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Keith Jennings
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AN APPLICATION OF SEQUENTIAL EXPERIMENTAL DESIGN
IN
CATALYST KINETIC STUDIES

A thesis submitted for the degree of
Doctor of Philosophy

by

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August 1984
To

Late Mrs Sharda Devi
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PREFACE

The conditions of the candidature for the degree of Doctor of Philosophy in the University of Sydney require that "the candidate must state generally in the preface and specifically in the notes the source from which his information is derived, the extent to which he has availed himself of the work of others and the portion of the work he claims as original"

The sequential experimental design criterion and reparameterization are frequently reported in literature for improving the precision of parameter estimates. The use of reparameterized kinetic model in sequential experimental design (Section 4.4) and comparative performance of design criteria (Section 4.5) are original. The stopping criterion of terminating the sequential experimental design programme is proposed by the author. The program (EXPDES) which performed the parameter estimation and sequential experimental design was written by the author. The Quasi-Newton minimisation code was taken from the NAG library.

The design of the differential reactor system (Chapter 5) and the major portion of the construction was carried out by the author. The reactor was operated by the author and all the experimental results and analysis of these results (Chapters 6 and 7) are original. From the kinetic results, a new mechanism (Section 6.2.4) for the ethylene hydrogenation reaction over palladium catalyst is proposed.
SUMMARY

Traditionally, the development of an accurate kinetic model and estimation of its parameters has been a costly and time consuming task, requiring extensive experimentation under laboratory conditions. Especially in gas-solid reaction systems, it is generally assumed that the accuracy and precision of the model is improved by increasing the amount of data collected. In a well designed experimental plan this assumption is usually true. However, in a poorly designed experimental plan, the collection of an increased volume of data rarely improves the accuracy and the precision.

The objective of this study was to assess the feasibility of applying the concepts of efficient sequential experimental design to the problem of parameter estimation in a laboratory study of catalyst kinetics.

In this work, available design criteria which have been proposed for sequentially designed experiments to estimate parameters precisely in kinetic models were compared. Criteria which seek to alter the shape of the joint confidence region of the parameter estimates, or to reduce cross correlation effects were proved useful, but the Minimum Volume Criterion of G E P Box and collaborators emerged as the most generally satisfactory.

It is well known that the precision of parameter estimates is reduced if they are strongly correlated and the experimental data are
noisy. Simulation studies were used to show that sequential experimental design can be used more effectively to reduce these problems if it is coupled with a reparameterized model. Better parameter estimates can be obtained with a more economical experimental programme, even in the presence of significant experimental noise. A natural criterion, expressed in terms of the number of function evaluations required to compute the optimal design, emerged as a means of terminating the sequential experimental design programme.

An experimental system was then developed based on an on-line computer controlled reactor with automatic sequencing of the designed experiments to study catalyst kinetics. The ethylene hydrogenation reaction over palladium/alumina (non-porous) catalyst was used as the test reaction system. This system was used to demonstrate experimentally the advantages over the conventional approach of using sequential experimental design strategy for catalyst kinetic studies.

A conventional kinetic study of the ethylene hydrogenation reaction over palladium/alumina catalyst was performed using a differential flow reactor. The catalyst was reproducible and showed no significant signs of deactivation in the temperature range 50°C to 90°C. A change in the activation energy was observed around 70°C. Different activities were observed for differently conditioned palladium catalysts; the hydrogen conditioned catalyst showed higher apparent activation energy compared to the nitrogen conditioned catalyst. A new mechanism involving reaction between an adsorbed ethyl radical and gaseous hydrogen was proposed, and two kinetic models were derived for the two differently conditioned catalysts. A good correlation between
the observed reaction rate and the proposed kinetic models was obtained.

The sequential experimental design strategy based on Minimum Volume Criterion was applied to the ethylene hydrogenation reaction. It was found that the sequential design achieved better precision with a fewer number of laboratory experiments compared to the conventional kinetic studies. The usefulness of the proposed criterion for terminating the sequential experimental design programme was also demonstrated.
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NOMENCLATURE

**Arabic Symbols**

- **A**: external surface area of catalyst
- **A**\_0**: pre-exponential factor in Arrhenius expression, Equation (3.15)
- **C**: overall correlation coefficient, Equation (3.24)
- **C**\_T\_D\_T**\_T^{-1}: denotes the matrix \((D^T D)^{-1}\)
- **C\_2H\_4**...**M**: adsorbed ethylene molecule
- **C\_2H\_5**...**M**: adsorbed ethyl radical
- **C\_2H\_6**...**M**: adsorbed ethane molecule
- **ΔC**: concentration difference between the catalyst surface and the bulk gas
- **c\_p**: specific heat
- **D**: \((nxp)\) matrix of element \(\partial f(X,K)/\partial k_j\)
- **D**: molecular diffusivity
- **E**: activation energy of reaction, kcal mole\(^{-1}\)
- **F**: reactant molar flow rate, kg mole hr\(^{-1}\)
- **H\_\_1**: hydrogen free radical
- **H**...**M**: adsorbed hydrogen atom
- **HM**: dissolved hydrogen atom
- **ΔH**: heat of adsorption
- **h**: heat transfer coefficient
k* reparameterized Arrhenius pre-exponential factor, Equation (3.17)
K vector of model parameters
K equilibrium constant
k rate constant
kg mass transfer coefficient
M catalyst active site
m number of operating variables
M_A, M_B Molecular weights of the gases
n number of model parameters
P total pressure, atm
P_{C_2H_4} partial pressure of ethylene, atm
P_{H_2} partial pressure of hydrogen, atm
Pr Prandtl number
R ideal gas constant
R correlation matrix of elements v_{ij} / \sqrt{v_{ii} v_{jj}}
Re Reynolds number
r_{C_2H_6} rate of formation of ethane
S sum of least squares function
s standard deviation of parameter estimates
Sc Schmidt number
St Stanton number
T absolute temperature (°K)
T* reference temperature
T' 1/T - 1/T*, Equation (3.19)
t t - distribution function
objective function

superficial velocity

variance-covariance matrix of parameter estimates

degrees of freedom (n - p)

catalyst weight, kg

weighting factor

vector of operating variable setting for experiment u

mole fraction of ethylene

mole fraction of hydrogen

(nx1) column vector of experimental values

(nx1) column vector of expected values

reaction order with respect to ethylene

reaction order with respect to hydrogen

constant defined in Equation (3.11)

expected error

defined in Equation (3.20)

ith eigenvalue of $(X^T X)$ matrix

viscosity

density

Lennard Jones constant, Equation (D.5)

variance of error in the observed dependent variable

defined in Equation (3.21)

reaction conversion
\( \omega_i \)  
ith principal axis of the joint confidence hyperellipsoid

\( \Theta_{AB} \)  
collision integral for the binary, Equation (D.5)

**Subscript**

\( H_2 \)  
hydrogen conditioned catalyst

\( N_2 \)  
nitrogen conditioned catalyst

\( o \)  
inlet condition

\( u \)  
experiment number

**Superscript**

\(-\)  
least square estimate

**Abbreviations**

RP  
reparameterized

JCR  
joint confidence region

NC  
nitrogen conditioned

HC  
hydrogen conditioned

MVD  
minimum volume design

SD  
shape design

CD  
correlation design
CHAPTER 1

INTRODUCTION

CONTENTS

1.1 Aims .................................................. 2
Kinetic studies are powerful tools for chemical engineers since they provide them with a better understanding of chemical reactions. They form bases for more accurate designs of new chemical reactors and also provide better insight into the behaviour of existing reactors.

In general, kinetic studies are performed: (a) to establish the form of a possible reaction model; (b) in selecting a model from a set of rival possibilities, also called "model discrimination"; and (c) in improving the precision of estimated parameters appearing in a model.

Traditionally, the development of an accurate kinetic model and estimation of its parameters has been a costly and time consuming task, requiring extensive experimentation under laboratory conditions. Especially in gas-solid reaction systems, the reaction rates have been measured by varying one variable at a time and subsequent correlations between the data obtained were used to provide a kinetic model and its parameters. In general, it is assumed that the accuracy and precision of the model is improved by increasing the amount of data collected. In a well designed experimental plan, this assumption is usually true. However, in a poorly designed experimental plan, the collection of an increased volume of data rarely improves the accuracy and the precision.

During the last decade, the use of a digital computer for real time data processing and direct digital control has found wide application in the chemical processing field, both in research and in industrial environments. The advent of high speed digital computation has also increased the application of optimization techniques. The significance of optimization techniques in this context lies in
attempting to adjust some system's variables to improve the performance of that system, measured in some way. One such application of these techniques is in the field of sequential experimental design applied to kinetic modelling. The sequential experimental design strategy has been shown to improve the precision of the parameter estimates of a kinetic model. To date, however, attention has only been devoted to establishing its theoretical importance for parameter estimation with little demonstration of its practical application.

This leads one to the idea that a possible application of computer technology is in the computer-aided development of reaction kinetic models for gas-solid catalyst systems.

The use of a computer for on-line control of a reactor for reaction kinetic experiments, including automatic sequencing of the designed experiments, could be the ultimate in reaction kinetic studies. This procedure would not only accelerate the collection of kinetic data and reduce the experimentation time, but it could also improve the precision of the parameter estimates for a kinetic model.

1.1 Aims

As implied above, the overall aim of this work was experimentally to demonstrate the advantages of using a sequential experimental design strategy for catalyst kinetic studies. The work was divided into four sections, each covering a single aspect of the overall plan.
1. A study of sequential experimental design by computer simulation of a reaction system. The following two additional objectives were taken into consideration when designing the simulation studies on the basis of the sequential experimental design strategy:

   i. to compare various design criteria focussing on their relative performance in the precision of the parameter estimation for a power law rate model.

   ii. to study the influence of reparameterization on sequential experimental design and on the accuracy and convergence of the parameter estimates at various noise levels.

2. To demonstrate experimentally, using a suitable test reaction system, that an on-line computer controlled reactor could be used to sequentially design and to perform experiments for catalyst kinetics measurements.

3. To carry out conventional kinetic studies for the selected ethylene hydrogenation reaction over supported palladium catalyst and to establish its mechanism and a kinetic rate model.

4. To estimate the kinetic parameters for the ethylene hydrogenation reaction on supported palladium catalyst by utilizing a sequential experimental design strategy.
CHAPTER 2

ETHYLENE HYDROGENATION

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2.6 Ethylene Hydrogenation Reaction over Supported Palladium Catalyst ........................... 26
2.1 INTRODUCTION

In this chapter, the relevant literature on the background of catalysis by metals and the metal catalysed ethylene hydrogenation reaction is reviewed. The reasons for selecting this reaction (ethylene hydrogenation) for the sequential experimental design studies are discussed.

2.2 Catalysis by Metals

The primary catalytic function of metals is hydrogenation and dehydrogenation; that is, metal catalysts are effective for reactions that involve the addition to or abstraction from a molecule of one or more molecules of hydrogen. This is because metals readily dissociate molecular hydrogen into hydrogen atoms and also catalyse the reverse process by virtue of their ability to adsorb the molecule in an appropriate manner (Bond (1962)). Very few metals act as oxidation catalysts because, generally speaking, even catalysed oxidation requires high temperature at which oxidation of the metal to the metal oxide is rapid. Thus only noble metals (such as platinum, palladium and silver) are commonly used as metallic oxidation catalysts.

Basically, the function of the metal catalyst is to render temporarily immobile one or more of the reacting molecules at the surface. This is the process known as adsorption and may involve simple attractive forces (physical adsorption) or a degree of chemical bonding (chemisorption). The latter is by far the most important in the process of catalysis. In the adsorbed state, the electronic rearrangement or
strains induced in the adsorbed molecule render it more vulnerable to attack by other molecules (which may or may not be adsorbed) or to rearrangement of the molecules on the surface. The surface intermediate so formed is desorbed as the product.

The strength with which the reactant molecule or the activated intermediate complex is adsorbed is one of the important factors in selecting the catalyst. For efficient catalysis, the strength of adsorption of the reactant(s) must lie within fairly wide limits. If a reactant is too strongly adsorbed it will be difficult to remove and it may then constitute a poison. On the other hand, if it is too weakly adsorbed, it will have little chance to react. For a given reaction it is therefore expected that there will be an inverse relationship between the strength of adsorption of reactant and the catalytic efficiency (Bond (1962)). This reflects the enormous importance of adsorption in the process of catalysis.

It has been found (Bond (1962)) with every metal so far investigated - with the single exception of gold - that the strengths of adsorption of those gases which do chemisorb fall in following sequence:

\[ \text{O}_2 > \text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{CO} > \text{H}_2 > \text{CO}_2 > \text{N}_2 \]

This indicates that oxygen has the highest strength of adsorption; that is, if oxygen is present in trace amounts in the reactants stream it can poison the metal catalyst.

To understand further details of metals as catalysts, the two important aspects of geometric factors and electronic factors will now be considered.
2.2.1 The Geometric Factor

In the field of catalysis, the term geometric factor refers to the lattice spacing of the atoms in a catalyst. Therefore, the geometric factor in this section will be discussed in terms of lattice spacing of metals only.

