frac{1}{2}} \quad \text{.......................3.05g}$$

The right hand side of the equation above can be expanded using binomial expansion according to Stroud, (1995).

$$\left[K_f C_N - K_r C_{CP}\right]^{\frac{1}{2}} = \left(K_f C_N\right)^{\frac{1}{2}} - \frac{1/2 K_f C_N^{1/2} K_r C_{CP}^{-1/2}}{1!} - \frac{(1/2-1) K_F C_N^{\frac{1}{2}-2} (K_r C_{CP})^2}{2!} -$$

$$\frac{-1/2(1/2-1)(1/2-2) K_F C_N^{\frac{1}{2}-3} (K_r C_{CP})^3}{3!} \quad \text{.........................3.06g}$$

Therefore

$$R^{1/2}\left[1 + \frac{C_m}{K_m} + \frac{C_B}{K_B} + \frac{C_T}{K_T} + \frac{C_{CP}}{K_{CP}} + K_N C_N\right] = \left[K_f C_N\right]^{1/2} - \frac{1}{2} K_1 C_N^{\frac{1}{2}-1} K_r C_{CP}^{-1/2}$$

$$R^{1/2} = K_f^{1/2} C_N^{1/2} - 1/2 K_F C_N^{-1/2} K_r C_{CP} - \frac{C_M}{K_M} R^{1/2} - \frac{C_B}{K_B} R^{1/2} - \frac{C_{CP}^{1/2}}{K_{CP}} - K_N C_N R^{1/2} \quad \text{..........3.07g}$$

Substituting concentration values at a set temperature at different W/Fs form matrices, which were solved using Gauss Jordan iterative method with the help of computer programming.

3.5 Date Processing

Calculation of rates of reaction

The rates of reactions were calculated by plotting the graph of fractional conversions against W/Fs. The slope at various points gives the rate of reaction. This graph is shown in Fig 3.1

$$r_A = F_{Ao}\left(\frac{dx}{dw}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.08g$$

3.6 Concentration values

Using the formular for the concentration of the inlet reactant (3 methyl hexane) the concentrations were obtained

$$C_d = 1/2\left(\frac{143.04\rho\Omega}{M.F.to.Treactor}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.09g$$

where

M = molecular weight of reactant

F = Flow rate mil/min

To = 20 secs. = 1/3 min

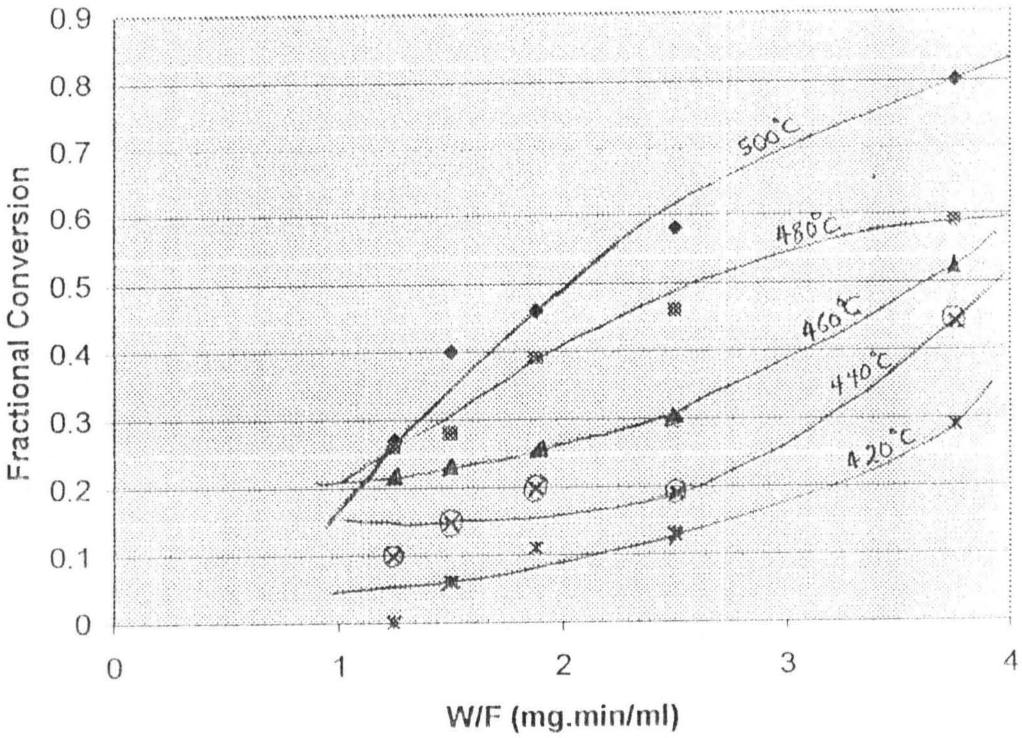
Ω = Pulse size = 1μL

ρ = density = 0.679 g/cm3

T = temperature oK

Cd = Concentration of the inlet reatant

The W/Fs considered are 3.75, 2.50, 1.88, 1.50 and 1.25. The Flow rates used are shown in Appendix E.



Fractional Conversion vs W/F (Nitrogen atmosphere)

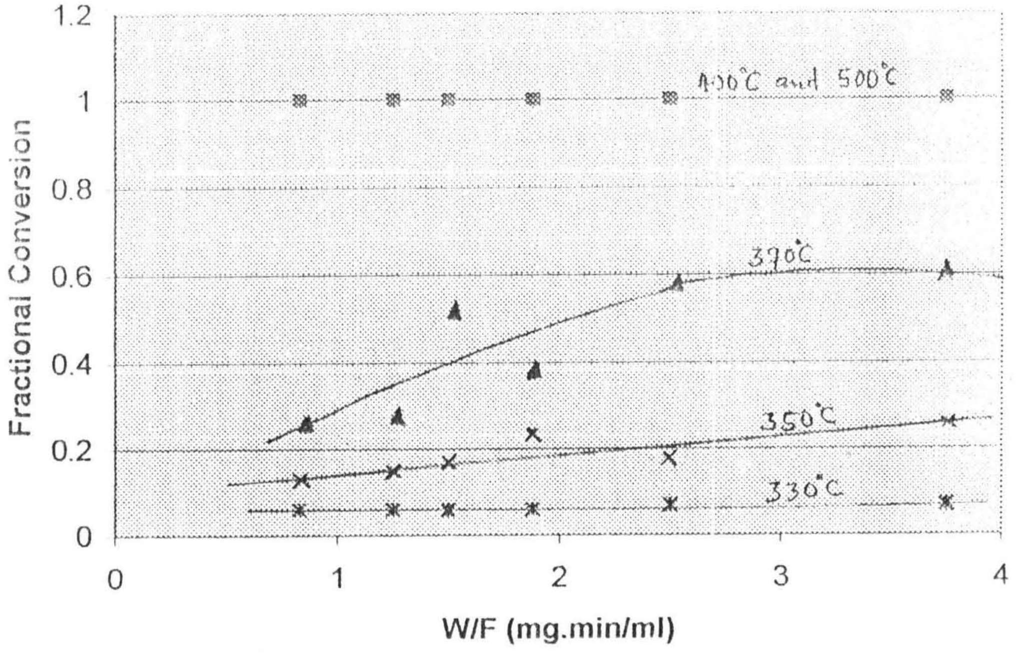


Fig3.1: **Fractional Conversion vs W/F (Hydrogen atmosphere)**

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Result

The rate and equilibrium constants obtained for 3-methylhexane aromatization in N_2 is shown in Appendix D for all reaction mechanism tested. The corresponding values in H_2 carrier gas are shown in Appendix H for reaction tested.

Under N_2, only reaction rate model 5 of Scheme 4 was fitted by experimental data and the value of rate and equilibrium constants obtained are shown in Table4.1. The rate equation for rate 5 is

$$r_5 = \frac{\dfrac{K_9 C_T C_{H2}}{K_i K_j^2} - \dfrac{K_{10} C_B C_{me}}{K_g K_k}}{\left(1 + \dfrac{C_B}{K_g} + \dfrac{C_T}{K_i} + \dfrac{C_{me}}{K_k} + K_N C_N\right)^2} \quad - - - 4.1$$

Also in H_2 atmosphere only model 3 of Scheme 2 was fitted by experimental data and the values of rate and equilibrium are as given in Table4.3 below.

$$r_3 = \frac{K_5 K_a C_I - \dfrac{K_6 K_g C_{Bt} C_{me}}{K_f K_e^3 K_d C_{H2}}}{1 + K_a C_I + \dfrac{C_{me}}{K_e} + \dfrac{C_{Bt}}{K_f} + \dfrac{C_{H2}^{1/2}}{K_g} + K_N C_N} \quad - - - - 4.2$$

Table 4.1: Rate and equilibrium constant for the best reaction rate (Scheme 4 rate 5). N2

Temp°C	KF	KR	KB	KT	Kme
420	-	-	-	-	-
440			1.483*106	1.981*107	9.577*106
460	4.691*101	2.652*105	2.610*105	3.804*106	3.597*106
480	6.191*101	5.539*105	8.487*106	3.480*106	5.476*105
500	1.249*102	1.609*106	1.553*105	1.613*106	1.263*105

From the concentration of the inlet reactant concentration of the products were arrived at using these formular below

$CI = Cd\,(1 - Xd)$

$Ccp = Cd\,Xcp$

$CB = Cd\,XB$

$CT = Cd\,XT$

$CH = Cd\,XH$

$Cme = Cd\,Xme$

Ccp, CB, CT, CH, Cme, CI are concentration of cracked product, Benzene, Toluene, Hydrogen and Methane. The X's represent their different mole fractions, W/F represents the contact time for the reaction

3.7 Optimization techniques

With the rate equations obtained, at different W/F and different temperature, the concentration values and rates were substituted to arrive at sets of simultaneous equations. Matrices were generated from these equations. Using Gauss Jordan iterative method of numerical analysis a computer program was written.

This known iterative method (Gauss Jordan) was used to solved the matrices via a programming software i.e. *Visual Basic* - Visual basic has the ability to handle matrices. The results obtained were given as the rate and equilibrium constants. Detailed of the computer program is in appendix **I**.

Original data used for this process was obtained from F. Aberuagba's Ph D thesis [Submitted in University of Lagos, Chemical Engineering department (1995)]

Table 4.2: rate and equilibrium constants for rate 3 Scheme 2. (Best model in N2)

Temp/ Oc	**KF**	**KR**	**KI**	**Kme**	**KBt**	**KH2**
350	$3.220*10^3$	$1.480*10^4$	$6.470*10^4$	$2.560*10^5$	$4.87*10^5$	$1.260*10^3$
370	$1.150*10^4$	$2.320*10^4$	$5.870*10^4$	$9.43*10^4$	$1.990*10^5$	$9.23*10^2$

The products of amortization of 3-mehyhexane reaction over $Pt/A_2\ 0_3$ catalyst in N_2 carrier gas are Toluene, Benzene, methane and cracked product. In H_2 carrier gas the product is cracked product due to high partial pressure of hydrogen the high partial pressure of hydrogen affects the formation of aromatics. This process is referred to as hydrogenolysis.

When the activation energies obtained (N_2 atmosphere. 58.93 KJ/mol forward reaction. 88.56 LK/mol reverse reaction: H_2 atmosphere, 203.6 KJ/mol forward reaction and 74.70 KJ/mol reverse reaction) were compared with activation energies obtained elsewhere i.e. activation every for reforming of n-Heptane are 27 and 39 KJ/mol for forward and reverse reaction, for reforming of n-octane. The activation energies were 21.2 and 14.3 Kcal/gmol. Values for aromatization of 3- methhlhexane obtained by Aberuagba (1999) were 107 and 202.03 KJ/mol in N2 and H2 respectively. This shows that the values obtained in this work are in the acceptable range.

4.2 Discussion

Parameter estimates were obtained for each model. Model generally gave a better fit to observed data with increasing temperature. Estimates were by no means unique, but were expected to follows a general trend. Rate constant were expected to show an increase with temperature while equilibrium constants were expected to show a decrease with temperature.

Model discrimination was based on a number of factors.

1. The agreement of estimated rate constants with the expected trend of increasing with increasing temperature.
2. The agreement of expected equilibrium constant with the expected trend of decreasing with increasing temperature.
3. The value of the objective functions at each temperature over the whole temperature range

Factor 1 examined the behaviour of rate constants with temperature and disqualifies most of the models except Scheme 1, model 6; Scheme 2, model 5; Scheme 4, model 9 and Scheme 5, model 3. Factor 2 examined the behaviour of equilibrium constants in relation to increase in temperature. At 420°C several of the results were not reliable because of zero values of concentration during calculation. The following models agree with the trend expected:

Scheme 1, Model 5;
Scheme 2, Model 5 and 7
Scheme 4, Model 5 and 9
Scheme 5, Model 3 and 5 other models were disqualified.

Factor 3 was used to eliminate Scheme 3 and Scheme 6, Scheme 3 shows negative values of the objective function that is not in agreement with the expected. Scheme 6 gave models that produce the same rate and equilibrium constants at all temperature. This scheme fail to show any trend and hence its disqualification.

Considering all the factors, Scheme 4, model 5 and 10 were the closest to the expected. Model 5 was finally selected as that which best describe the aromatization of 3-Methlyhexane over Pt/Al2O3 catalyst over the temperature range investigated from the Models examined.

This model described the reaction of Toluene to give benzene and methane as rate controlling step with the dissociative adsorption of hydrogen on the catalyst surface. And Arrhenius plot of the rate constants i.e. forward and reverse reaction for model 5 of Scheme 4 gave the activation energies as 58.8 KJ/mol and 88.56 KJ/mol respectively.

Table 4.3: Goodness of fit of model (N_2 atmosphere)

Sheme	Best fit model
1	1
2	5 and 7
3	None
4	5 and 10
5	3 and 5
6	None

Table 4.4: Showing rate constant and temperature (R_5 in N_2)

		Forward reaction		Reversed reaction	
T(K)	1/K	K	Log K	K	Log K
713	1.40 E-3	4.86E2	2.68	3.67E5	5.56
733	1.36 E-3	4.69E1	1.67	2.65E5	5.42
753	1.33 E-3	6.91E1	1.79	5.54E5	5.74
773	1.30 E-3	1.24E2	2.10	1.61E5	5.21

Forward reaction

$$Slope = \frac{2.096 - 1.670}{0.0013 - 0.00136} = 7.1$$

$$E = 7.1 * 8.314 = 59.03 KJ/gmol$$

Reversed reaction

$$slope = \frac{5.74 - 5.42}{(133 - 136)x10^{-5}} = 10.67$$

$$E = 10.67 * 8.314 = 88.71 KJ/gmol$$

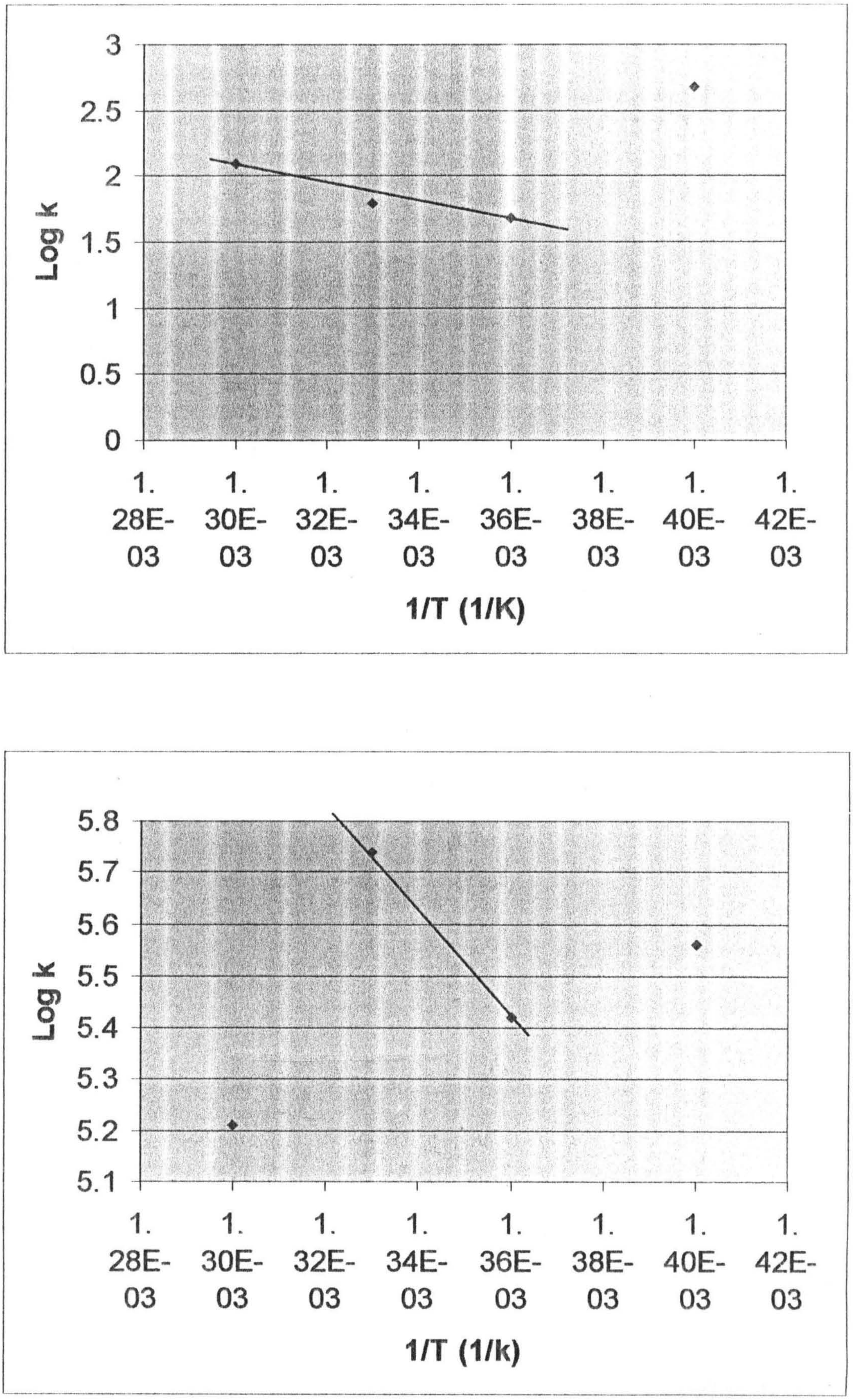


Fig4.1. ACTIVATION ENERGY(NITROGEN ATMOSPHERE)

4.2.1 Analysis of Parameters (Hydrogen atmosphere)

In hydrogen atmosphere, there was high hydrogen partial pressure, which, eventually affect the formation of aromatics. Here, cracked products were formed. The products formed referred to as cracked products here are methane and butane.

From the experimental data, at temperature $500^{o}C$ and $400^{o}C$ there was complete conversion of methylhexane to cracked product, which gave a horizontal line on the graph of fractional conversion against W/F. This eventually, led to zero value of slope. Rate value could not be accounted for at this range of temperature. At $330^{o}C$ reaction were almost impossible, at different W/F, the conversion was uniform hence, affecting the calculation of the rate of reaction.

Factor 1 agrees with the Scheme 1, model 1, model 4 and model 5. Also included are model 1, 2, 3 and 7 of Scheme 2. Other models were disqualified by this factor.

Factor 2 disqualified Scheme 1 completely and all model in Scheme 2 except model 3 and 6. Model 5 of Scheme 2 have the same value at all temperature. Therefore, it is said not to have followed any known trend.

All factors approve of scheme 2 model 3 therefore; the model is the modal model that fits the reaction of the 3 - methylhexane in hydrogen atmosphere over Pt/Al2O3 catalyst.