Over fifty years ago, Sherman and Eyring (1932) calculated the magnitude of the activation energies of adsorbed hydrogen molecules on different metals and concluded that the lattice spacing affects the magnitude of the activation energy. It is apparent that for a given reaction involving the adsorption of specific molecules, certain lattice spacing will favour adsorption with the correct strength. Chemical adsorption, shown in Figure 2.1, takes place during the ethylene hydrogenation reaction over nickel (Twigg and Rideal (1940)). If the Ni-C bond length is taken to be the same as that in Ni(CO)$_4$ (1.82 Å) and the C-C bond length is that of paraffins (1.54 Å), the Ni-C-C valence angle can be calculated for various values of the Ni-Ni distance. The principal lattice planes which are exposed at the surface of nickel correspond to Ni-Ni distances of 2.48Å and 3.51Å (Figure 2.2). Using simple geometry the Ni-C-C angle is very close to 105° on the 2.48Å spacing and to 123° on 3.51Å spacing. Now, the strain free tetrahedral angle is 109°28' (Thomas and Thomas (1967)). Hence the complex would be strained to a greater extent if adsorbed on the 3.51Å spacing and the more stable situation (strongest adsorption) would occur on the 2.48Å spacing. This would lead to expectation of a higher reaction rate on the 3.51Å spacing. The (110) lattice plane of nickel contains many such spacings and is observed to be more active than
FIGURE 2.1: Adsorbed ethylene molecule on nickel (Pratt (1979)).
Figure 2.2: Representation of the spacing in three lattice planes in a crystal of nickel (Thomas and Thomas (1967)).
randomly oriented nickel surfaces for the ethylene hydrogenation reaction (Beeck et. al. (1940)). This idea has been extended to the other metals, as shown in Figure 2.3, where the optimum spacing is exhibited by rhodium (Beeck (1950)).

The considerations above are simple to visualise, but it is important to note that surface parameters (lattice spacing etc.) are often different from the bulk values used for illustrations and that the metal does not exist as extensive plane faces but rather as small irregular crystallites on the support.

2.2.2 The Electronic Factor

The electronic factor in metal catalysis is generally related to the electronic properties of metals. In a simple way, it can be said that there is a relationship between the catalytic activities and the electronic structure of the bulk solid. Also, it is clear from the last sub-section that catalysis involves the making and breaking of bonds at the catalyst surface. In other words, the transfer of electrons between the reactant molecule and the solid catalyst surface takes place. Therefore, the electronic structure of the bulk solid metal is an important factor in the catalysis.

Many theories have been put forward to explain the metal electronic structure. Among these theories, Pauling's Theory (Pauling (1949)) visualised metal crystals as being held together by covalent bonds between the adjacent atoms. Pauling attempted to distinguish between those electrons involved in the formation of the covalent bonds
FIGURE 2.3: Activation of various metallic film as a function of metal lattice distance. (Beeck (1950)).
and those which are non-bonding and are responsible for the magnetic and electrical properties of a metal. The former form \(dsp\)-type hybrid orbitals, while the latter remain as atomic \(d\)-orbitals. For transition metals, Pauling's theory calculated the extent to which the \(d\)-electrons participate in \(dsp\)-orbitals and expressed this as the 'percentage \(d\)-character of the bond' \((\delta)\). The higher the value of \(\delta\), the fewer the number of atomic \(d\)-orbitals available at each atom. In other words, \(\delta\) is the measure of the unavailability of electrons for the atomic \(d\)-orbitals. Now, if chemisorption is considered to be a covalent type of bond (see Section 2.1.1), the strength of the bond will depend upon the availability of bonding electrons in the atomic \(d\)-orbitals; that is, a high strength bond will occur if \(\delta\) is low.

Boudart (1950) indicated that the variation of the catalytic activity of a number of transition metals for the hydrogenation of ethylene could be represented in the form of a plot of the percentage \(d\)-character \((\delta)\) against the logarithm of the rate constant for the reaction. Beeck (1950) also observed such dependence (see Figure 2.4). As mentioned previously (see Section 2.1.1), rhodium, as in Figure 2.4, has the highest activity.

The geometric and electronic factors are important in catalysis. As such, however, these factors do not completely distinguish one catalyst from another. The advantages of these factors for selecting the metal catalyst for the ethylene hydrogenation reaction will be considered and discussed in the following sub-Section.
FIGURE 2.4: Variation of the percentage d-character of a range of metals against the activity of metals for the ethylene hydrogenation reaction (Beeck (1950)).
2.3 Reaction Kinetics and Mechanism

The hydrogenation of ethylene in the presence of metallic catalysts has been the subject of intensive investigation since its discovery at the turn of the century. However, the actual kinetics of the simple overall reaction

\[ \text{H}_2 + \text{C}_2\text{H}_4 \xrightarrow{\text{Catalyst}} \text{C}_2\text{H}_6 \]  

are still controversial and have been further complicated by the poisoning effects which are frequently encountered.

Most of the earlier work was carried out in closed systems, often on metal films, and the progress of the reaction was followed by noting the change of system pressure with time. In recent years more attention has been devoted to flow systems using supported metal catalyst. Often, nickel was used in different forms as the catalyst for the kinetic studies. A summary of these studies is given in Table 2.1 which reveals that there is general agreement that the reaction is first order in hydrogen partial pressure and shows lower activation energies for static systems. The order in ethylene is more controversial but where this has been determined a value of less than 0.4 is usually obtained. One unusual feature of the reaction is that the activation energy tends to decrease with rise in temperature (Rideal (1922), Kato et. al. (1969)) and there seems to be a reaction mechanism shift between 150 and 200°C (Fulton and Crosser (1965)).

Earlier studies on nickel catalyst suggest that the reaction proceeds through an associative adsorption of ethylene but opinions
### TABLE 2.1: Summary of the Kinetic Studies of Catalytic Hydrogenation of Ethylene on Nickel.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Conditions</th>
<th>System</th>
<th>Test</th>
<th>Activation Energy (kcal/mole)</th>
<th>Rate Relation and/or Reaction Mechanism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nickel Foil</strong></td>
<td>75°C to 200°C, P = 1 atm</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>1.8</td>
<td>r = k ⃗PA, 8 excess</td>
<td>Readel (1922)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>r = k ⃗PB, A excess</td>
<td>Schuster (1932)</td>
</tr>
<tr>
<td><strong>Nickel on Charcoal</strong></td>
<td>-64°C to 50°C</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>3.6</td>
<td>r = k ⃗PA</td>
<td>Parase et al (1934)</td>
</tr>
<tr>
<td><strong>Nickel Wire</strong></td>
<td>20°C to 250°C, Pₐ, P₈ = 7 to 20 atm</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>---</td>
<td></td>
<td>Toyama (1937)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Toyama (1938)</td>
</tr>
<tr>
<td><strong>Nickel Powder</strong></td>
<td>-78°C to 0°C, Pₐ, P₈ = 10 to 130 atm</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>6.1</td>
<td>r = k ⃗PA, 8 constant</td>
<td>Twigg and Readel (1939)</td>
</tr>
<tr>
<td><strong>Nickel Wire</strong></td>
<td>99°C to 165°C, Pₐ, P₈ = 10 to 40 atm</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>---</td>
<td></td>
<td>Twigg and Readel (1939)</td>
</tr>
<tr>
<td></td>
<td>156°C</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>14</td>
<td></td>
<td>Eley (1948)</td>
</tr>
<tr>
<td><strong>Nickel Wire</strong></td>
<td>62 to 206°C, Pₐ, P₈ = 38 to 304 atm</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>---</td>
<td></td>
<td>Beeck (1950)</td>
</tr>
<tr>
<td><strong>Evaporated Nickel Film</strong></td>
<td>-80°C to 150°C</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>10.7</td>
<td></td>
<td>Twigg and Readel (1950)</td>
</tr>
<tr>
<td><strong>Nickel on Kieselgur</strong></td>
<td>156°C, Pₐ = 50 mm Hg</td>
<td>Closed</td>
<td>C₂H₄, H₂, D₂</td>
<td>---</td>
<td></td>
<td>Jenkins and Readel (1955)</td>
</tr>
<tr>
<td><strong>Nickel Film</strong> (carbided)</td>
<td>20°C to 170°C, Pₐ = 2 to 10 mm Hg</td>
<td>Closed, C₂H₄, H₂ agitated</td>
<td></td>
<td>10.2</td>
<td>r = k ⃗PA, 8 excess</td>
<td>Pauls et al (1958)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Nickel-on-alumina</strong> (carbided)</td>
<td>70°C, P = 1 to 5 atm, Xₐ = 0.4 to 0.9</td>
<td>Flow</td>
<td>C₂H₄, H₂</td>
<td>11.6</td>
<td>r = k ⃗PA ⃗PB, 8 excess</td>
<td>Tull and Farnsworth (1961)</td>
</tr>
<tr>
<td><strong>Nickel Plate</strong></td>
<td>16°C to 95°C, Pₐ, P₈ = 10 atm</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>---</td>
<td></td>
<td>Tsuji and Ziegler (1971)</td>
</tr>
<tr>
<td><strong>Evaporated Nickel Film</strong></td>
<td>-40°C to 40°C, Pₐ = 38 atm, P₈ = 49 mm Hg</td>
<td>Closed</td>
<td>C₂H₄, H₂</td>
<td>---</td>
<td></td>
<td>Tsuji and Ziegler (1971)</td>
</tr>
<tr>
<td><strong>Nickel-on-arsenious alumina</strong> (carbided)</td>
<td>60°C to 100°C, Xₐ = 0.27</td>
<td>Flow</td>
<td>C₂H₄, H₂</td>
<td>10.3</td>
<td>r = k ⃗PA ⃗PB, 8 excess</td>
<td>Tsuji and Ziegler (1971)</td>
</tr>
<tr>
<td><strong>Nickel on silica</strong> (carbided)</td>
<td>90°C to 100°C, Xₐ = 0.05 to 0.4</td>
<td>Flow</td>
<td>C₂H₄, H₂</td>
<td>12.0</td>
<td>r = k ⃗PA ⃗PB, 8 excess</td>
<td>Roh and Hughes (1974)</td>
</tr>
</tbody>
</table>

* Subscript A denotes hydrogen, and B designates ethylene

P = total pressure
X = mole fraction
differ as to whether the subsequent reaction goes via a Langmuir-Hinshelwood mechanism with adsorbed hydrogen or by an Eley-Rideal reaction with gas phase or Van der Waals adsorbed hydrogen. Farkas and Farkas (1938), on the basis of exchange experiments suggested a reaction involving dissociatively adsorbed hydrogen and adsorbed ethylene. Horiuti and Polanyi (1934) proposed that the reaction goes through a half-hydrogenated state. Later, Jenkins and Rideal (1955) postulated a mechanism involving reaction between adsorbed hydrogen on the nickel surface and gaseous ethylene. The dissociative adsorption of ethylene with the formation of poisonous acetylenic residues on the active site was suggested to account for the observed adverse effect of ethylene on the reaction rate.

Beeck (1950) suggested that some ethylene molecules are adsorbed on that part of the surface not covered by acetylenic complexes and that the rate controlling step is the reaction between adsorbed ethylene and adsorbed hydrogen. A fast reaction between ethylene and adsorbed hydrogen also occurs. Using the exchange reaction with deuterium, Twigg (1950) concluded that hydrogen is first dissociated into atoms on the nickel surface through reaction with adsorbed ethylene. Hydrogenation then occurs with the addition of another hydrogen atom.

Investigations with flow systems have received significantly less attention. Pauls et al. (1959) and Kostenblatt and Ziegler (1971) carried out experiments using flow systems with nickel on alumina catalyst. Both sets of authors obtained a rate equation which suggested a reaction between adsorbed ethylene and gaseous hydrogen, but because
of poisoning effects caused by ethylene, the results were interpreted in terms of the Jenkins – Rideal mechanism (Jenkins and Rideal (1955)). In this mechanism hydrogen is adsorbed on dual sites and reacts with gaseous ethylene, but with no adsorption possible on that fraction of the surface occupied by ethylene or acetylenic complexes.