Model 3 of Scheme 2 describe the reaction of 3 – methylhexane to give butane and propane before the production of metane. It is the rate controlling step. Arrhenius plot of the rate constant for forward and reverse reaction gave activation energies of 203.6 Kj/mol and 74.70 Kj/mol respectively.

Table 4.5: Goodness of fit of model (H_2 atmosphere)

Scheme	Best fit model
1	-
2	3 and 6

Table 4.6: Showing rate constant and temperature. (R_3 in H_2)

		Forward reaction		Reversed reaction	
T	1/T	K	Log K	K	log K
622	1.61E-3	3.22E3	8.80	1.48E4	9.60
643	1.56E-3	1.15E4	9.35	2.32E4	10.05

Forward reaction

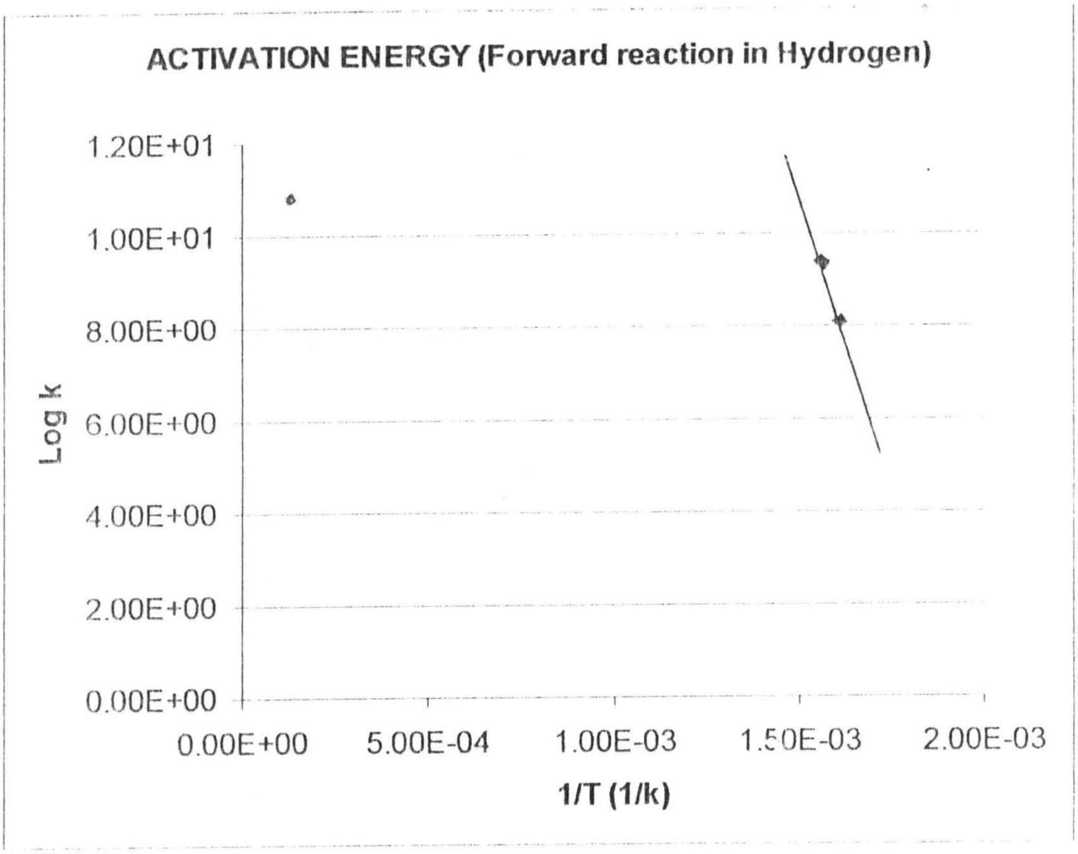
$$Slope = \frac{9.35-8.01}{(156-161)*10^{-5}} = 24.54$$

$$E = 24.54*8.314 = 203.6KJ/\,gmol$$

Reversed reaction

$$\text{Slope} = \frac{10.05-9.60}{(156-161)*10^{-5}} = 9.00$$

$$\text{E} = 9.00*8.314 = 74.7\text{KJ/gmol}$$



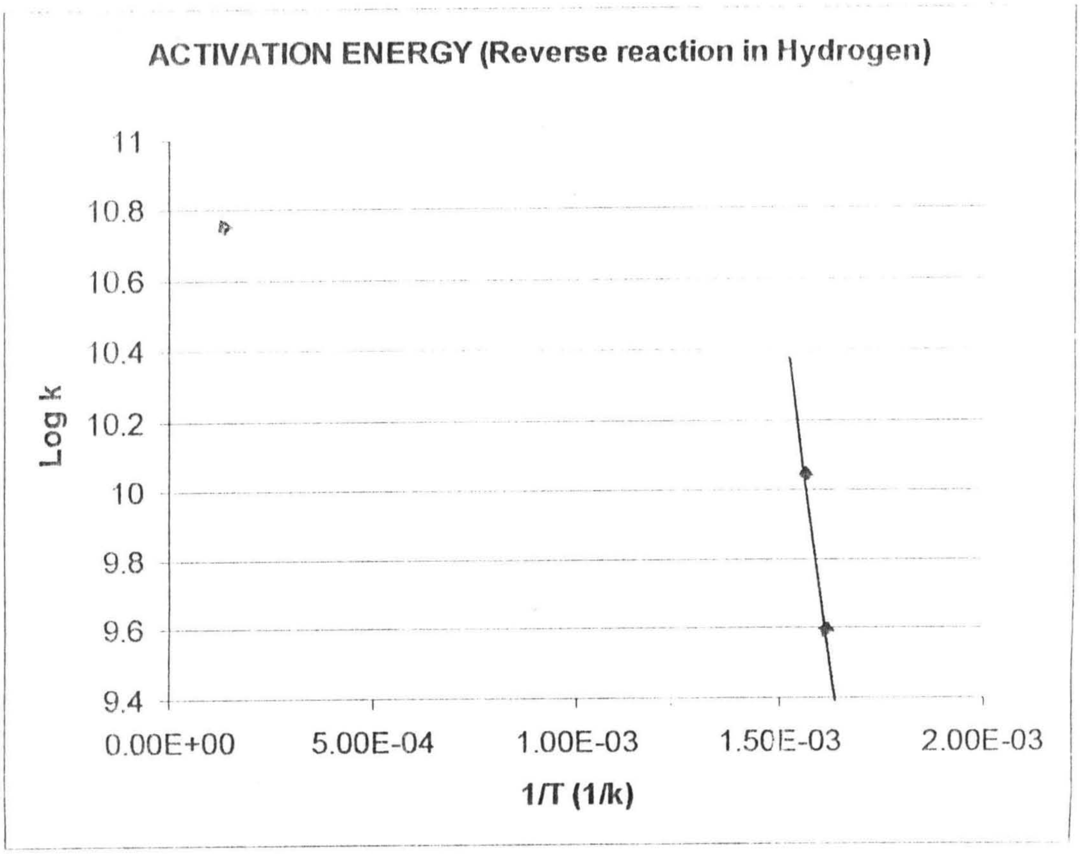


Fig. 4.2 Activation energy (H_2 atmosphere)

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In the modeling of aromatizatio of 3-methyl hexane over Pt/Al_2O_3 catalyst, the product of the reaction in N_2 atmosphere were toluene, benzene, methane and cracked product. The rate controlling step is reaction of toluene to form adsorbed benzene and adsorbed methane i.e. model 5 scheme 4 in the scheme considered for the temperature range of 420 to 500^0C. The activation energies for forward and backward reaction of the rate controlling step were determined to be 58.93 KJ/mol and 88.56 KJ/mol respectively

In hydrogen atmosphere, the best model is model 3 of scheme 2 which describe the reaction of 3 – methylhexane to butane and propane. Activation energies for forward reaction for the rate controlling were obtained as 203.60 KJ/mol and 74.70KJ/mol within the temperature range of 330 to 500^0 C

5.2 RECOMMENDATION

1. A computer packaged that could handle very small values in a simultaneous equation should be developed and made available to ease the work.

2. Kinetic study is a complex body of knowledge. Therefore there is need to split the work into parts for easy understanding

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APPENDIX A

SOURCE OF DATA

Commercial Pt/Al_2O_3 catalyst containing 180 m^2/g pure volumes of 0.5ml/g was used for the experiment reported herein.

Reagent grade 3 – methylhexane was used for the reactions. Purity cylinder H_2 and N_2 were used as the carrier gases. N_2 was passed through a bed of reduced copper oxide at 300^oC to removed traces of oxygen and through a bed of silica gel to removed traces of water vapour, whilst hydrogen was passed through a bed of deoxo catalyst (Pb/Al_2O_3) at room temperature to remove traces of oxygen and through a bed of silica gel to remove traces of water vapour.

0.15g of Pt/Al_2O_3 catalyst of particle size 53 – 57μm was charged into a pulse micro-reactor, which is a 5cm stainless tube. The particles were held in place by glass wool. The micro-reactor was inserted into the center of a vertical redcroft furnance while temperature control was achieved by temperature indicating controller.

The catalyst was dried at 110°C in the flow of 40ml/min N_2 and reduced at 500°C in the flow of 40ml/min H_2 for 2 hours. This method of pre-treatment of catalyst has been reported to give a stable catalyst surface.

The aromatisation of 3 – methylhexane was undertaken in several experiments to ascertain the total conversion and product distribution behaviour of 1μL pulses of 3 – methylhexane reaction with temperature and contact time (W/F) and H_2 and N_2 atmospheres. The products were monitored by an on line G.C which contained a stainless steel supelco column labeled 15% FEAP on 80/100 chromosorb W.A.W containing carbon wax and substituted terephthalic acid.

The experiment was performed at a total pressure of 4.0 KG/cm^2. The kinetic data were obtained on a stable catalyst surface. Usually 3 – 5 pulses are required to obtain steady state condition.