Recently, Koh and Hughes (1974) carried out an interesting study of hydrogenation of ethylene over a supported nickel/silica-alumina catalyst in a differential reactor. They claimed that the purification of the ethylene feed from all oxygen impurities removed all poisoning effects observed in previous studies. A gradual decrease in catalyst activity was observed due to some black carbonaceous deposits at higher temperatures (> 140°C), but this phenomenon was not observed at lower temperatures. This non-selective behaviour could not be explained by dissociative adsorption of ethylene. The results were interpreted on the basis of ethylene adsorption with no adsorption of hydrogen or ethane and with the reaction between adsorbed ethylene and gaseous hydrogen as the rate controlling step. This leads to the rate equation:

\[ r_{\text{C}_2\text{H}_6} = \frac{k P_{\text{C}_2\text{H}_4} P_{\text{H}_2}}{1 + K_{\text{C}_2\text{H}_4} P_{\text{C}_2\text{H}_4}} \]  

The same equation has been proposed by others (Pauls et. al. (1959), Koestenblatt and Ziegler (1971)) but based on different interpretations. Koh and Hughes (1974) observed a break in their Arrhenius plot at about 130° to 150°C and interpreted the decrease in apparent activation energy at high temperature as due to low surface coverage of ethylene. Similar observations were also made by Fulton and Crosser (1965).
With the exception of Koh and Hughes (1974) all other studies of the ethylene hydrogenation reaction on nickel catalyst indicated that the nickel undergoes some sort of poisoning during the hydrogenation reaction. It has also been observed that the extent of poisoning depends upon the ratio of ethylene and hydrogen in the reaction mixture (Beeck (1950), Jenkins and Rideal (1955), Pauls et. al (1959)).

To understand the surface chemistry of the ethylene adsorption, in recent years there have been several studies of the adsorption of ethylene on transition metal surfaces. Different molecular beam scattering studies for adsorption of ethylene have found that, on nickel and platinum, ethylene is adsorbed irreversibly and dissociatively (Morgan and Somorjai (1969), McCarroll and Thomson (1970), Weinberg et. al. (1974), Zuhr and Hudson (1977)). Studies of chemisorption of ethylene by means of Auger electron spectroscopy (Tescari (1977)) and various techniques of infrared (IR) spectroscopy (Wojtczat et. al. (1975), Prentice et. al. (1976)), including IR reflection spectroscopy (Ito and Suetake (1977)), found that two types of ethylene adsorption exist: \( \pi \) and \( \sigma \) adsorbed ethylene. The adsorbed species are represented as follows:

\[
\begin{align*}
 \text{H}_2\text{C} = \text{CH}_2 \\
 \text{H}_2\text{C} - \text{CH}_2 \\
 \text{M} \\
 \text{M} \quad \text{M}
\end{align*}
\]

\( \pi \)-adsorbed ethylene \hspace{1cm} \( \sigma \)-adsorbed ethylene

The symbol \( \text{M} \) represents the surface metal atom. \( \pi \)-adsorbed ethylene is very unstable and is found in the majority when ethylene is exposed to palladium and platinum surfaces (Prentice et. al. (1976), Soma
(1979, 1982)). On the other hand, \( \sigma \)-adsorbed ethylene is comparatively stable and dominant on a nickel surface (Morrow and Shappard (1969)).

Also, there is general agreement among the different ethylene adsorption studies (IR spectroscopy studies by Erkelens and Liefkens (1967) and Morrow and Sheppard (1969), field emission techniques by Whalley et al. (1970), ultraviolet photo-emission by Demuth and Estman (1974)) that strong, dissociative chemisorption of ethylene takes place on the nickel surface. Recently, Zuhr and Hudson (1977) studied the interaction of ethylene gas with a nickel(110) surface using a combination of modulated beam mass spectrometry and Auger electron spectroscopy techniques. They observed that the interaction of ethylene on a clean nickel(110) surface at a temperature above 150°C leads to the formation of a chemisorbed carbonaceous layer and the carbon concentration was essentially one carbon atom per surface metal atom. A similar phenomenon was utilized by Jenkins and Rideal (1955) and Pauls et al. (1959) and later by Ziegler and coworkers (1971, 1979) for stabilizing their nickel catalyst by pretreating with ethylene at 170°C. Koh and Hughes (1974) also observed the carbonaceous material above 140°C and were not able to explain the formation at low temperature.

With the above discussions on adsorption studies of ethylene on a nickel surface, it is clearly demonstrated that ethylene adsorption on a nickel surface takes place via a \( \sigma \)-adsorption which could lead to the formation of a poisonous acetylenic complex or carbonaceous material. This phenomenon is also clear by geometric and electronic factors. As discussed in sub-Section 2.1 nickel has the tendency to adsorb ethylene strongly at its surface.
The use of nickel as a catalyst for the hydrogenation reaction in the past was merely due to economical reasons in comparison to the more active noble metals such as platinum and palladium. The selection of the metal catalyst for the ethylene hydrogenation reaction for the present study will be discussed in the following section.

2.4 The Choice of Ethylene Hydrogenation Reaction for Sequential Experimental Design Studies

The sequential experimental design strategy has proved to be a significantly important tool in reaction kinetic studies and is generally utilized to improve the precision of parameter estimates of a known kinetic model (Draper and Smith (1966), Beck and Arnold (1977)). The literature has principally addressed its theoretical importance with very little consideration given to its practical application in real kinetic studies. Therefore, it was the purpose of the present study to utilize this statistically proven method in a simple and clean reaction with a known kinetic model.

From a study of the literature it was found that the ethylene hydrogenation reaction on a metal surface is a simple reaction. The study of the ethylene hydrogenation reaction is not commercially significant. However, the general reaction - the hydrogenation of olefinic material on heterogeneous metallic catalysts - is of considerable importance commercially. In addition, the system chosen offers the following advantages:

1. The chemistry of the reaction is well known.
ii. Pyrolysis does not occur at the operating temperatures.

iii. The reaction is essentially irreversible with no significant by-products.

iv. The homogeneous rate of reaction is negligible.

v. Composition analysis is straight-forward (by gas chromatography).

vi. The form of the rate expression is well established.

2.5 Catalyst Selection

The selection of a catalyst is the most important factor in heterogeneous catalysis. As such, the topic is very wide and complicated, particularly when the reaction is complex. For the simple ethylene hydrogenation reaction transition metals have mostly been used. Recently, a few metal oxides (such as ZnO, MgO, CaO) were utilized for this reaction (Dent and Kokes (1969), Inoue and co-workers (1980, 1981)). Amongst the transition metals, as indicated in the last sub-Section, nickel has been used predominantly and its selection was commonly based on economical reasons in comparison to the much more active noble metals such as palladium and platinum.

The following points were taken into consideration for selecting the metal catalyst for the present study of the kinetics of the ethylene hydrogenation reaction utilizing the sequential experimental design technique:

i. Ethylene should not adsorb strongly at the metal surface.
ii. The catalyst should not lose its activity during the sequential experimentation.

These two points are interrelated because strong adsorption of ethylene on the metal surface leads to poisoning effects (see Section 2.2).

If metals as bulk are examined and grouped according to their chemisorption ability then the selection of the metal will be understood easily. Table 2.2 gives a classification of metals according to the number of different gases which can be chemisorbed (Bond (1962)). Hydrogenation activity requires the adsorption of hydrogen and so is confined to groups A, $B_1$, and $B_2$. Group A was rejected since nitrogen gas was to be used as a diluent for the present experimental studies. In group $B_1$, nickel and cobalt are the only two metals. Nickel has been used in different forms for the ethylene hydrogenation reaction and has shown susceptibility to poisoning due to dissociative adsorption of the ethylene (see Section 2.2). Kokes (1969) observed that the cobalt activity was similar to that of nickel for the ethylene hydrogenation reaction except for their bulk structural differences. Therefore, on the ground of poisoning effects and strong adsorption of the ethylene on the metal surface, metals of group $B_1$ were rejected.

Thus, only group $B_2$ is left for consideration. Palladium seems to be the only metal which satisfies both criteria based on recent adsorption studies of ethylene. These studies (Prentice et al. (1976), Soma (1979)) suggested that the ethylene adsorbs as a weakly $\pi$ bonded ethylene complex on the palladium surface. To understand its activity, geometric and electronic factors can be examined.
Table 2.2: A classification of metals according to their abilities in chemisorption (Bond (1962)).

(+ means that strong chemisorption occurs; - means that it is weak or unobservable)

<table>
<thead>
<tr>
<th>Gases</th>
<th>Group</th>
<th>Metals</th>
<th>O₂</th>
<th>C₂H₄</th>
<th>C₂H₆</th>
<th>CO</th>
<th>H₂</th>
<th>CO₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>B₁</td>
<td>Ni, Co</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>B₂</td>
<td>Rh, Pd, Pt, Ir</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Al, Mn, Cu, Au</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>K</td>
<td>+</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>Mg, Ag, Zn, Cd, In, Si, Ge, Sn, Pb, As, Sb, Bi</td>
<td>+</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*These metals absorb hydrogen weakly

The principal lattice planes which are exposed at the surface of palladium correspond to Pd-Pd distances of 2.74Å and 3.87Å (Figure 2.5). If adsorption of ethylene on palladium is considered to be similar to that on nickel (see Figure 2.1), Pd-C-C valance angles may be calculated for these spacings. The calculations gave a picture similar to that for nickel and demonstrated that the adsorption at a spacing of 3.87Å will be strained. On the other hand, if the percentage d-character (δ) is examined for the competitive metals, as shown in Table 2.3, the bonding of the ethylene molecule at the palladium surface is seen to be weaker than on nickel and platinum surfaces (also see Figure...
FIGURE 2.3: Representation of the spacing in three lattice planes in a crystal of palladium.
2.4). This phenomenon is well explained by recent adsorption studies of ethylene on the palladium surface by Soma (1979) which demonstrated the predominant occurrence of $\pi$-adsorbed ethylene.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\sigma$-character (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>39.5</td>
</tr>
<tr>
<td>Ni</td>
<td>40</td>
</tr>
<tr>
<td>Pt</td>
<td>44</td>
</tr>
<tr>
<td>Pd</td>
<td>46</td>
</tr>
<tr>
<td>Rh</td>
<td>50</td>
</tr>
</tbody>
</table>

It is also noteworthy that supported palladium catalyst has not been reported in the literature for use in kinetic studies of the ethylene hydrogenation reaction using a flow system. This point was also taken into consideration in the catalyst selection. Therefore, for the present study of the kinetics of the ethylene hydrogenation reaction the supported palladium on alumina was taken as the catalyst (see Section 5.5.2 for its preparation).

2.6 Ethylene Hydrogenation Reaction Over Palladium Catalyst

From a study of the literature it was found that palladium metal as a catalyst has always been the exception in hydrogenation reactions compared to other transition metal catalysts due to its extraordinary absorption abilities for hydrogen. Therefore, the study of the catalytic activities of hydrogen on palladium has received much more attention than the kinetic studies of hydrogenation reactions. In most cases the ethylene hydrogenation reaction system was chosen for establishing the catalytic activity of the palladium catalyst. Often
these studies were carried out in closed systems using various forms of the palladium metal. A summary of the kinetic studies of the ethylene hydrogenation reaction using palladium as a catalyst is given in Table 2.4 which shows that the reaction orders with respect to hydrogen and ethylene as well as the activation energy are controversial. This can be understood due to the fact that the palladium has extra hydrogen absorption ability. Palczewska (1975) has also revealed this behaviour in his review article on the catalytic reactivity of hydrogen on palladium. He emphasised that this behaviour could be due to the formation of a distinct phase of the metal-hydrogen system, called the hydride phase or $\beta$-phase and could lead to self-poisoning effects. The exact conditions under which the self-poisoning takes place are still not known.

Frackiewicz et. al. (1977) studied the rate of ethylene hydrogenation on a thin film of palladium and palladium hydride in a differential flow reactor and observed that, depending on the hydrogen pressure, the 480 Å layer of palladium deposited on glass was completely or partially transformed to palladium hydride (PdH). A hysteresis was also observed in the relation between reaction rate and the phase composition of the catalyst layer. This may be accounted for by the rapid disappearance of PdH from the catalyst surface during a decrease in hydrogen concentration in the gas mixture.