During experimentation, the stability of the catalyst was checked every two (2) hour at definite condition. When a deviation from the expected activity at a defined condition is observed, the catalyst is regenerated by burning off coke in airflow of 150ml/min at temperature of 400°C for 30 min. The catalyst is then reduced in 40ml/min H_2 at 500°C for 2 hours.

APPENDIX B

Table B1: EFFECT OF W/F (mg – min/ml) ON 3-METHYLHEXANE REFORMING IN NITROGEN CARRIER GAS ON PLATINUM/ALUMINA CATALYST.

PL – S_Z = 1.0 microlitre; P = 4.0 Kg/Sq. – cm

500°C

W/F	3.75	2.50	1.88	1.50	1.25
X_C	0.16	0.09	0.07	0.04	0.03
X_{MH}	0.20	0.42	0.54	0.60	0.73
X_B	0.12	0.09	0.07	0.07	0.05
X_T	0.05	0.03	0.04	0.02	0.00
Xme	0.12	0.09	0.07	0.07	0.05
X_H	0.35	0.28	0.21	0.02	0.14
X_o	0.80	0.58	0.46	0.40	0.27

480°C

W/F	3.75	2.50	1.88	1.50	1.25
X_C	0.12	0.07	0.06	0.04	0.02
X_{MH}	0.41	0.54	0.61	0.72	0.74
X_B	0.09	0.07	0.07	0.05	0.05
X_T	0.04	0.03	0.00	0.00	0.00
Xme	0.09	0.07	0.07	0.05	0.05
X_H	0.26	0.21	0.20	0.14	0.15
X_O	0.59	0.46	0.39	0.28	0.26

460^{O}C

W/F	3.75	2.50	1.88	1.50	1.25
X_C	0.10	0.05	0.04	0.02	0.02
X_{MH}	0.46	0.69	0.75	0.77	0.78
X_B	0.08	0.05	0.04	0.04	0.04
X_T	0.04	0.02	0.00	0.00	0.00
Xme	0.08	0.05	0.04	0.04	0.04
X_H	0.24	0.15	0.12	0.12	0.12
X_O	0.54	0.31	0.25	0.23	0.22

440^{O}C

W/F	3.75	2.50	1.88	1.50	1.25
X_C	0.06	0.04	0.03	0.02	0.01
X_{MH}	0.58	0.81	0.80	0.85	0.90
X_B	0.06	0.03	0.03	0.03	0.20
X_T	0.04	0.02	0.00	0.00	0.00
Xme	0.06	0.03	0.03	0.03	0.02
X_H	0.02	0.08	0.10	0.08	0.05
X_O	0.42	0.19	0.21	0.15	0.10

420^{O}C

W/F	3.75	2.50	1.88	1.50	1.25
X_C	0.05	0.04	0.02	0.01	0.00
X_{MH}	0.71	0.87	0.89	0.94	1.00
X_B	0.04	0.02	0.02	0.01	0.00

X_T	0.03	0.00	0.00	0.00	0.00
X_{mc}	0.04	0.02	0.02	0.01	0.00
X_H	0.13	0.05	0.05	0.03	0.00
X_O	0.29	0.13	0.11	0.06	0.00

Table B2: Data in Hydrogen atmosphere

EFFECT OF W/F ON 3-METHYLHEXANE CRACKING IN HYDROGEN CARRIER GAS ON Pt/ALUMINA CATALYST.

PL – SZ = 1.0 microlitre; P = 4.0 Kg/Sq – cm

500^{O}C

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_C	1.00	1.00	1.00	1.00	1.00	1.00
X_{MH}	0.00	0.00	0.00	0.00	0.00	0.00
X_B	0.00	0.00	0.00	0.00	0.00	0.00
X_T	0.00	0.00	0.00	0.00	0.00	0.00
X_O	1.00	1.00	1.00	1.00	1.00	1.00
X_O	1.00	1.00	1.00	1.00	1.00	1.00

400^{O}C

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_C	1.00	1.00	1.00	1.00	1.00	1.00
X_{MH}	0.00	0.00	0.00	0.00	0.00	0.00
X_B	0.00	0.00	0.00	0.00	0.00	0.00
X_T	0.00	0.00	0.00	0.00	0.00	0.00

370°C

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_C	0.54	0.50	0.33	0.44	0.29	0.23
X_{MH}	0.46	0.50	0.67	0.56	0.71	0.77
X_B	0.00	0.00	0.00	0.00	0.00	0.00
X_T	0.00	0.00	0.00	0.00	0.00	0.00
X_O	0.54	0.50	0.33	0.44	0.29	0.23

350°C

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_C	0.22	0.15	0.19	0.14	0.12	0.11
X_{MH}	0.78	0.85	0.81	0.86	0.88	0.89
X_B	0.00	0.00	0.00	0.00	0.00	0.00
X_T	0.00	0.00	0.00	0.00	0.00	0.00
X_O	0.22	0.15	0.19	0.14	0.12	0.11

330°C

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_C	0.06	0.06	0.05	0.05	0.05	0.05
X_{MH}	0.94	0.94	0.95	0.95	0.95	0.95
X_B	0.00	0.00	0.00	0.00	0.00	0.00
X_T	0.00	0.00	0.00	0.00	0.00	0.00
X_O	0.06	0.06	0.05	0.05	0.05	0.05

APPENDIX C

Table C1: – 3 - Methylhexane conversion (N_2 Atm.)

	W/F (Mg.min/ml)	Conversion
500°C	3.75	0.80
	2.50	0.58
	1.88	0.46
	1.50	0.40
	1.25	0.27
480°C	3.75	0.59
	2.50	0.46
	1.88	0.39
	1.50	0.28
	1.25	0.26
460°C	3.75	0.54
	2.50	0.31
	1.88	0.25
	1.50	0.23
	1.25	0.22
440°C	3.75	0.44
	2.50	0.19
	1.88	0.20
	1.50	0.15
	1.25	0.10

420°C	3.75	0.29
	2.50	0.13
	1.88	0.11
	1.50	0.06
	1.25	0.00

APPENDIX D

RATES (N_2)

Rates were obtained from the graph of conversion against W/F

$r_A = F_{AO}\,(dx/dw)$

Table D1: Showing the value of rates obtained

W/F \ Temp	420°C	440°C	460°C	480°C	500°C
1.250	0.250	0.200	0.050	0.200	0.180
1.500	0.165	0.167	0.050	0.143	0.170
1.875	0.132	0.143	0.080	0.160	0.160
2.500	0.100	0.133	0.114	0.114	0.150
3.750	0.075	0.100	0.240	0.075	0.147

APPENDIX E

DETERMINATION OF INLET CONCENTRATION (NITROGEN ATMOSPHERE)

Concentration of the inlet reactants from the given equation.

$$C_d = 1/2\left(\frac{143.04\rho\Omega}{M * F * to * Treactor}\right)$$

M = molecular weight of reagent

F = flow rate mol/min

to = 20 sec = 1/3 min

Ω = pulse size = 1 μL

ρ = density = 0.679 g/cm^3

T = temperature °K

C_d = Concentration of inlet reagent

e.g. at 500°C = 773K, F = 40

$$C_d = 1/2\left(\frac{143.04 * 0.679 * 1 * 10^{-6}}{100.2 * 40 * 1/3 * 773}\right) = 4.70 * 10^{-5}\, gmol/\min$$

Table E1: SHOWING INLET CONCENTRATION IN N_2

		TEMPERATURE				
F	**W/F**	**500°C**	**480°C**	**460°C**	**440°C**	**420°C**
40	3.75	4.70	4.83	4.96	5.10	5.24
60	2.50	3.13	3.22	3.30	3.40	3.50
80	1.88	2.35	2.41	2.48	2.55	2.62
100	1.50	1.88	1.93	1.98	2.04	2.10
120	1.25	1.56	1.61	1.65	1.70	1.75

Concentration x 10^{-5} gmol/ml

TABLE E2: CONCENTRATION IN EXIT STREAM

			CONCENTRATION IN EXIT STREAM (g mol/m^3)					
T	F	W/F	C_{CP}	C_{MH}	C_B	C_T	C_{ME}	C_H
420^{O}	40	3.75	2.62	37.20	2.10	1.57	2.10	6.81
	60	2.50	1.40	30.45	0.70	0.00	0.70	17.50
	80	1.88	0.52	23.37	0.52	0.00	0.52	1.31
	100	1.50	0.21	19.74	0.21	0.00	0.21	0.65
	120	1.25	0.00	17.50	0.00	0.00	0.00	0.00
440^{0}	40	3.75	3.06	28.54	3.57	2.04	3.57	10.20
	60	2.50	1.36	27.53	1.02	0.68	1.02	2.72
	80	1.88	0.76	20.39	0.76	0.00	0.76	2.55
	100	1.50	0.41	17.33	0.61	0.00	0.61	1.63
	120	1.25	0.17	15.29	0.31	0.00	0.34	0.85
460^{0}	40	3.75	4.96	22.81	3.97	1.98	3.97	11.90
	60	2.50	1.65	22.81	1.65	0.66	1.65	4.96
	80	1.88	0.99	18.60	0.99	0.00	0.99	2.98
	100	1.50	0.40	15.27	0.79	0.00	0.79	2.38
	120	1.25	0.33	12.89	0.66	0.00	0.66	1.98
480	40	3.75	5.79	19.79	4.34	1.93	4.34	12.55
	60	2.50	2.25	17.38	2.25	0.97	2.25	6.76
	80	1.88	1.45	14.72	1.69	0.00	1.69	4.83
	100	1.50	0.77	13.90	0.97	0.00	0.97	2.70
	120	1.25	0.32	12.39	0.80	0.00	0.80	2.41