Yamabe et. al. (1973) studied the sorption and desorption of hydrogen by palladium supported on silica-alumina catalyst, and found that the hydrogen is absorbed by palladium in three states; that is, weakly adsorbed $H_2$, dissolved $H$, and strongly adsorbed $H$. In
### TABLE 2.4: Summary of the Kinetic Studies of Catalytic Hydrogenation of Ethylene on Palladium.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Conditions</th>
<th>System</th>
<th>Test</th>
<th>Activation Energy (kcal/mole)</th>
<th>Rate Relation* and/or Reaction Mechanism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium on Alumina</td>
<td>-36° to 77°C</td>
<td>Closed</td>
<td>$D_2$, $C_2H_4$</td>
<td>$11.4 \pm 7.0$</td>
<td>$r = k P_A$</td>
<td>Bond et al (1966)</td>
</tr>
<tr>
<td></td>
<td>$P_A = 25$ to 350mm Hg</td>
<td></td>
<td></td>
<td>(50°-70°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$P_B = 25$ to 200mm Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palladium on silica-alumina</td>
<td>-20° to 20°C</td>
<td>Closed</td>
<td>$H_2$, $C_2H_4$</td>
<td>2.5</td>
<td>$r = k P_A P_B^0$</td>
<td>Yamabe et al (1974)</td>
</tr>
<tr>
<td></td>
<td>$P_A = P_B = 25$mm Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palladium film</td>
<td>75°C</td>
<td>Flow</td>
<td>$H_2$, $C_2H_4$</td>
<td>---</td>
<td>$2Pd + H_2 \rightarrow 2PdH$</td>
<td>Frackiewicz et al (1977)</td>
</tr>
<tr>
<td></td>
<td>$P_A = 50$ to 300mm Hg</td>
<td></td>
<td></td>
<td></td>
<td>$2PdH + C_2H_4 \rightarrow C_2H_4 + 2Pd$</td>
<td></td>
</tr>
<tr>
<td>Palladium membrane</td>
<td>50° to 100°C</td>
<td>$H_2$, $C_2H_4$</td>
<td>---</td>
<td>$r \alpha P_{C_2H_4}$</td>
<td>Nagamoto and Inoue (1981)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$P_A 0.1$ to 1 atm</td>
<td>permeating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$P_B 0.05$ to 0.95 atm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palladium black</td>
<td>Perchloric acid</td>
<td>Electro-</td>
<td>$H^+$, $C_2H_4$</td>
<td>---</td>
<td>$r \alpha P_A^{1.8}$ $P_B^{0.4}$ ($P_B &lt; 0.3$ atm)</td>
<td>Sakellaropoulos and Langer (1981)</td>
</tr>
<tr>
<td></td>
<td>+0.6 to 0 V</td>
<td>chemical</td>
<td></td>
<td></td>
<td>$r \alpha P_A^{1.8}$ ($P_B &gt; 0.3$ atm)</td>
<td></td>
</tr>
</tbody>
</table>

* Subscript A denotes hydrogen and B designates ethylene.
continuation of their work, Yamabe et. al. (1974a,1975) have observed that the strongly adsorbed B readily reacts with gaseous ethylene in the ethylene hydrogenation reaction to form ethane.

Yamabe et. al. (1974b) extended their work on palladium supported on silica-alumina catalyst to the hydrogenation of ethylene. They observed in repeated experiments on the same catalyst that the apparent activation energy increased from 3 to 5 kcal (mole)$^{-1}$ while catalyst activity gradually decreased to a low steady value. For the catalyst with the steady activity the rate of the hydrogenation was first order in hydrogen and slightly negative order in ethylene. Yamabe et. al concluded that the irreversible adsorption of ethylene could be responsible for the gradual decrease in the catalytic activity during the repeated experiments. The low activation energy could well be due to the influence of diffusional effects between the bulk-gas and the catalyst surface as they did not have gas agitation.

Dus (1975) used the static capacitor technique for measuring the surface potential changes accompanying adsorption and hydrogenation of ethylene on an evaporated palladium film. It was found that the ethylene is adsorbed in two forms, $\sigma$ and $\pi$. The $\sigma$ form is adsorbed with decomposition, whereas the $\pi$ form is adsorbed with no decomposition. It was also observed that only the $\pi$ form was active in the hydrogenation with gaseous hydrogen. The hydrogen adsorbed in $\pi$ form (similar to the strongly adsorbed B of Yamabe et. al. (1974a)) at the palladium surface was active in the hydrogenation of the ethylene.

Dus and Lisowask (1979) have recently extended their work and proposed a mechanism for ethylene self-hydrogenation in which ethylene
molecules ($\pi$-form) adsorbed in the second layer reacted readily with hydrogen whereas those which form the first layer ($\sigma$-form) did not.

Recently, Sakellaropoulos and Langer (1981) carried out an electrocatalytic hydrogenation of ethylene over palladium at positive potential to establish the reaction kinetics. They proposed a mechanistic model involving the surface insertion of ethylene to adsorbed hydrogen atoms followed by slow hydrogen addition to the resulting surface ethyl radicals. A complex behaviour was observed with the ethylene. For partial pressure above 0.3 atmosphere the reaction order with respect to ethylene was effectively zero. Below this pressure, an order of 0.4 was observed.

Nagamato and Inoue (1981) also recently analysed the mechanism of ethylene hydrogenation by hydrogen permeating a palladium membrane. The behaviour of ethylene was similar to that observed by Sakellaropoulos and Langer (1981), but an approximate first order was observed for ethylene for a partial pressure less than 0.2 atmosphere.

To date, no thorough kinetic studies of the ethylene hydrogenation have been carried out using a flow system. Therefore, it was one of the aims of the present study to carry out a kinetic investigation of the reaction using a differential flow reactor. Also, these studies are of interest in view of the practical application of palladium catalysts in hydrogenation of unsaturated hydrocarbons.
CHAPTER 3

PRECISE PARAMETER ESTIMATION

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3.3 Sequential Experimental Design for Parameter Estimation .......................... 45
3.1 Introduction

One of the fundamental tasks in chemical kinetics is the extraction of information from the available data on the reaction. Parameter estimation is a discipline that provides tools for the efficient use of data in the estimation of constants appearing in the mathematical kinetic model.

In the mathematical model, there are dependent and independent variables and also certain constants. The constants are generally called parameters.

In experiments, the dependent variables may be measured directly but the parameters cannot be. Approximate values of the parameters are inferred from the dependent and independent variables. Since only approximate parameter values are found, the parameters are said to be estimated. Section 3.2 discusses the precision and problems associated with the estimation.

Carefully designed experiments can result in greatly increased accuracy of the estimates. This has been demonstrated by various authors. Box and co-workers (Box and Lucas (1959), Box and Hunter (1965)) were pioneers in this area. The common measure of the precision of the estimate is its variance; the smaller the variance, the greater the precision. Section 3.3 discusses the various design criteria based on the variance of parameter estimates. In this section it is assumed that the form of the model is known although it contains unknown parameters. If the form of the model is unknown, the search for an optimal design strategy may be quite difficult, involving model
discrimination. The problem of discrimination between various proposed models is beyond the scope of the present studies. This problem has been discussed by Box and Hill (1967) and Hunter and Reiner (1965).

3.2 Estimation of Parameters

The prediction of the behaviour of a reaction system is usually approached by postulating a mathematical model and determining its parameters by some criterion of best fit to experimental data. The least squares criterion has proved to be of significant value for this purpose (Graybil (1961)). For the case of data on the kinetics of heterogeneous catalytic reactions, the fit of the model and the estimated values of parameters should satisfy the following constraints:

i. The estimated adsorption and rate constants should be positive.

ii. A logarithmic plot of the rate constant against the reciprocal absolute temperature should be linear with negative slope.

iii. Logarithmic plots of adsorption constants should be linear with positive slopes (exothermic adsorption) and generally have negative intercepts (decrease in entropy with adsorption).

iv. The model should adequately fit the data.
3.2.1 Least Squares Theory

The model representing the relationship between a dependent variable and independent variables can be given by

\[ \bar{y}_u = f(X_u, K) \]  

where \( \bar{y}_u \) represents the predicted dependent variable for the \( u \)-th experimental run \((u=1,2,...,n)\). \( f(X_u, K) \) is the function of the \( m \) independent variables \( X_u = (x_{1u}, x_{2u}, ..., x_{mu}) \) for an experimental run \( u \), and of \( K = (k_1, k_2, ..., k_p)^T \), the \( p \) parameters to be estimated. Under the least squares criterion, the function to be minimised is given as

\[ S = \sum_{u=1}^{n} w_u (y_u - \bar{y}_u)^2 \]  

where \( y_u = (y_1, y_2, ..., y_n)^T \) are \( n \) observed experimental values of the dependent variable and \( w_u \) are weighting factors. The weights \( w_u \) can be chosen arbitrarily, but usually one of the three standard approaches is used:

1. The sum of squares of the errors is minimised if \( w_u = 1 \)
2. The sum of squares of the percentage errors is minimised if \( w_u = (1/y_u)^2 \)
3. The probability of a set of errors occurring is minimised if \( w_u = (1/\epsilon_u)^2 \)

where \( \epsilon_u \) is the expected error in the measurement \( y_u \). When the sum of squares of the errors are minimised the process is called unweighted...
least squares, otherwise it is called weighted least squares.

When the function $f(X_u, K)$ is linear in $K$, then Equation (3.1) can be given in matrix notation as

$$\bar{y} = X K$$  \hspace{1cm} (3.3)

where $\bar{y} = (\bar{y}_1, \bar{y}_2, \ldots, \bar{y}_n)^T$ is the $(n \times 1)$ column vector of expected values of the dependent variable and $X$ is an $(n \times p)$ matrix of independent variables. For a linear problem the estimated parameter $\bar{K}$ defining the minimum value of the scalar $S$ in Equation (3.2), when the sum of squares of the errors are minimised, is given by

$$\bar{K} = (X^T X)^{-1} (X^T y)$$  \hspace{1cm} (3.4)

where $y = (y_1, y_2, \ldots, y_n)^T$ is an $(n \times 1)$ column vector of experimental values of the dependent variable. The process is known as linear least squares estimation. The matrix $(X^T X)$ is often badly conditioned and its inversion leads to some problems (see Appendix-B). Discussion of the methods of circumventing such problems are covered in detail elsewhere (Draper and Smith (1966), Kittrell (1970), Beck and Arnold (1977)).

When the function $f(X_u, K)$ is non-linear the process of estimation involves iterative minimisation techniques and is known as non-linear least squares estimation. This introduces numerous complications, such as initial estimates of parameters (Appendix-B), efficiency and effective convergence of minimisation algorithms (Section 4.2) and multiple minima in the least squares surface condition. Some of these problems are covered by Marquardt (1963) and Fletcher and Powell (1963).
3.2.2 Confidence Region of Estimated Parameters

The minimum value of the least squares function (Equation (3.2)) obtained by the iterative minimisation method may not be sufficiently informative to allow much confidence in the parameter estimates obtained. Consequently, one must turn to procedures which indicate the size of the region within which the true parameter values might be expected to lie. Beale (1960) has presented a comprehensive discussion of confidence regions for parameters in non-linear models.

There are two methods which are very common and easily applied to measuring the uncertainty associated with the parameter estimates. In the first method, the approximate magnitudes of the confidence intervals of the unweighted least squares estimates $\bar{X}$ can be obtained from the variance - covariance matrix $V(\bar{X})$ of $\bar{X}$:

$$V(\bar{X}) = (\bar{X}^T \bar{X})^{-1} \sigma^2$$  \hspace{1cm} (3.5)

where $\sigma^2$ is the variance of normally and independently distributed error in the observed dependent variable. If the model is adequate, the quantity

$$S(\bar{X}) / (n-p)$$  \hspace{1cm} (3.6)

is usually called $s^2$ and is an unbiased estimate of $\sigma^2$. $S(\bar{X})$ denotes the sum of the squares of residuals at the least squares estimates $\bar{X}$ (Equation (3.2)). A corresponding approximation for a non-linear model is given as

$$V(\bar{X}) = (D^T D)^{-1} s^2$$  \hspace{1cm} (3.7)
where $D$ is an $(n \times p)$ matrix. An element of $D$, $d_{ju}$ is the partial derivative with respect to the $j$-th parameter evaluated for the $u$-th experimental conditions at the least squares estimates $K=\bar{K}$:

$$d_{ju} = \left[ \frac{\partial f(X_u,K)}{\partial k_j} \right]_{K=\bar{K}}$$

(3.8)

If the matrix $(D^T D)^{-1}$ is denoted as $C$, the approximate standard deviation of the parameters is given as

$$s_{ii}^2 = s^2 c_{ii}$$

(3.9)

where $s_{ii}$ represents the standard deviation of the parameter estimate $\bar{k}_i$ and $c_{ii}$ is the $ii$-th element of the matrix $C$. These can be used to calculate the individual $100(1-\alpha)$% confidence interval for the various parameters separately from the formula (Beck and Arnold (1977)):

$$\bar{k}_i \pm s_i t(1-\nu_2 \alpha)(\nu)$$

(3.10)

where $t(\nu)$ is the $t$ - distribution and $\nu$ is the number of degrees of freedom, frequently $(n-p)$.

The above method provides an approximate interval estimate for any single parameter, but does not describe the joint region of uncertainty for the parameter estimates considered collectively.

The second method utilizes the joint confidence region (JCR) of the parameter estimates. The JCR of the parameter estimates for a linear model is represented by

$$(K-K)(X^T X)(K-K) = 0$$

(3.11)
where $\delta$ is a constant, depending upon the number of degrees of freedom with which the parameters have been estimated, the selected probability level and the error variance $\sigma^2$. If the model is non-linear in the parameters, Equation (3.11) is only approximately valid.

Since $(X^TX)$ is a positive definite matrix and all its eigenvalues, $\lambda_i$, are positive, Equation (3.11) can be transformed into (Hosten(1974)):

$$\frac{\omega_1}{\sqrt{\delta/\lambda_1}} + \frac{\omega_2}{\sqrt{\delta/\lambda_2}} + \ldots + \frac{\omega_p}{\sqrt{\delta/\lambda_p}} = 1 \quad (3.12)$$

From Equation (3.12) it is clear that Equation (3.11) defines a closed hyper-ellipsoid surface. The length of the principal axes ($\omega_i$) of this hyper-ellipsoid are inversely proportional to the square roots of the eigenvalues of the matrix $(X^TX)$.