500	40	3.75	7.50	9.40	5.60	2.35	5.60	16.00
	60	2.50	2.82	13.20	2.82	0.94	2.80	8.64
	80	1.88	1.60	12.70	1.60	0.94	1.60	4.90
	100	1.50	0.75	11.30	1.30	0.38	1.30	3.76
	120	1.25	0.47	11.40	0.78	0.00	0.78	2.19

concentration $\times 10^{-6}$

$C_{MH} = C_d (1 - X_d) = C_d X_{MH}$

$C_{CP} = C_d X_{CP}$

$C_T = C_d X_T$

$C_{me} = C_d X_{me}$

$C_B = C_d X_B$

Table E3: Showing Inlet Concentration in Hydrogen

F	**W/F**	**500°C**	**400°C**	**370°C**	**350°C**	**330°C**
40	3.75	4.70	5.40	5.65	5.83	6.02
60	2.50	3.13	3.60	3.76	3.88	4.01
80	1.88	2.35	2.70	2.82	2.91	3.01
100	1.50	1.88	2.16	2.26	2.33	2.41
120	1.25	1.56	1.80	1.88	1.94	2.00
140	1.83	1.34	1.54	1.62	1.67	1.72

$\times 10^{-5}$ gmol/ml

APPENDIX F

Table F1: Rates and equilibrium constants (N_2)

	T	K_f	K_r	K_T	K_{cp}	K_M	K_B
Model 1	420	14.285	8.86E20	3.31E19	1.20E13	3.378E10	
	440	14.457	2.633E16	2.081E12	2.72E12	2.027E2	
	460	2.157	4.852E16	1.451E15	1.253E12	2.718E3	
	480	6.339	1.969E14	4.473E18	1.864E11	1.836E3	
	500	762.378	6.889E12	1.221E12	8.686E9	9.343E3	
Module 2	420	14.285	2.397	1.977E15	5.550E12		1.894E3
	440	18.123	203.22	1.605E10	4.64E7		6.258E2
	460	52.508	3.631E3	4.346E11	4.659E9		5.834E4
	480	10.117	126.567	3.160E9	3.767E6		7.197E2
	500	17.314	39.617	3.149^8	2.529E5		8.826E0
Model 3	420	14.285	2.397	1.977E5	5.550E12	1.894E2	
	440	18.123	203.22	1.605E10	4.64E7	6.258E2	
	460	52.508	3.631E3	4.346E11	4.659E9	5.834E4	
	480	10.117	126.567	3.160E9	3.767E6	7.197E2	
	500	17.314	39.617	3.149E8	2.529E5	8.826E0	
Model 4	420	14.285	3.823E24	4.919E12	3.324E10	3.173E15	
	440	14.459	6.567E15	2.720E12	2.032E2	6.093E6	
	460	2.155	4.100E3	1.255E12	2.717E3	1.094E7	
	480	6.341	1.107E14	1.864E11	1.836E3	4.353E6	
	500	8.266	1.379E10	2.080E7	6.108E2	5.243E2	

	T	K_f	K_r	K_T	K_{cp}	K_M	K_B
Model 5	420	9.587E9	57.14	3.71E2	2.286E11	2.361E2	
	440	8.501E6	72.475	5.899E2	2.500E8	2.314E1	
	460	8.651E6	1.319E3	2.548E3	3.387E8	2.550E4	
	480	2.356E5	7.429E1	3.379E2	1.335E7	2.347E2	
	500	5.496E4	8.839E1	2.088E2	4.721E6	5.115E2	
Model 6	420		NOT	RELIABLE			
	440	2.769E-6	1.798E-3	1.808E3	2.248E2	1.810E1	
	460	8.651E-4	2.190E-1	3.955E4	6.677E4	1.242E2	
	480	4.366E-6	6.894E-4	1.027E3	1.029E3	8.154E0	
	500	1.241E-4	4.468E-2	4.557E4	7.027E4	5.115E2	
Model 7	420	27.990	1.120E4	57.143	3.833E2		2.121E2
	440	19.125	1.299E4	73.419	6.467E2		5.921E1
	460	34.591	9.316E4	1.431	1.167E3		3.356E3
	480	11.136	4.570E3	7.709E1	3.619E2		1.825E2
	500	23.660	1.393E4	1.069E2	3.460E2		1.320E2
Model 8	420		NOT	RELIABLE			
	440	1.070E-1	4.560E0	7.233E1	5.777E2	4.538E1	
	460	2.521E0	6.671E2	9.750E2	8.3862E3	9.221E2	
	480	3.698E1	7.809E2	2.278E2	4.065E3	9.343E4	
	500	1.410E0	6.397E2	2.760E2	1.324E3	3.820E2	

SCHEME 2

	T	K_f	K_r	K_T	K_{cp}	K_M	K_B
Model 1	420	1.429E1	2.19E2	4.584E3	1.010E1	1.099E3	
	440	1.807E1	2.335E2	3.885E3	2.359E2	1.270E2	
	460	1.425E2	3.779E2	4.366E4	7.976E2	4.028E4	
	480	7.691E0	2.987E1	1.270E3	1.103E3	3.970E2	
	500	6.452E-1	1.123E3	7.822E3	2.774E2	8.247E2	
Model 2	420			NOT RELIABLE			
	440	1.460E-1	4.539E0	7.233E1	1.142E0	5.777E2	
	460	2.687E0	6.671E2	9.755E2	2.447E1	8.386E3	
	480	1.577E0	7.809E2	2.278E2	1.249E1	4.086E3	
	500	1.901E-1	2.001E3	8.852E1	1.132E0	1.649E2	
Model 7	420	4.130E5	7.315E1	5.714E1	2.213E2	3.814E2	
	440	1.600E5	3.467E1	7.288E1	3.386E1	6.168E2	
	460	3.367E6	1.798E2	1.844E2	6.781E3	1.307E3	
	480	3.917E4	1.329E1	7.656E1	1.959E2	3.430E2	
	500	4.260E4	9.223E0	9.223E1	7.308E1	2.375E2	

SCHEMES 3

NOT RELIABLE

SCHEMES 4

	T	K_f	K_r	K_T	K_{cp}	K_M	K_B
Model 1	420	1.429E1	1.588E2	1.203E1	8.888E2	1.480E3	
	440	1.704E1	1.729E1	1.129E2	2.863E3	2.555E3	
	460	1.227E0	6.943E1	4.332E1	2.317E2	6.333E2	
	480	2.670E-1	1.903E1	3.598E1	9.756E2	1.014E2	
	500	2.996E1	1.152E2	9.588E1	2.422E3	6.471E2	
	T	K_F	K_R	K_B	K_T	K_{me}	
Model 5	420			NOT RELIABLE			
	440	4.864E2	3.665E5	1.483E6	1.981E7	9.577E6	
	460	4.691E1	2.652E5	2.610E5	3.804E6	3.597E6	
	480	6.191E1	5.559E5	8.487E5	3.480E6	5.476E5	
	500	1.219E2	1.609E6	1.553E5	1.613E6	1.263E5	
Model 9	420			NOT RELIABLE			
	440	2.606E3	1.536E2	8.343E1	1.001E2	1.094E4	
	460	4.536E2	1.194E2	1.108E3	4.376E1	2.696E3	
	480	1.436E2	2.010E1	1.352E2	3.014E1	7.297E2	
	500	1.275E3	1.600E1	3.036E1	4.318E1	3.869E3	
Model 10	420			NOT RELIABLE			
	440	1.638E-1	1.421E1	1.841E3	2.124E3	1.856E3	
	460	8.165E-2	1.123E0	7.095E2	1.617E3	2.570E2	
	480	7.974E-2	4.014E0	5.572E2	6.462E2	6.714E1	
	500	4.664E0	2.090E1	1.461E4	3.604E4	3.019E4	

SCHEME FIVE

	T	K_f	K_r	K_T	K_{cp}	K_M	K_B
Model 1	420	1.429E1	2.158E0	1.975E0	5.616E0	3.280E3	
	440	1.907E1	2.684E24	2.086E25	2.844E13	1.342E3	
	460	2.06E8	1.153E23	4.404E23	1.662E14	2.406E3	
	480	9.149E0	2.964E21	4.072E22	1.092E13	1.963E3	
	500	8.342E0	3.089E12	2.109E13	1.468E3	1.959E3	
Model 3	420		NOT	RELIABLE			
	440	1.998E4	1.350E5	6.268E1	3.517E2	3.790E0	
	460	4.043E2	6.389E4	4.136E2	5.719E3	1.243E4	
	480	9.006E2	6.415E4	3.501E1	9.643E2	1.515E4	
	500	3.549E3	3.296E5	6.910E2	1.281E4	3.674E4	
Model 5	420	9.950E6	5.897E2	7.685E7	5.714E1	6.569E2	
	440	1.706E8	6.673E2	1.798E9	1.358E2	2.435E4	
	460	2.384E6	4.870E2	2.635E7	6.160E2	1.006E4	
	480	2.306E6	4.715E1	2.295E7	2.383E2	2.925E3	
	500	2.724E6	2.580E1	1.888E7	9.380E1	1.990E2	

APPENDIX G

Table G1: Mole fraction in Hydrogen atmosphere

500^0

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_I	0.00	0.00	0.00	0.00	0.00	0.00
X_{me}	0.75	0.75	0.75	0.75	0.75	0.75
X_{Bt}	0.25	0.25	0.25	0.25	0.25	0.25
X_H	0.00	0.00	0.00	0.00	0.00	0.00
X_O	1.00	1.00	1.00	1.00	1.00	1.00

400^0

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_I	0.00	0.00	0.00	0.00	0.00	0.00
X_{me}	0.75	0.75	0.75	0.75	0.75	0.75
X_{Bt}	0.25	0.25	0.25	0.25	0.25	0.25
X_H	0.00	0.00	0.00	0.00	0.00	0.00
X_O	1.00	1.00	1.00	1.00	1.00	1.00

370^OC

W/F	3.75	2.50	1.88	1.50	1.25	0.83
X_I	0.405	0.444	0.619	0.505	0.662	0.728
X_{me}	0.356	0.333	0.229	0.297	0.203	0.163
X_{Bt}	0.119	0.111	0.076	0.099	0.068	0.054
X_H	0.119	0.111	0.076	0.099	0.068	0.054
X_O	0.595	0.556	0.381	0.495	0.338	0.272