Alternatively, the $100(1-\alpha)$% JCR of the parameter estimates may be approximately calculated for a non-linear model by

$$S(K) = S(\bar{K}) [1 + \frac{p}{(n-p)} F(p,n-p,1-\alpha)] \quad (3.13)$$

where $F(p,n-p,1-\alpha)$ is the $(1-\alpha)$ point of the $F$-distribution with $p$ and $n-p$ degrees of freedom. $S(K)$ denotes the sum of squares of residuals of a set of parameters $K$ at a confidence level $\alpha$. 
3.2.3 Correlation between Parameters

Correlation between parameters in reaction rate modelling can be derived from the $(X^TX)^{-1}$ matrix. A complete correlation between parameters means that a change in the value of one parameter can be completely compensated by a change in another parameter so that an equally good fit to the experimental results is achieved. Figure 3.1 shows plots of equal confidence for a two parameter system. The ellipses show the relationship between the two parameters which give equally good fits to experimental data. This means the result can offer no information on the individual values of the parameters when there is high correlation. Degree of correlation is shown by the correlation coefficient, with 1.0 (or -1.0) denoting complete positive (or negative) correlation and 0.0 complete independence. In general, correlation is not a problem unless the correlation coefficient is higher than $\pm 0.95$ (Rose (1981)).

Correlation, which in linear least squares estimation simply means that the individual values of the parameters cannot be specified, is a much more serious problem in nonlinear least squares estimation. Correlation between two parameters has the effect of minimising the response surface into a long narrow valley instead of a circular pit, as shown in Figure 3.2. Hence, the optimisation routine has great difficulty in moving along the valley, particularly if it is curved, and there is difficulty in locating the parameter values. This means that, at least, the computational time is long or, at worst, the minimisation routine completely fails to locate the minimum. In this case more experiments have to be included, chosen so as to reduce this
FIGURE 3.1: Correlation between parameters.
FIGURE 3.2: Approximate 95% confidence region for $A_0$ and $E$ (Equation (3.15)).
Non-linear models are particularly susceptible to correlation problems due to the form of the model and the value of the parameters. Correlation problems are not due solely to the selection of uneven experimental points, as is the case with the linear models.

The correlation matrix $R = (r_{ij})$ for the least squares estimates is defined as

$$r_{ij} = \frac{v_{ij}}{(v_{ii}v_{jj})^{1/2}}$$

where $v_{ij}$ is an element of the variance-covariance matrix $V(\bar{R})$. Each diagonal element of the symmetric matrix $R$ is unity and an off-diagonal element $r_{ij}$ is a dimensionless measure of the linear association between the estimated parameters $\bar{k}_i$ and $\bar{k}_j$.

### 3.2.4 Reparameterization

The problem of correlation described in the last sub-section can frequently be reduced by improving the surface conditioning through reparameterization. Reparameterization means writing the model in an equivalent mathematical form, but with different parameters. Reparameterization for estimation purposes is often carried out by redefining the independent variables so that the centre of their coordinate system is near the centre of the experimental design (Box (1960)). In kinetic models, one type of reparameterization frequently needed is that associated with the exponential dependence of parameters upon temperature. In particular, the Arrhenius equation for the reaction
rate constant

\[ k = A_0 \exp\left( \frac{-E}{RT} \right) \]  \hspace{1cm} (3.15)

is invariably redefined as

\[ k = k^* \exp\left( -\frac{E}{T} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right) \]  \hspace{1cm} (3.16)

where

\[ k^* = A_0 \exp\left( \frac{-E}{RT} \right) \]  \hspace{1cm} (3.17)

and \( T^* \) is a reference temperature. To ensure a non-negative pre-exponential factor \( (A_0) \) and activation energy \( (E) \), the transformation suggested by Box (1966) can be incorporated. The final reparameterized expression for a reaction rate constant can be written as

\[ k = \exp(\theta) \exp\left( -T^* \exp(\rho) \right) \]  \hspace{1cm} (3.18)

where

\[ T^* = \frac{1}{T} - \frac{1}{T^*} \]  \hspace{1cm} (3.19)

\[ \exp(\theta) = k^* \]  \hspace{1cm} (3.20)

\[ \exp(\rho) = \frac{E}{R} \]  \hspace{1cm} (3.21)

The change in contour of the sum of squares is shown in Figures 3.2 and 3.3. The parameters \( \theta \) and \( \rho \) are thus more rapidly obtained than \( A_0 \) and \( E \); the initial parameter estimates are not as critical and the estimation routine converges more rapidly to the minimum. Reparameterization and examples of its usefulness have been discussed in more detail elsewhere (Box (1960), Box and Draper (1965),
FIGURE 3.3: Approximate 95% confidence region for \( \psi \) and \( \phi \) (Equation (3.18)).
3.3 Sequential Experimental Design for Parameter Estimation

Parameter estimation for a model of known form has been discussed in the last section. The estimates thus obtained are likely to be approximate since experiments are probably poorly designed over the desired experimental range. They may still be too imprecise for real reactor design purposes. Box and Lucas (1959) developed an experimental design procedure for decreasing the amount of uncertainty associated with the estimates of parameters. It aims at reducing the volume of the JCR associated with the estimates.

Box and Lucas (1959) have shown that the choice of the experimental variables, $X_u$, for an non-linear model which minimises the determinant:

$$| (D^T D)^{-1} |$$

or, equivalently, maximises the determinant:

$$| (D^T D) |$$

will also minimise the volume of the JCR of the parameter estimates (see Appendix-B). The square root of this determinant (Equation (3.23)) is proportional to the volume of the JCR of the estimates.

Box and Lucas (1959) dealt with the simultaneous planning of exactly as many experiments as there are parameters in the model. Later Box and Hunter (1965) established a criterion for a sequential experimental design, generally known as the "Minimum Volume" design.
(MVD) criterion, where all available experimental results are analysed each time an additional experiment is performed and the current information is then used for the design of the next experiment. The general scheme which they proposed is shown in Figure 3.4. Box and Hunter (1965) also indicated that this strategy not only minimises the size of the JCR of the parameter estimates but also the correlation between them. St. John and Draper (1975) have recently reviewed this criterion and its applications to real experimental studies in the field of chemical kinetics have been reported by Mezaki (1969), Froment and Mezaki (1970), Graham and Stevenson (1972), and Jucisola et.al. (1972).

Instead of minimising the volume of the JCR associated with the estimates, Hosten (1974) proposed to aim for a more spherically shaped JCR by maximum contraction of the longest principal axis of the confidence region hyperellipsoid. From Equation (3.12) it follows that this contraction is performed by those experiments which maximise the smallest eigenvalues of the \((X'X)^{T}\) matrix. Since this criterion specifically acts upon the shape of the JCR, it will be called the "Shape" design (SD) criterion. When both criteria were applied to twenty three experiments in the kinetic study of saccharose hydrolysis (Hosten (1974)), it was found that the ultimate volume of the JCR obtained with the MVD was about 2.7 times smaller than with the SD. This was achieved, however, at the expense of superfluous contraction of some axes of the hyperellipsoid which were already much smaller than the longest at the early stages of the design. Owing to its specific action, the shape criterion arrives at a longest axis which is only about two thirds of that obtained by MVD. In addition, in this example at least, the correlation between the parameters was much smaller with the shape
FIGURE 3.4: Sequential experimental design strategy.
Later, Hosten and Eming (1975) applied the SD criterion to the parameter estimation in differential equations that cannot be analytically integrated.

Pritchard and Bacon (1978) have more recently proposed a new design criterion which measures the overall extent of correlations present among the parameter estimates; that is, a measure of the size of the correlation matrix $R$. They used the root mean square of the individual pairwise correlations

$$C = \left( \sum_{i,j} r_{ij} / (p^2 - p) \right)^{1/2}$$

(3.24)

as a design criterion. Since this criterion specifically acts upon the correlations among the parameter estimates, it will be called the "Correlation" design (CD) criterion. When both design criteria (MVD and CD) were applied to the design of fifteen experiments for the kinetic study of catalytic oxidation of o-xylene, it was found that the use of CD led to reductions in both correlation and the size of the JCR for the parameter estimates (Pritchard and Bacon (1978)). However, MVD led to a reduction in the size of the JCR alone, about five times smaller than CD. The use of CD also revealed that the extremely high correlations among estimates of the Arrhenius parameters (Equation (3.15)) were essentially irreducible.

Section 4.4 of Chapter 4 compares these design criteria, focussing on their relative performance in the precision of the parameter estimates for a rate model.
CHAPTER 4

SIMULATIONS OF SEQUENTIAL EXPERIMENTAL DESIGN

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   4.5.1 Results and Discussion ......................... 68
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4.1 Introduction

This chapter discusses simulation studies applied to sequential experimental design. The simulations were used to provide information in two principal areas. Firstly, the influence of reparameterization on the experimental design was considered and secondly, the performances of the design criteria in the estimation of the parameters were compared.

The effect of reparameterization on the convergence of the parameter estimates at various noise levels (Section 4.4) and design criteria evaluation (Section 4.5) were investigated by utilizing a common reaction rate model, discussed in Section 4.2.

The choice of optimisation algorithm used to minimise the objective functions for the parameter estimation and the sequential experimental design is discussed in Section 4.3.

4.2 Reaction Model

The ethylene hydrogenation reaction system (see Chapter 2 for details) studied by Barton (1976) was used for the simulation studies. In Barton's work the hydrogenation of ethylene was investigated over supported nickel catalyst at atmospheric pressure in a differential reactor. The rate model for the reaction was:

\[ r_{C_2H_6} = A_0 \exp \left( \frac{-E}{RT} \right) \left( X_{C_2H_4} \right)^{\alpha} \left( X_H \right)^{\beta} \]  

(Model 1)
where, \( r_{C_2H_6} \) is the rate of formation of ethane, \( X_{C_2H_4} \) and \( X_{H_2} \) are the mole fractions of ethylene and hydrogen respectively. Incorporating the reparameterized Equation (3.18) for the Arrhenius reaction rate constant, the rate Model 1 can be rewritten as

\[
\text{MODEL 2 : } r_{C_2H_6} = \exp(\theta) \exp(-T'\exp(\rho))(X_{C_2H_4})^\alpha (X_{H_2})^\beta \tag{4.2}
\]

Model 1 and Model 2 were used to examine the effect of reparameterization on the precision of the parameter estimates when utilizing the MVD criterion in sequential experimental design (Section 4.4). Also, Model 2 was used to compare the three design criteria (Section 3.3) based on the relative precision of the parameter estimates obtained (Section 4.5).

The original parameter estimates, hereafter referred to as the 'true' values, were taken from Barton's analysis. The values were: \( A_0=4.629E+03 \), \( E=11.6 \) kcal/mole, \( \alpha=0.33 \), \( \beta=1.0 \). The values for \( \theta \) and \( \rho \) were calculated on the basis of an average temperature of 338°K (Table 4.1).

An initial set of six experiments was planned so as to span the range of variables in a fairly arbitrary way. This set was used to initiate the simulated design programmes. The continuous operating region chosen was defined by \( X_{C_2H_4} \) from 0.1 to 0.4, \( X_{H_2} \) from 0.4 to 0.8 and \( T \) from 313° to 363°K. Constraints from the actual experiments were used to bound the allowable space. Thus an upper limit for the reaction rate was set at 1.5E-04 kg mole sec\(^{-1}\) (kg catalyst\(^{-1}\)) because higher reaction rates gave run-away conditions (Barton (1976)). The mole fractions were restricted by: \( X_{C_2H_4} + X_{H_2} \leq 1.0 \), with nitrogen used as
Table 4.1: Orders of magnitude comparison of 'true' parameter values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>4.629E+03</td>
<td>$\theta$</td>
<td>-8.822</td>
</tr>
<tr>
<td>$E$</td>
<td>1.160E+04</td>
<td>$\rho$</td>
<td>8.672</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.33</td>
<td>$\alpha$</td>
<td>0.33</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.0</td>
<td>$\beta$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
an inert diluent when necessary.

The data from each set of experiments consisted of one set of independent variables (mole fractions of ethylene and hydrogen and reaction temperature) together with the dependent variable obtained by adding errors to the true values calculated from Equations (4.1) and (4.2). The errors used were calculated from

\[
\text{% Error} = \text{Random Number} \times \text{% Noise} \quad (4.3)
\]

The random numbers were generated from a Gaussian normal distribution with zero mean and a constant standard deviation of 0.5. 10% and 40% noise levels were used for model performance comparison but only a 10% noise level was employed when comparing the performance of the three design criteria.

4.3 Choice of Minimisation Routine

An important problem in parameter estimation and the statistical design of experiments is the choice of the numerical minimisation technique. Two factors, computational time and robustness, were considered when selecting a suitable routine in the present study. A good measure of computational time is the number of times the objective function has to be evaluated.

Two objective functions were examined in choosing the optimisation routine:

1. The MVD criterion for optimal experimental design i.e.
minimise \( U_{\text{Design}} = \frac{1}{|D^T D|} \) \hspace{1cm} (4.4)

This is equivalent to maximising the determinant \(|D^T D|\).

2. The least squares criterion for the parameter estimation i.e.

\[
\text{minimise} \quad U_{\text{Estimation}} = \sum_{u=1}^{n} \left( \frac{1}{y_u} \right)^2 (y_u - \hat{y}_u)^2
\]  \hspace{1cm} (4.5)

Three algorithms were tested. Their convergence is compared in Tables 4.2 and 4.3. The Quasi-Newton routine (Gill and Murray (1972)) was clearly the best, converging to a smaller minimum more rapidly than the other techniques. Of the remaining methods, the pattern search Simplex algorithm (Nelder and Mead (1965)) performed slightly better than the Powell algorithm (Powell (1964)). No method had difficulty in finding the flat valley that is the typical of least squares problems. However, the progress of both the Powell and Simplex methods was slow. The Quasi-Newton routine continued to make progress until very near to the minimum. This result was consistent with the published results of Bard (1970) who found that the Gauss-Newton class of technique was better than several other common types of minimisation algorithms in solving least squares parameter estimation problems.

The Quasi-Newton technique was clearly the best choice for minimisation of the present objective functions.

A computer program was developed to design the optimum experimental conditions and estimate the kinetic parameters for the design. The flow-diagram and program listings are given in Appendix C.
Table 4.2: Comparison of minimisation algorithms for the MVD criterion for experimental design.

<table>
<thead>
<tr>
<th>Minimisation Method</th>
<th>Starting Function Value</th>
<th>Optimum Function Value</th>
<th>Experiment Number Designed</th>
<th>Number of Function Evaluations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quasi-Newton</td>
<td>0.1195</td>
<td>0.0132</td>
<td>7</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>0.1251</td>
<td>0.1131</td>
<td>15</td>
<td>62</td>
</tr>
<tr>
<td>Simplex</td>
<td>0.1195</td>
<td>0.0133</td>
<td>7</td>
<td>1119</td>
</tr>
<tr>
<td></td>
<td>0.1251</td>
<td>0.1142</td>
<td>15</td>
<td>708</td>
</tr>
<tr>
<td>Powell</td>
<td>0.1195</td>
<td>0.0147</td>
<td>7</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>0.1251</td>
<td>0.1140</td>
<td>15</td>
<td>928</td>
</tr>
</tbody>
</table>

*Algorithm did not converge.

Table 4.3: Comparison of minimisation algorithms for the least squares parameter estimation function.

<table>
<thead>
<tr>
<th>Minimisation Method</th>
<th>Starting Function Value</th>
<th>Optimum Function Value</th>
<th>Number of data Points</th>
<th>Number of Function Evaluations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quasi-Newton</td>
<td>0.32199</td>
<td>9.279E-16</td>
<td>4</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>0.64001</td>
<td>0.29652</td>
<td>11</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>0.15350</td>
<td>0.11486</td>
<td>24</td>
<td>94</td>
</tr>
<tr>
<td>Simplex</td>
<td>0.32199</td>
<td>2.899E-05</td>
<td>4</td>
<td>428</td>
</tr>
<tr>
<td></td>
<td>0.64001</td>
<td>0.29652</td>
<td>11</td>
<td>377</td>
</tr>
<tr>
<td></td>
<td>0.15350</td>
<td>0.11486</td>
<td>24</td>
<td>186</td>
</tr>
<tr>
<td>Powell</td>
<td>0.32199</td>
<td>0.05518</td>
<td>4</td>
<td>211</td>
</tr>
<tr>
<td></td>
<td>0.64001</td>
<td>0.29652</td>
<td>11</td>
<td>327</td>
</tr>
<tr>
<td></td>
<td>0.15350</td>
<td>0.11486</td>
<td>24</td>
<td>217</td>
</tr>
</tbody>
</table>
4.4 Use of Reparameterized Model in Sequential Experimental Design

It has already been shown in Section 3.2.4 that the high correlation between the pre-exponential factor \( A_0 \) and the activation energy \( E \) in the Arrhenius expression for a reaction rate constant \( k \):

\[
k = A_0 \exp\left(\frac{-E}{RT}\right)
\]

(4.6)
can be reduced by reparameterization:

\[
k = k^* \exp\left[-\frac{E}{R} (1/T - 1/T^*)\right]
\]

(4.7)

where

\[
k^* = A_0 \exp\left(-\frac{E}{RT^*}\right)
\]

(4.8)

and \( T^* \) is a reference temperature. Whilst the use of a reparameterized (RP) model is undoubtedly successful in parameter estimation, its effect on the design of experiments to provide the data has not received any attention. In the present work the influence of reparameterization on the sequential design and the accuracy and convergence of the parameter estimates was studied for various noise levels.

4.4.1 Results and Discussion

Table 4.4 shows the initial block of six experiments and subsequent simulated experiments for Models 1 and 2. As expected, the two designs led to somewhat different experimental conditions except for the first few experiments.
TABLE 4.4 : Simulated experimental conditions*.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Temperature (°C)</th>
<th>$X_{C_{2}H_{4}}$</th>
<th>$X_{H_{2}}$</th>
<th>Noise %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model 1</td>
<td>Model 2</td>
<td>Model 1</td>
<td>Model 2</td>
</tr>
<tr>
<td>1</td>
<td>45.0</td>
<td></td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>53.0</td>
<td></td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>60.0</td>
<td></td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>68.0</td>
<td></td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>75.0</td>
<td></td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>85.0</td>
<td></td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>90.00</td>
<td>90.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>8</td>
<td>82.09</td>
<td>82.09</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>9</td>
<td>85.80</td>
<td>85.80</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>10</td>
<td>67.43</td>
<td>67.43</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>11</td>
<td>90.00</td>
<td>67.51</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>12</td>
<td>80.76</td>
<td>74.67</td>
<td>0.21</td>
<td>0.40</td>
</tr>
<tr>
<td>13</td>
<td>67.81</td>
<td>90.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>14</td>
<td>70.82</td>
<td>72.71</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>15</td>
<td>82.09</td>
<td>68.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>16</td>
<td>80.82</td>
<td>90.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>17</td>
<td>80.82</td>
<td>90.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>18</td>
<td>80.82</td>
<td>86.80</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>19</td>
<td>82.47</td>
<td>82.03</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>20</td>
<td>90.00</td>
<td>82.10</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>21</td>
<td>82.09</td>
<td>82.09</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>22</td>
<td>80.82</td>
<td>85.60</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>23</td>
<td>80.82</td>
<td>85.60</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>24</td>
<td>80.82</td>
<td>85.60</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* Nitrogen is used as diluent.
The parameters $A_0$ and $E$ for Model 1 and their re-calculated values for Model 2, estimated after each simulated experiment in sequence for each of two noise levels, are shown in Figures 4.1 and 4.2. It is seen that both the parameters are slightly better estimated using the RP model (Model 2) for 10% noise and much better estimated for 40% noise. It is also evident that, for both the models at a low noise level, the parameters converge to the true values after a few experiments. At the higher noise level the parameter estimates in the non-RP model (Model 1) show some signs of instability, and do not necessarily approach the true values. In fact, on Figure 4.1, the values of $A_0$ from the non-RP model with 40% noise level is completely off scale after the 8th experiment. In the RP model, however, the parameters converge towards the expected values.

This convergence or lack of convergence could be interpreted by postulating that, at low noise, the surface of the experimental design criterion as a function of operating variables rapidly becomes flat. This flatness was also noted by Graham and Stevenson (1972). It is proposed that this phenomenon can easily be used as a stopping criterion for sequentially designed experiments by observing the number of function evaluations for the experimental design. It is evident from Figure 4.3 that as the response surface becomes flat the number of function evaluations to design the independent variables increases sharply for the low noise case, for both models. Figure 4.4, however, shows that at higher noise the design surface for the non-RP model does not exhibit such well defined behaviour, whilst the design surface of the RP model is quite immune to noise effects.
FIGURE 4.1: Estimated pre-exponential factor ($A_0$) vs simulated experimental number.
FIGURE 4.2: Estimated activation energy (E) vs simulated experimental number.
Fun Evaluation for Design

Effect of Model
10% Noise

FIGURE 4.3: Number of function evaluations for optimal experimental design vs simulated experimental number (10% Noise).
FIGURE 4.4: Number of function evaluations for optimal experimental design vs simulated experimental numbers (40% Noise).
Table 4.5 compares the parameter values and their deviation from the true values, for 40% noise, at the 15th designed experiment, after which the response surface becomes flat. It is evident that the values of $E$ and $\alpha$ were estimated very accurately even at high noise by the RP model, while values of $A_o$ and $\beta$ were reasonably good when compared to the non-RP model. The deviations in $A_o$ and $\beta$ are still significant because the correlation between $\theta$ and $\beta$ in the RP model (Equation (4.2)) is relatively high (Table 4.6). However, the correlation between $\theta$ and $\rho$ in the RP model is reduced to the negligible value of 0.10 compared to the correlation between $A_o$ and $E$ (of greater than 0.99) in the non-RP model.

The effects of noise and reparameterization on the size of the parameter confidence region (measured by $(\mathbf{D}^T \mathbf{D})^{1/2}$) are shown in Figure 4.5 which clearly demonstrates the negligible effect of noise on the confidence region of the RP model. The size of the confidence region for the parameters is a measure of uncertainty in the estimates and its shape and size depends upon the the parameter values (Section 3.2). In the RP model all four parameters are of comparable order of magnitude (see Table 4.1), whilst in the non-RP model the values span four orders of magnitude. This point emphasises that a model should always be a candidate for some type of reparameterization or transformation of parameters if the parameter values span more than an order of magnitude.

Figure 4.6 shows the effect of noise on the fractional residual,

\[
\text{Fractional Residue} = \frac{\text{Observed Rate} - \text{Predicted Rate}}{\text{Observed Rate}}
\]
Table 4.5: Parameter estimates at the 15th experiment (40% Noise).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Value</th>
<th>Relative Deviation (%)</th>
<th>Parameter Value</th>
<th>Relative Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>$1.029e+05$</td>
<td>+2.1E+03</td>
<td>$2.799e+03$</td>
<td>-39.5</td>
</tr>
<tr>
<td>$E$</td>
<td>$1.334e+04$</td>
<td>+15.0</td>
<td>$1.153e+04$</td>
<td>-0.6</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.522</td>
<td>+58.2</td>
<td>0.309</td>
<td>-6.4</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.870</td>
<td>+87.0</td>
<td>0.611</td>
<td>-38.9</td>
</tr>
</tbody>
</table>
### TABLE 4.6: Correlation coefficients between parameters (40% Noise).

<table>
<thead>
<tr>
<th></th>
<th>Correlation Coefficients</th>
<th></th>
<th>Correlation Coefficients</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model 1</td>
<td>Model 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_0$ $E_0$ $\alpha$ $\beta$</td>
<td>$\theta$ $\phi$ $\alpha$ $\beta$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After Preliminary Experiments</td>
<td>1 0.9993 0.9770 0.9317</td>
<td>1 0.9699 0.9874 0.9574</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 0.9709 0.9226</td>
<td>1 0.9700 0.9251</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 0.9026</td>
<td>1 0.9035</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 15th Experiment</td>
<td>1 0.9973 0.5187 0.5191</td>
<td>1 -0.1055 0.5658 0.7278</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 0.4603 0.4681</td>
<td>1 0.4113 0.4070</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 0.6615</td>
<td>1 0.3630</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4.5: Volume of parameter confidence region vs simulated experimental number.
FIGURE 4.6: Fractional residuals vs simulated experimental number.
for sequential experiments. It is apparent that the RP model is far superior to the non-RP model, with the RP residuals lying almost entirely within an envelope defined by the non-RP residuals. Also, the number of function evaluations in the parameter estimation is much smaller for the RP-model compared to the non-RP model (Figure 4.7). For example, 110 and 553 respectively for the 7th experiment at 10% noise.

4.5 Comparative Performance of Design Criteria

No thorough testing of the design criteria (Section 3.3) on a common model has been published. It is the purpose of this section to compare the design criteria focusing on their relative performance in the precision of parameter estimates for the rate Model 2 discussed in Section 4.2.

4.5.1 Results and Discussion

The initial block of six experiments and subsequent simulated experiments for the design criteria are shown in Figure 4.8. The design criteria led to different experimental conditions. As expected, the MVD criterion used the overall operability region and the designed experimental conditions lay on the boundaries. However, localized designed conditions were observed for SD and CD criteria. No replicate experiments were observed with the CD criterion.

After eight designed experiments, the MVD criterion became insensitive to variations in the choice of experimental conditions due to a flat surface. This flatness in the response surface of the design
FIGURE 4.7: Number of function evaluations for the parameter estimation vs simulated experimental number.
FIGURE 4.8: Simulated experimental conditions for preliminary (○) and designed experiments by Minimum Volume Design (●), Correlation Design (■) and Shape Design (▲) criteria.
criterion as a function of experimental conditions has been discussed in Section 4.4. However, a comparable flatness in the response surface was not observed for the SD and CD criteria.