350°C

W/F	**3.75**	**2.50**	**1.88**	**1.50**	**1.25**	**0.83**
X_I	0.739	0.819	0.773	0.831	0.854	0.866
X_{me}	0.156	0.208	0.136	0.101	0.087	0.080
X_{Bt}	0.052	0.036	0.045	0.034	0.029	0.027
X_H	0.052	0.036	0.045	0.034	0.029	0.027
X_O	0.261	0.181	0.227	0.169	0.146	0.134

330°C

W/F	**3.75**	**2.50**	**1.88**	**1.50**	**1.25**	**0.83**
X_I	0.926	0.926	0.938	0.938	0.938	0.938
X_{me}	0.044	0.044	0.037	0.037	0.037	0.037
X_{Bt}	0.015	0.015	0.012	0.012	0.012	0.012
X_H	0.015	0.015	0.012	0.012	0.012	0.012
X_O	0.074	0.074	0.062	0.062	0.062	0.062

APPENDIX H

Table H1: Fractional Conversion (Hydrogen atmosphere)

T	W/F	CONVERSION
500°C	3.75	1.00
	2.50	1.00
	1.88	1.00
	1.50	1.00
	1.25	1.00
	0.83	1.00
400°C	3.75	1.00
	2.50	1.00
	1.88	1.00
	1.50	1.00
	1.25	1.00
	0.83	1.00
370°C	3.75	0.60
	2.50	0.56
	1.88	0.38
	1.50	0.50
	0.83	0.27
350°C	3.75	0.26
	2.50	0.18
	1.88	0.23
	1.50	0.17
	1.25	0.15
	0.83	0.13

330°C	3.75	0.07
	2.50	0.07
	1.88	0.06
	1.50	0.06
	1.25	0.06
	0.83	0.06

RATE

Table H2: Rates of reaction in Hydrogen

$r_a = F_{AO} (dx/dw)$

Temp W/F	500	400	370	350	330
3.75	0.00	0.00	0.03	0.02	0.00
2.50	0.00	0.00	0.15	0.05	0.00
1.88	0.00	0.00	0.17	0.06	0.00
1.50	0.00	0.00	0.22	0.07	0.00
1.25	0.00	0.00	0.23	0.09	0.00
0.83	0.00	0.00	0.20	0.12	0.00

Rates $X10^{-3}$

APPENDIX I

Table II: Concentration in exit stream (Hydrogen atmosphere)

Temp.	**F**	**40**	**60**	**80**	**100**	**120**	**140**
	W/F	**3.75**	**2.50**	**1.88**	**1.50**	**1.25**	**0.83**
500°C	C_I	0.000	0.000	0.000	0.000	0.000	0.000
	C_{me}	3.523	2.345	1.763	1.410	1.170	1.005
	C_{Bt}	1.175	0.783	0.588	0.470	0.390	0.335
	C_H	0.000	0.000	0.000	0.000	0.000	0.000
400°C	C_I	0.000	0.000	0.000	0.000	0.000	0.000
	C_{me}	4.050	2.700	2.025	1.620	1.350	1.155
	C_{Bt}	1.350	0.900	0.675	0.540	0.450	0.385
	C_H	0.000	0.000	0.000	0.000	0.000	0.000
370°C	C_I	2.288	1.669	1.746	1.141	1.245	1.179
	C_{me}	2.011	1.252	0.646	0.671	0.382	0.264
	C_{Bt}	0.672	0.417	0.214	0.223	0.128	0.087
	C_H	0.672	0.417	0.214	0.223	0.128	0.087
350°C	C_I	4.308	3.178	2.249	1.936	1.657	1.446
	C_{me}	0.909	0.419	0.890	0.235	0.169	0.134
	C_{Bt}	0.303	0.140	0.131	0.079	0.056	0.045
	C_H	0.303	0.140	0.131	0.079	0.056	0.045
330°C	C_I	5.575	3.713	2.823	2.261	1.876	1.613
	C_{me}	0.265	0.176	0.111	0.089	0.074	0.064
	C_{Bt}	0.090	0.060	0.036	0.029	0.024	0.035
	C_H	0.090	0.060	0.036	0.029	0.024	0.035

Concentration x10^{-5}gmol/ml

APPENDIX J

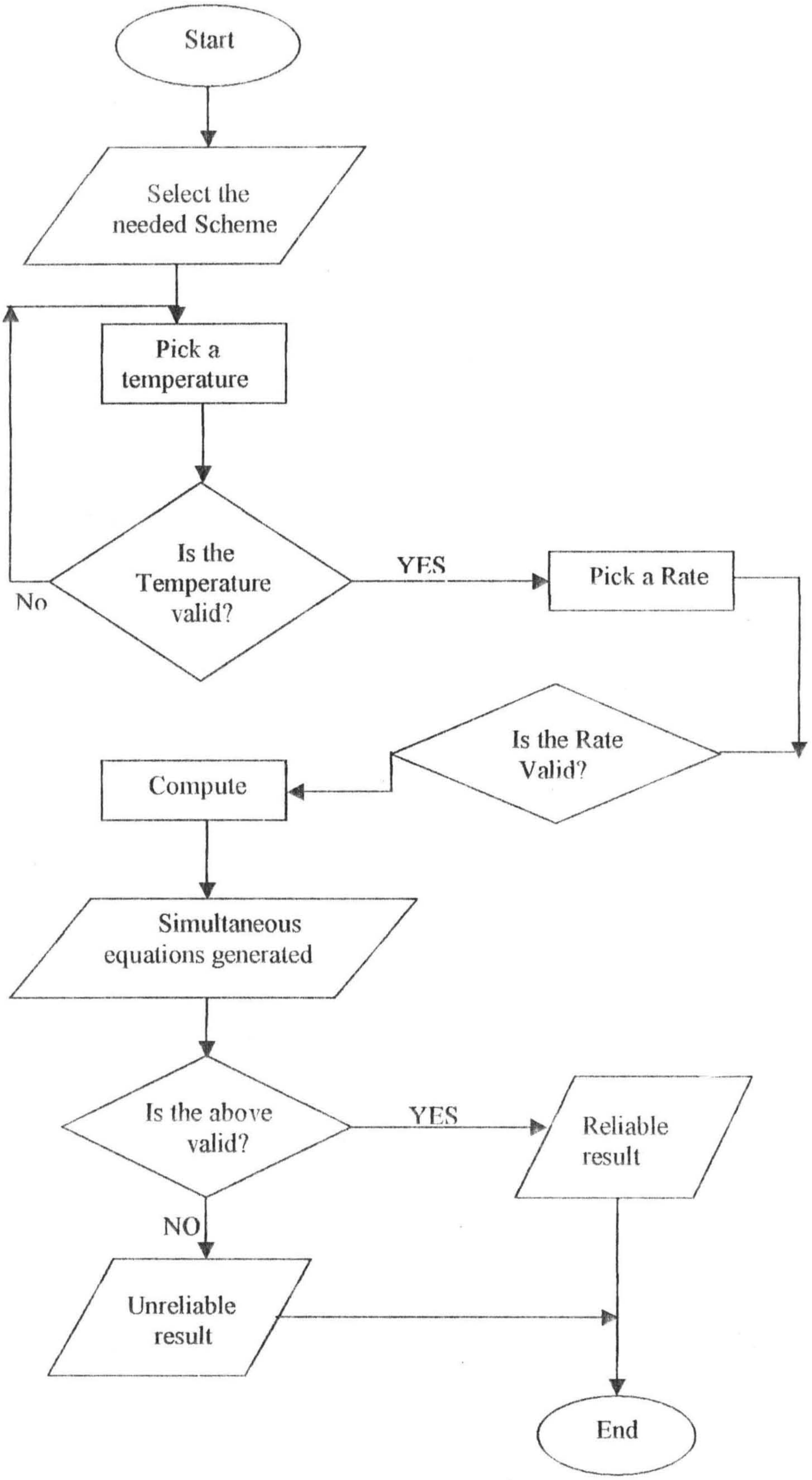
Table J1: Rate and Equilibrium constants
SCHEME ONE (Hydrogen atmosphere)

	TEMP. (^{O}C)	K_F	K_r	K_{me}	K_{Bt}	K_{H2}	K_N
Model 1	350	6.035E3	1.0E13	4.68E5	4.75E-2	2.14E-2	2.595E-2
	370	1.55E4	4.44E13	4.07E7	1.21E8	4.80E-1	8.17E11
		K_F	K_r	K_I	K_{Me}	K_{Bt}	K_{H2}
Model 2	350	6.60E3	4.03E-2	5.13E-2	6.47E-2	8.63-2	1.12E-1
	370	4.46E3	1.31E-2	1.60E-1	2.10E-1	2.24E-1	3.88E2

SCHEME TWO

	Temp.(^{O}C)	K_F	K_r	K_{me}	K_{Bt}	K_{H2}	K_N
Model 1	350	8.64E2	1.79E9	1.21E6	2.38E-2	4.61E-2	6.93E-2
	370	9.46E3	1.14E4	2.16E5	8.2E-2	3.22E-2	1.18E-4
		K_F	K_r	K_I	K_{me}	K_{Bt}	K_{H2}
Model 2	350	1.14E1	3.60E-2	4.68E-2	5.98E-2	8.00E-2	1.12E-1
	370	1.16E1	1.26E-1	1.53E-1	2.02E-1	2.16E-1	3.21E0
		K_F	K_r	K_I	K_{me}	K_{Bt}	K_{H2}
Model 3	350	3.22E3	1.48E4	6.47E4	2.56E5	4.87E5	1.26E3
	370	1.15E4	2.32E4	5.87E4	9.43E4	1.99E5	9.23E2
		K_F	K_r	K_I	K_{me}	K_{Bt}	K_{H2}
Model 4	350	2.27E3	8.28E13	5.50E4	1.87E5	1.28E5	9.99E2
	370	2.07E2	3.29E5	5.18E4	1.93E6	5.42E6	1.20E3