Table 4.7 gives the parameter estimates obtained by different design criteria. It is seen that the estimates are slightly better for parameters $A_0$ and $E$ with the MVD criterion than the SD and CD criteria and the parameter $\beta$ by the SD and CD criteria than with the MVD criterion. The parameter $\alpha$ was not estimated particularly well by any of the design criteria due to the strong correlation between $\theta$ and $\alpha$ (Table 4.8).

Table 4.8 gives the binary correlation coefficients between the parameter estimates before and after the application of the design criteria. It is evident that the magnitude of the correlations among the parameter estimates is:

$$\text{MVD > SD > CD}$$

The SD and CD criteria were able to reduce the weaker correlation to negligibly small values, with the CD criterion achieving better reduction as anticipated. Table 4.9 compares the values of overall correlation ($C$). It is evident that the CD criterion reduced the $C$ values drastically after eight designed experiments but a further eight experiments achieved only marginal improvement. The SD criterion showed a similar trend with slightly larger $C$ values. The MVD criterion on the other hand showed a progressive reduction in the $C$ values, but with a more substantial correlation persisting.


**TABLE 4.7**: Results of parameter estimation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>After Preliminary Experiments</th>
<th>After 8th Designed Experiment</th>
<th>After 16th Designed Experiment</th>
<th>True Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MVD</td>
<td>SD</td>
<td>CD</td>
<td>MVD</td>
</tr>
<tr>
<td>$A_0 \times 10^{-3}$</td>
<td>20.987</td>
<td>5.511</td>
<td>5.638</td>
<td>5.955</td>
</tr>
<tr>
<td>$E_0 \times 10^{-4}$</td>
<td>1.235</td>
<td>1.163</td>
<td>1.167</td>
<td>1.169</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.519</td>
<td>0.397</td>
<td>0.390</td>
<td>0.390</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.261</td>
<td>1.072</td>
<td>1.029</td>
<td>1.047</td>
</tr>
</tbody>
</table>
### TABLE 4.8: A Comparison of correlation coefficients between parameter estimates obtained by different design criteria.

#### After Preliminary Experiments

<table>
<thead>
<tr>
<th></th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9637</td>
<td>0.9876</td>
<td>0.9698</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.9760</td>
<td>0.9201</td>
<td>0.9243</td>
<td>1</td>
</tr>
</tbody>
</table>

#### After 8 Designed Experiments

**Minimum Volume Design**

<table>
<thead>
<tr>
<th></th>
<th>0.5212</th>
<th>0.9443</th>
<th>0.5991</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6519</td>
<td>0.5820</td>
<td>0.4572</td>
<td>1</td>
</tr>
</tbody>
</table>

**Correlation Specific Design**

<table>
<thead>
<tr>
<th></th>
<th>0.0999</th>
<th>0.5577</th>
<th>0.5432</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3317</td>
<td>0.0109</td>
<td>-0.3408</td>
<td>1</td>
</tr>
</tbody>
</table>

**Shape Design**

<table>
<thead>
<tr>
<th></th>
<th>0.3348</th>
<th>0.7296</th>
<th>0.2690</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4715</td>
<td>0.1715</td>
<td>-0.3738</td>
<td>1</td>
</tr>
</tbody>
</table>

#### After 16 Designed Experiments

**Minimum Volume Design**

<table>
<thead>
<tr>
<th></th>
<th>-0.2472</th>
<th>0.7378</th>
<th>0.5854</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3118</td>
<td>0.4028</td>
<td>0.5290</td>
<td>1</td>
</tr>
</tbody>
</table>

**Correlation Specific Design**

<table>
<thead>
<tr>
<th></th>
<th>0.0352</th>
<th>0.5072</th>
<th>0.5568</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1106</td>
<td>0.0258</td>
<td>-0.3969</td>
<td>1</td>
</tr>
</tbody>
</table>

**Shape Design**

<table>
<thead>
<tr>
<th></th>
<th>0.3303</th>
<th>0.6875</th>
<th>0.2573</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5247</td>
<td>0.0322</td>
<td>-0.4531</td>
<td>1</td>
</tr>
</tbody>
</table>
TABLE 4.9: A comparison of overall correlation (C).

<table>
<thead>
<tr>
<th></th>
<th>Overall Correlation (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MVD</td>
</tr>
<tr>
<td>After Preliminary Experiments</td>
<td>0.957</td>
</tr>
<tr>
<td>After 8 Designed Experiments</td>
<td>0.645</td>
</tr>
<tr>
<td>After 16 Designed Experiments</td>
<td>0.498</td>
</tr>
</tbody>
</table>
TABLE 4.10: Characteristics of the joint confidence region of the parameter estimates before and after the application of designs criteria.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>After Preliminary Experiments</th>
<th>After 8th Designed Experiment</th>
<th>After 16th Designed Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MVD</td>
<td>SD</td>
<td>CD</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>2.29E+17</td>
<td>3.43E+15</td>
<td>1.10E+16</td>
</tr>
<tr>
<td>$\lambda_1$</td>
<td>1.26E-07</td>
<td>5.40E-07</td>
<td>3.07E-07</td>
</tr>
<tr>
<td>$\lambda_2$</td>
<td>7.38E-09</td>
<td>1.63E-08</td>
<td>8.33E-09</td>
</tr>
<tr>
<td>$\lambda_3$</td>
<td>1.04E-09</td>
<td>7.27E-09</td>
<td>2.03E-09</td>
</tr>
<tr>
<td>$\lambda_4$</td>
<td>1.97E-11</td>
<td>1.33E-09</td>
<td>1.60E-09</td>
</tr>
</tbody>
</table>
It is interesting now to examine how the joint confidence region has been modified by the design criteria. Table 4.10 gives the $\Delta$ values, the volume of the joint confidence region of the parameter estimates (measured by $\left( |D^TD| \right)^{-1/2}$) and the principle axes length in terms of the eigenvalues $\lambda_i$ of the $(D^TD)$ matrix, before and after the application of the design criteria.

It is seen that the volumes of the JCR of the parameter estimates, obtained after eight designed experiments by the SD and the CD criteria are about 3 and 5 times larger respectively than those obtained from the MVD criterion. A reduction by a further factor of 1.5 was obtained by the SD and CD criteria, compared to a factor of 9.4 with the MVD criterion, after eight additional experiments. As might be expected, the longest axis (corresponding to $\lambda_4$) has been shortened to the greatest extent by the SD criterion after the 8th designed experiment. However, after the 16th designed experiment, the longest axis has been shortened most by the MVD criterion.

Hosten (1974) defended the SD criterion by saying that the MVD criterion arrives at a smaller volume of the JCR due to the superfluous contraction of some axes which were already far smaller than the largest axis. Hosten's aim was to make the JCR as spherical as possible so as to estimate all parameters with an equal degree of precision. However, this is almost impossible to do with the naturally occurring large span in the orders of magnitude of the parameters (Table 4.1). A reparameterization or transformation of parameters, as used in this work, is a much better way of achieving a close approach to a spherical region.
It is apparent from Tables 4.7 and 4.10 that after the first eight designed experiments little if any significant improvement in parameter estimates was achieved. With the SD and CD criteria there is no simple way of deciding when to terminate the experimental sequence, other than by judgement of convergence of the estimates, or the criteria values. In fact, for high noise levels, as may occur in industrial experimentation, it was found that the SD criterion failed to converge, whilst the CD criterion showed signs of instability due to a tendency to produce a localized design. However, the MVD criterion did not show such instability and the parameters converged towards the expected values. Further, it has been shown (Section 4.4) that the MVD criterion provides a natural convergence criterion for terminating the sequential experimental design programme.

4.6 Conclusions

The performance of available design criteria for the sequential design of experiments to estimate the kinetic parameters have been compared using a common reaction model. The design criteria proposed by Hosten (1974) and Pritchard and Bacon (1978) proved useful, but failed to cope with noisy data which might arise in industrial experimentation. However, the design criterion of Box et. al. (1959,1965) gave satisfactory results in all situations.

The criterion of Box et. al. was used to study the influence of reparameterization on the parameter estimates. It is seen from the example that the RP model led to better parameter estimates in a sequentially designed experimental programme, even with strongly
correlated parameters and high experimental noise levels. This model not only reduced the correlation among the parameters, but reduced significantly the volume of the confidence region of the estimated parameters. Its use should lead to more economical experimentation, with saving in computational time and the potential for equivalent parameter precision with fewer experiments. Whilst the availability of a statistical technique less sensitive to noise should not be advocated as an excuse to permit poorly designed or performed experiments, it appears that the RP model will tolerate very noisy data and allow an experimental programme to converge to meaningful results not otherwise obtainable. This is of significance in awkward industrial experimental situations.

Finally, with the RP model, a sudden increase in the number of function evaluations for the optimum design appears a useful criterion for terminating the sequential experimental programme.
CHAPTER 5

EXPERIMENTAL METHOD

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5.1 Introduction

Estimating the parameters in a kinetic model as precisely as possible is an essential part of the design, development, and control of the chemical reactor. However, the collection of the reaction data, its interpretation and the estimation of parameters are tedious and time consuming tasks.

Brisk (1969) has discussed an approach which accelerates the collection of kinetic data. The method utilizes an on-line computer controlled laboratory reactor. The computer’s tasks include data collection, simple data reduction such as rate calculation and control of the operating variables.

In Chapters 3 and 4 the advantages of the sequential experimental design strategy as a means of improving the precision of parameter estimates was discussed. Also, as observed later (Chapter 7), sequential design also reduces the number of experiments needed to achieve parameter estimates in comparison to conventional methods. Brisk’s (1969) approach could be extended by including the sequencing of the designed experiments in the computer’s tasks. Therefore, by utilizing a real time computer it should be possible both to reduce the experimentation time and also improve the precision of the parameter estimates for a kinetic model.

In general, the computer controlled apparatus would require a micro- or mini-computer to perform the real time tasks of equipment operation for the experimentation stages. However, the computations required for the optimal design and parameter estimation steps require
non-linear multivariable search algorithms (see Section 4.3), are generally too demanding for mini-computers, especially if the computer is also to perform the time critical tasks of data collection and apparatus control. Therefore, a hierarchy of computers was initially proposed to perform the various control and computational functions needed to automate the entire process of the catalyst kinetics measurements.

This chapter gives a brief description of such a hierarchy of computers and discusses the experimental apparatus eventually used to study the ethylene hydrogenation reaction over supported palladium catalyst.

5.2 The Computer Hierarchy

Figure 5.1 shows the computer systems originally planned to perform the present kinetic studies. The upper level was to be a large mini-computer which was also time shared amongst many others users and tasks, in the manner of a "mainframe" machine. In the present case this computer was a PDP 11/60, with substantial disc storage and a wide range of peripherals, supporting up to 20 time-sharing users. This level would be required for the heavy computational tasks of parameter estimation and sequential experimental design which need to be done rapidly, but not as real time operations. The large on-line storage could also receive logged chromatographic analytical data for subsequent processing. All programming at this level was to be in the FORTRAN language.
LEVEL #2
LARGE MINICOMPUTER
Experimental Design
Parameter Estimation
Complex Data Logging
Logged Data Storage

Other Users

LEVEL #1
MICROCOMPUTER
Data Collection
Regulatory DDC
Local Logging
Sequence Execution
Alarm Recognition

REACTOR
RIG
LOCAL VDU
CONSOLE

FIGURE 5.1: The Computer Hierarchy.
A Motorola M6800 microprocessor-based system was to be used at the lower level to handle the real time logging sequence, and direct digital control (DDC) functions to operate the reactor and to collect the data. Figure 5.2 is a schematic diagram representing the hardware structure of the micro-computer and its interfaces. The program at this level is written in assembler and stored permanently in ROM. Details of the M6800 software are described elsewhere (Rowles and Brisk (1979)).

It was originally planned to use these on-line facilities on the kinetic reactor used for present studies. However, they were not fully applied due to the following limitations:

i. The non-linear multivariable search algorithms used for optimal design and parameter estimation along with the main computational program could not be readily run on the PDP 11/60 due to their size and were run on a large mainframe machine (CYBER 173). The flame ionization chromatograph for the analysis of the gas mixture was not interfaced to the micro-computer in time.

ii. The five control loops, to be discussed later, interacted with each other in DDC mode and it was more satisfactory to operate without DDC once the desired conditions were obtained.

In the present studies, the M6800 was used at the start of the experiment to bring the desired variables to the required level and later it was used to monitor the conditions of the experiment. The data collected was entered manually into the CYBER computer where it was processed.
FIGURE 5.2 : The Schematic Diagram of micro-computer hardware and its Interfaces.
5.3 The Experimental Apparatus

The Figure 5.3 is a schematic diagram showing the overall flow system and instruments used for the manual or automatic catalyst kinetic measurements.