		K_F	**K_r**	**K_I**	**K_{Bt}**	**K_{H2}**	**K_N**
Model 5	350	0	0	0	0	0	1
	370	0	0	0	0	0	1
		K_F	**K_r**	**K_I**	**K_{me}**	**K_{H2}**	**K_N**
Model 6	350	1.18E-1	1.17E4	8.50E3	2.88E5	2.22E3	5.03E0
	370	6.80E-2	3.35E3	4.034E3	2.37E4	1.89E2	2.71E0
		K_F	**K_r**	**K_I**	**K_{me}**	**K_{Bt}**	**K_{H2}**
Model 7	350	1.15E1	3.60E-2	4.68E-2	5,98E-2	8.00E-2	1.12E-1
	370	1.16E1	1.26E-1	1.53E-1	2.03E-1	2.17E-1	3.21E0


Start
Select the needed Scheme
Pick a temperature
Is the Temperature valid?
No
YES
Pick a Rate
Is the Rate Valid?
Compute
Simultaneous equations generated
Is the above valid?
YES
Reliable result
NO
Unreliable result
End

FLOWCHART

APPENDIX I

```
Private Sub Command1_Click()
Unload Me
Load frm1
frm1.Show

End Sub

Private Sub Command2_Click()
Dim labb As Double
Text1.Text = ""

If ((Label1.Caption = "" Or Label2.Caption = "")) Then
   msg% = MsgBox("Pick one in each of the Option above, Please", vbOKOnly, "Error
Entering")
      If msg% = 1 Then
         Exit Sub
      End If
Else
      lab$ = Label2.Caption
      For t = 0 To 4
         ff = Val(frm1.Text2(t).Text)
         Call main
         If Label2.Caption = "Rate1" Then
            X1 = ci
            X2 = -1 * cp
            X3 = -1 * ch * r11
            X4 = -1 * cb * r11
            X5 = -1 * cme * r11
            X6 = -1 '************

         ElseIf Label2.Caption = "Rate2" Then
            X1 = ch
            X2 = -1 * ch
            X3 = -2 * cp * r11
            X4 = -1 * ct * r11
            X5 = -1 * cb * r11
            X6 = -1 * cme * r11

         ElseIf Label2.Caption = "Rate3" Then
            X1 = ci
            X2 = -1 * ch ^ 2 * r11
            X3 = -1 * ct ^ 2 * r11
            X4 = -1 * cb ^ 2 * r11
            X5 = -1 * cme ^ 2 * r11
            X6 = -1 * cp ^ 2 * r11

         ElseIf Label2.Caption = "Rate4" Then
            If ch <> 0 Then
               X1 = ci / ch
            Else
```

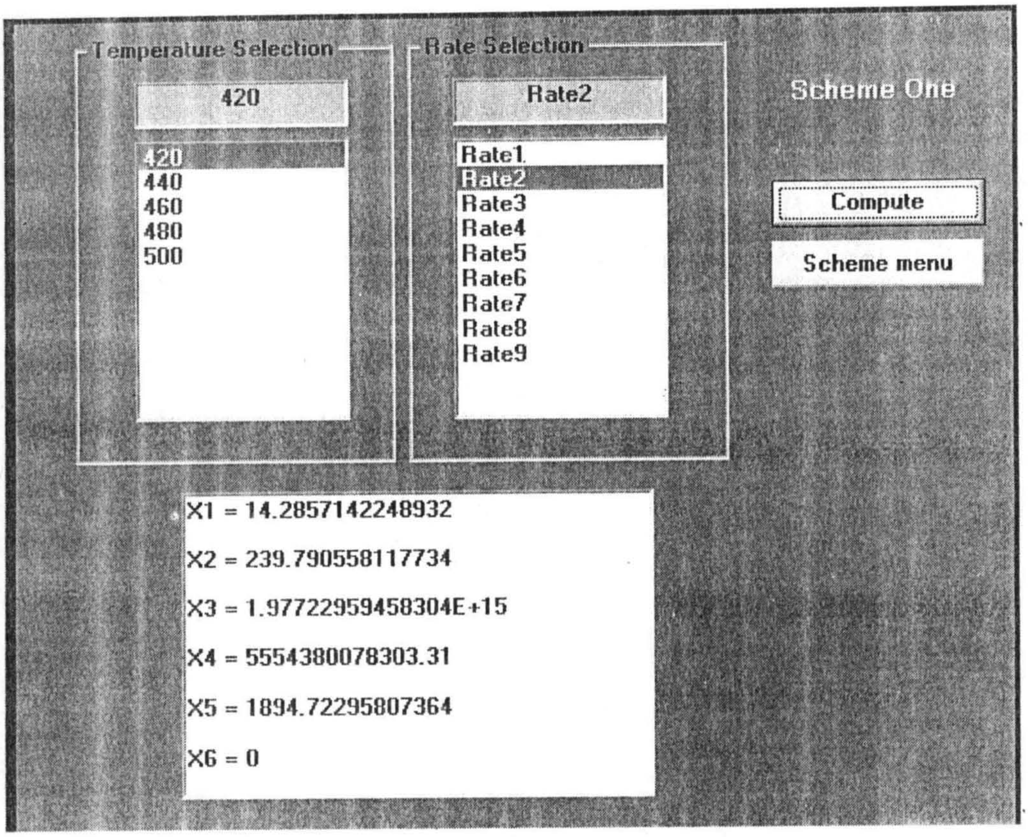
```
        X1 = ci
    End If
    X2 = -1 * ch ^ 4 * r11
    X3 = -1 * ct ^ 4 * r11
    X4 = -1 * cb ^ 4 * r11
    X5 = -1 * cme ^ 4 * r11
    X6 = -1 * cp ^ 4 * r11

ElseIf Label2.Caption = "Rate5" Then
    X1 = ct * ch
    X2 = -1 * cb * cme
    X3 = -4 * cp ^ 2 * r11
    X4 = -1 * ct ^ 2 * r11
    X5 = -1 * cb ^ 2 * r11
    X6 = -1 * cme ^ 2

ElseIf Label2.Caption = "Rate6" Then
    X1 = ci
    X2 = -1 * cp
    X3 = -1 * ch * r11
    X4 = -1 * ct * r11
    X5 = -1 * cb * r11
    X6 = -1 * cme * r11

ElseIf Label2.Caption = "Rate7" Then
    If cme <> 0 Then
        X1 = ct * ch / cme
    Else
        X1 = ct * ch
    End If
    X2 = -1 * cb
    X3 = -2 * cp * r11
    X4 = -1 * ch * r11
    X5 = -1 * ct
    X6 = -1 * cme * r11

ElseIf Label2.Caption = "Rate8" Then
    X1 = ci
    X2 = -1 * cp
    X3 = -1 * ch * r11
    X4 = -1 * ct
    X5 = -1 * cb
    X6 = -1 * cme

ElseIf Label2.Caption = "Rate9" Then
    If ch <> 0 Then
        X1 = cb * cme / ch
    Else
        X1 = cb * cme
    End If
```

```
        X2 = -1 * ct
        X3 = -2 * cp * r11
        X4 = -1 * ch * r11
        X5 = -1 * cb * r11
        X6 = -1 * cme

      ElseIf Label2.Caption = "Rate10" Then
        X1 = ch
        X2 = -1 * ch
        X3 = -2 * cp * r11
        X4 = -1 * cb * r11
        X5 = -1 * cme * r11
        X6 = -1 * 0.546 '*****************

      ElseIf Label2.Caption = "Rate11" Then
        If cb <> 0 Then
          X1 = ch * ct / cb
        Else
          X1 = ch * ct
        End If
        X2 = -1 * cme
        X3 = -2 * cp * r11
        X4 = -1 * ch * r11
        X5 = -1 * cb * r11
        X6 = -1 * ct
      End If

      X6 = X6 * 0
   X6 = r11 - X6
      Call mat(matric())
    Next t

    Call matGauss(matric())

'Result Display

Text1.Visible = True
For b = 0 To 4
  Text1.SelText = "X" & b + 1 & " = " & matric(b, 5)
  Text1.SelText = vbCrLf & vbCrLf
Next b
Text1.SelText = "X6 = " & 0

End If
End Sub

Private Sub Form_Load()
Text1.Visible = False

List1.AddItem "330"
```

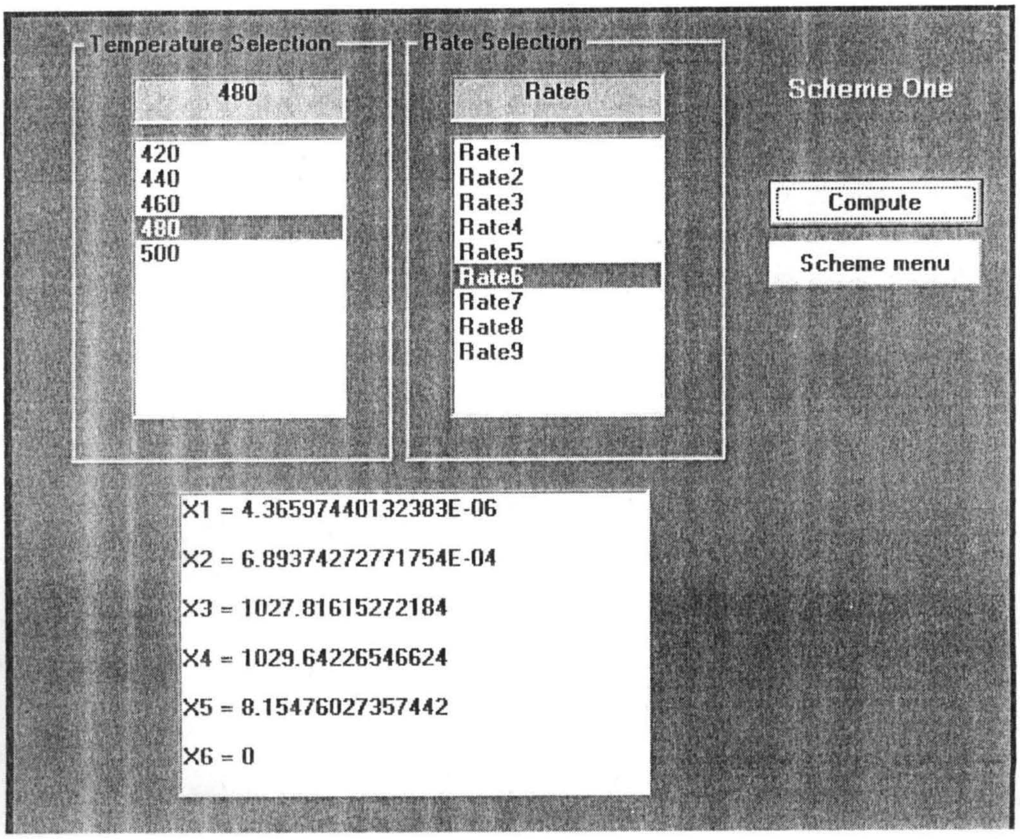
```
List1.AddItem "350"
List1.AddItem "370"
List1.AddItem "400"
List1.AddItem "500"

List2.AddItem "Rate1"
List2.AddItem "Rate2"
List2.AddItem "Rate3"
List2.AddItem "Rate4"
List2.AddItem "Rate5"
List2.AddItem "Rate6"
List2.AddItem "Rate7"
List2.AddItem "Rate8"
List2.AddItem "Rate9"
List2.AddItem "Rate10"
List2.AddItem "Rate11"

End Sub

Private Sub Form_QueryUnload(Cancel As Integer, UnloadMode As Integer)
  'Cancel = True
End Sub

Private Sub List1_Click()
Label1.Caption = List1.List(List1.ListIndex)
End Sub

Private Sub List2_Click()
Label2.Caption = List2.List(List2.ListIndex)
End Sub


Private Sub Command2_Click()

'End

End Sub

Private Sub Form_Load()
Command1.TabIndex = 0
For y = 0 To 29
  Text1(y).Visible = False
Next y

For g = 0 To 5
  Text2(g).Visible = False
Next g
End Sub

Private Sub Form_QueryUnload(Cancel As Integer, UnloadMode As Integer)
```

```
  'Cancel = True
End Sub

Private Sub Option1_Click()
If Option1 = True Then
   Unload Me
   Load Form1
   Form1.Show
   Form1.Label1.Caption = ""
   Form1.Label2.Caption = ""
   Form1.Text1.Text = ""
End If
End Sub

Private Sub Option2_Click()
If Option2 = True Then
   Unload Me
   Load Form2
   Form2.Show
   Form2.Label1.Caption = ""
   Form2.Label2.Caption = ""
   Form2.Text1.Text = ""
End If
End Sub

Private Sub Option3_Click()
If Option3 = True Then
   Unload Me
   Load Form3
   Form3.Show
   Form3.Label1.Caption = ""
   Form3.Label2.Caption = ""
   Form3.Text1.Text = ""
End If
End Sub

Private Sub Option4_Click()
If Option4 = True Then
   Unload Me
   Load Form4
   Form4.Show
   Form4.Label1.Caption = ""
   Form4.Label2.Caption = ""
   Form4.Text1.Text = ""
End If
End Sub

Private Sub Option5_Click()
If Option5 = True Then
   Unload Me
```

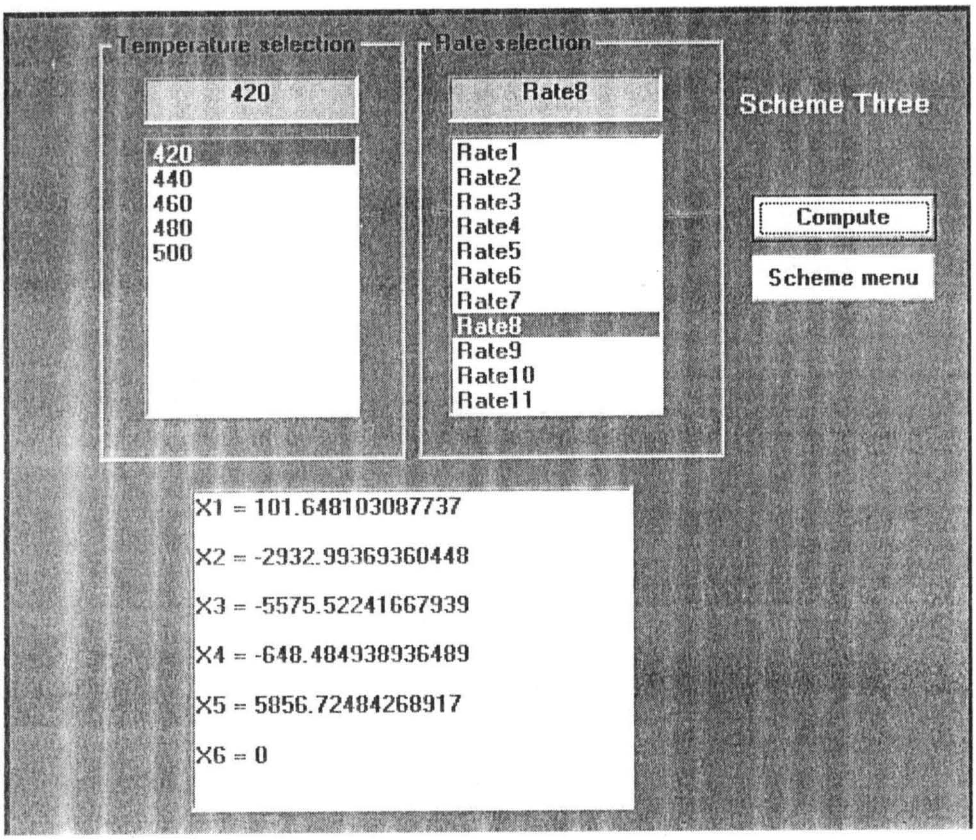
```
    Load Form5
    Form5.Show
    Form5.Label1.Caption = ""
    Form5.Label2.Caption = ""
    Form5.Text1.Text = ""
End If
End Sub

Private Sub Option6_Click()
If Option6 = True Then
    Unload frm1
    Load Form6
    Form6.Show
    Form6.Label1.Caption = ""
    Form6.Label2.Caption = ""
    Form6.Text1.Text = ""

End If
End Sub
```



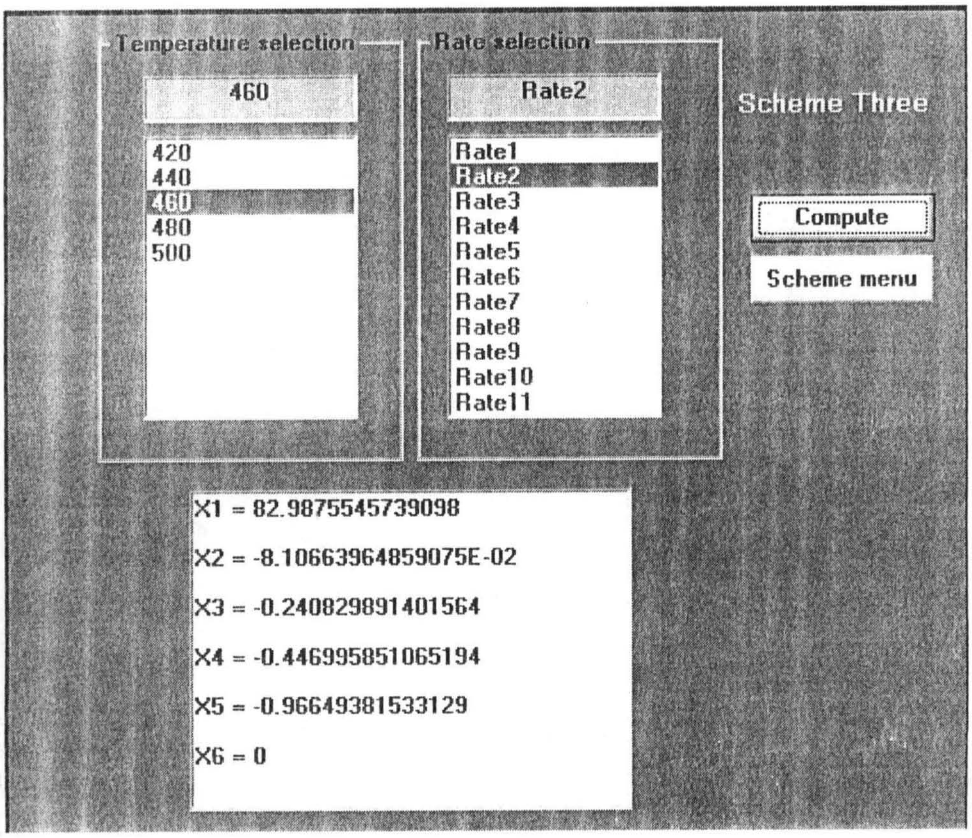
```
X1 = 14.2857142248932

X2 = 239.790558117734

X3 = 1.97722959458304E+15

X4 = 5554380078303.31

X5 = 1894.72295807364

X6 = 0
```



```
X1 = 4.36597440132383E-06

X2 = 6.89374272771754E-04

X3 = 1027.81615272184

X4 = 1029.64226546624

X5 = 8.15476027357442

X6 = 0
```



```
X1 = 101.648103087737

X2 = -2932.99369360448

X3 = -5575.52241667939

X4 = -648.484938936489

X5 = 5856.72484268917

X6 = 0
```



```
X1 = 82.9875545739098

X2 = -8.10663964859075E-02

X3 = -0.240829891401564

X4 = -0.446995851065194

X5 = -0.96649381533129

X6 = 0
```