5.3.1 A General Description

The apparatus was designed to accommodate three separate gas phase feed streams for ethylene, hydrogen and diluent nitrogen. Each of the reactant feed lines was connected to a nitrogen purge stream and was separately passed through a series of two tubes (0.46 m long and 0.25 m OD) of 3A molecular sieves and Drierite to remove any traces of water present in the reactant feed. A brass filter (Nupro 'F' series) with a mean pore diameter of 60 μm was connected before the controlled needle valve on each feed stream. Its function was to remove any particulate material, to avoid any blockage of the capillary tube used for measuring the gas flow, and for trouble free operation of the fine metering needle valves. The flow rate of each stream could be controlled either manually using the rotameter as a flow indicator, or automatically by the M6800 which measured the differential pressure across the capillary. The gases then passed through a mixing point where the three gas streams were mixed together at a controlled mixing pressure of 100 kPa(g). The mixed gases then passed to the catalytic reactor via a pre-heating coil. The reaction pressure was set downstream of the reactor by a needle valve. The mixing and reactor pressures could be controlled either manually or automatically. The product gases passed through a water cooled heat
Figure 5.3: Schematic diagram of reactor flow system.
exchanger before being vented to atmosphere. Sampling of the reactant and product gases was provided by a continuous bleed stream set at a low flow rate. The compositions of reactant and product gases were determined using a flame ionization chromatograph.

The surging effect in the ethylene gas feed line was overcome by using a large surge vessel and a two stage pressure regulator.

5.3.2 Flow Measurements and Control

The following arrangements were utilized to control gas flow rates, mixing and reactor pressures either manually, or directly by micro-computer.

Normally closed solenoid valves were fitted in the feed lines and pressure compensated needle valves (Flow-stat) were used to control the flow rates of each gas feed stream. These valves were operated using Phillips 4-phase unipolar stepper motors operated by electronic switching. Micro-switches were utilized to limit the range of the needle valves.

Each feed stream was fitted with a rotameter to enable measurement of gas flow rate and to provide visible evidence of gas flow when the apparatus was operating under computer control. A pre-determined length of capillary was used to provide a differential pressure drop for each feed stream. The pressure drop across each capillary was measured by a "Yamatake - Honeywell" differential pressure to current transmitter. These 4-20 ma current signals were converted into voltage signals across precise 250 ohm resistors to provide analog input to the
computer for automatic flow control (see Figure 5.4). Voltage measurements across the resistance were more precise than the rotameter readings. Therefore, the flow rates of each feed stream were calibrated against the voltage readings for manual operation.

The mixing point and reactor pressures were controlled by "Nupro" fine metering needle valves. A pressure gauge of range 0 - 160 kPa displayed the measured pressure at each location. For computer measurements of these pressures, differential pressure to current converters, identical to those described above, were used. In this case, however, the low pressure end of the transmitter was open to atmosphere to provide gauge pressure measurements. The needle valves controlling the pressure could be driven either manually or automatically by stepper motors. Figure 5.5 is a photograph of part of the experimental rig showing the arrangements discussed above.

5.3.3 The Reactor

The reactor was made from 4.2 mm ID by 100 mm long stainless steel tube. Five thermocouple positions were provided for the reactor bed temperature measurements during the reaction. Stainless steel sheathed iron-constantan thermocouples were used. Figure 5.6 shows the details of the reactor. The reactor was immersed in a constant temperature fluidized sand bath, designed and constructed by Barton (1976). Figure 5.7 provides a side view of the sand bath showing the position of the 1200 W heating element. A West Gardian 3 term controller was used to control the temperature of the fluidized sand bath. A Leeds and Northrup's temperature recorder was used to record the
FIGURE 5.4: Flow Rate Measuring System.

ADC - Analog to digital convertor
HP - High Pressure
LP - Low Pressure
Figure 5.5: Photograph of part of the experimental rig to show the flow measurement and control equipments.
All dimensions are in millimeters.

FIGURE 5.6: Differential packed bed flow reactor for kinetic studies.
FIGURE 5.7: Cross-section of Fluidized Sand Bath (Barton (1976)).

All dimensions are in millimeters.
temperatures from the reactor bed and the temperature of the fluidized sand bath.

Figure 5.8 is a schematic diagram of the air supply system for the fluidized sand bath. Air was taken from a 690 kPa line and passed through a series of filters to remove any oil or moisture present. A three stage precision pressure regulator was used to provide a constant fluidization pressure in the sand bath and facilitated control of the fluidized sand bath's temperature to within ±1°C.

A by-pass line was provided to facilitate change-over of settings of variables for the next experiment allowing the catalyst bed to be kept under an atmosphere of desired conditions.

As discussed earlier, the reactor pressure could be maintained either by DDC or manually using a downstream needle valve driven by a stepping motor. A pressure of 20 kPa(g) was used for the present study.

5.3.4 Measurements of Conversion

A Pye 104 series flame ionization gas chromatograph was used for all conversion measurements. The sampling system is shown in Figure 5.9. The Pye 13440 sampling valve could be activated manually or remotely by the control computer. A 1 ml sampling loop was used. A continuous bleed of either the feed stream or reactor product stream could be selected by solenoid valves and directed to the sampling valve of the chromatograph. The operating conditions for the chromatograph were:
Compressed Air (690 kPa)

To fluidized sand bath

24K Metric Rotameter

Air Supply System for Fluidized-sand Bath.

FIGURE 5.8: Air Supply System for Fluidized-sand Bath.
FIGURE 5.9: Chromatograph Sampling System.
Oven temperature = 40.0°C
Carrier gas flow rate = 1.0E-03 m³ sec⁻¹
Hydrogen flow rate = 2.4E-03 m³ sec⁻¹
Air flow rate = 3.6E-02 m³ sec⁻¹
Detector oven temperature = 75°C
Sample gas flow rate = 1.17E-06 m³ sec⁻¹

The output from the chromatograph amplifier was sent to a Shimadzu’s Chromatopac ELA integrator.

5.4 Calibration Procedures

5.4.1 Thermocouples

The thermocouples were calibrated over the range 40°C to 110°C using the fluidized bed (as a constant temperature bath) and a calibrated mercury-in-glass thermometer. The results showed that:

i. There was no significant difference between individual thermocouples.

ii. The actual temperature was a linear function of the temperature as measured by the thermocouple/multi-point recorder combination. A linear regression program was used to determine the line of best fit through the data from all thermocouples.
5.4.2 Flow Rates

The ethylene, hydrogen and nitrogen flowmeters were calibrated at a mixing pressure of 100 kPa(g) using a wet-test meter and/or soap bubble meter. These flow rates were measured against the voltage across the precise resistance (see Section 5.3.2) and the volumetric flow rates were fitted to a second order polynomial after they were corrected to STP.

5.4.3 Gas Chromatograph

Special gas mixtures of ethylene, ethane and hydrogen were used for the gas chromatograph calibration. The ethane mole percentage ranged from 0.8% to 2.1% and the ethylene mole percentage ranged from 5% to 30%, with the balance being hydrogen. The instrument was prepared according to the procedure discussed in Section 5.3.4. Samples were introduced into the column using the sample valve. A linear regression was applied to determine the line of best fit through the data.

5.5 Materials

5.5.1 Gases

The following gases were used for the present studies:

1. Ethylene, CP grade (> 99.5% pure with remainder inert).

2. High purity hydrogen (>99.98% pure).
3. Oxygen-free high purity nitrogen.

5.5.2 Catalyst

5.5.2.1 Catalyst Support

Alcoa T162 non-porous alumina pellets (supplied as nominal 1/8 in = 3.2 mm balls) were used for catalyst support. Pellets were crushed to -12 +14 mesh size (average diameter 1.27E-03 m) in a Tima mill. The crushed pellets were first digested in concentrated hydrochloric acid to remove any iron on the pellet surface originating from the Tima mill and then thoroughly washed with warm distilled water to remove any chloride ions. The washed pellets were dried at 120°C. These dried pellets were used as the catalyst support.

5.5.2.2 Method of Preparation

The palladium/alumina catalyst was prepared by an impregnation technique. A measured amount of PdCl₂ was dissolved in a small quantity of concentrated HCl (12M). The solution was then evaporated to dryness at 70°C, and distilled water was added to obtain the required amount of salt solution which was just enough to wet the alumina pellets. This salt solution was mixed with the alumina pellets and stirred vigorously. The excess water was removed by vacuum drying using a rotary vacuum evaporator.

The impregnated sample was dried at 120°C for two hours then reduced under flowing hydrogen, first at 200°C for one hour to preclude
AlCl₃ formation (Veduraz et. al. (1978)) and then at 330°C for two hours. The catalyst was washed repeatedly with hot distilled water until the elimination of chloride ions was complete. After drying, the sample was further reduced in a hydrogen stream under the previous conditions.

A 0.01% palladium on alumina pellet catalyst was prepared by the above method for the present studies.

5.6 Analysis of Reactor Data

With the small amount of conversion (less than 5%), it was assumed that the reactor operated differentially. Thus, rate could be computed directly from the feed parameters and the measured ethane content in the product gas. For a differential mass of catalyst and plug flow conditions, the reaction rate in terms of ethane formation can be expressed as (see Appendix A for details):

\[
\dot{r}_{C_2H_6} = \frac{F_0}{(1 + X_{C_2H_6})^2} \frac{dX_{C_2H_6}}{dW} \quad (5.1)
\]

For the case of no ethane in the reactor feed, Equation (5.1) may be written in the form

\[
\dot{r}_{C_2H_6} = \frac{F_0}{W} \left[ \frac{(X_{C_2H_6})_f}{1 + (X_{C_2H_6})_f} \right] \quad (5.2)
\]

where
\( F_0 \) = molar feed rate

\( (X_{C_2H_6})_f \) = mole fraction of ethane in product gas

\( W \) = mass of catalyst

The reaction conversion was calculated from the feed parameters and the mole fraction of ethane in the product gas (see Appendix A for details).

\[
X = \frac{X_{C_2H_6}}{(X_{C_2H_4})_o (1 + X_{C_2H_6})} \tag{5.3}
\]

The subscript \( o \) refers to the inlet conditions.
CHAPTER 6

KINETIC STUDIES OF THE ETHYLENE HYDROGENATION REACTION

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6.1 Introduction

This chapter presents a discussion of the results obtained from the conventional kinetic experiments performed with the equipment described in the previous chapter. The results were used to establish the reaction mechanism of the hydrogenation of ethylene over a supported palladium/alumina catalyst. The initial estimates of the parameters of the proposed rate model were calculated to provide the basis of the sequential experimental design technique described in Chapter 3.

6.2 Results and Discussion

The reaction experiments were carried out using hydrogen rich gas mixtures containing 10 to 30% of ethylene. To ensure that the catalytic data were obtained in a region where mass transfer was not controlling, a high total gas flow rate of $42E-06 \text{ m}^3\text{ sec}^{-1}$ was used for the present studies. Theoretical calculations were performed for interparticle effects, confirming that the experimental studies were free from any external diffusion effects (for details see Appendix D). The intraparticle effects were assumed to be negligible as the impregnated catalyst was prepared using a non-porous alumina support of negligible internal surface area. A temperature range of $50^\circ \text{C}$ to $90^\circ \text{C}$ was used for the present study and a fixed amount of the active catalyst was used (about $1.5E-04 \text{ kg before dilution}$).

All experiments were carried out at a conversion below 5% to maintain the differential behaviour of the reactor and also to justify the use of Equation (5.2) to calculate the reaction rate. During some
initial experiments it was established that the maintenance of a small axial temperature gradient was more important than achieving low conversion.

The temperature in the reactor was controlled by separating the active catalyst particles with inert support of the same size. This procedure reduced the longitudinal temperature gradient to a maximum of $5^\circ C$. It was assumed that there was no significant radial temperature gradient due to the small reactor diameter.

Temperatures were measured at five different locations in the reactor (see Section 5.3.3). The rate computed from Equation (5.2) was based on a temperature corresponding to the arithmetic average of these temperature values. This average was considered an improvement over taking the average of inlet and outlet temperatures of the reactor, which has been the practice in the past (Pauls et al. (1959), Koestenblatt and Ziegler (1971)).

Blank experiments in which the reactor contained only catalyst support established that no measurable conversion occurred under these conditions throughout the temperature range investigated.

Previous published studies demonstrated that ethane had no effect on the reaction other than that of an inert diluent. Hence no experiments were performed with ethane added to the feed.

6.2.1 Catalyst Activity

It has been observed that the activity of the palladium
supported on alumina catalyst stabilizes after an initial declining period. The activity during the initial period was dependent upon two factors; firstly, the composition of the gaseous mixture and secondly, the gaseous atmosphere before the exposure of the catalyst to the reaction mixture. Two gaseous atmospheres were investigated: an inert atmosphere with nitrogen gas and a preconditioning atmosphere of hydrogen gas. The behaviour of the fresh catalyst in each atmosphere was the same; that is, an initial decline in the activity followed by a constant activity (see Figures 6.1 and 6.2). Similar phenomena were observed by Yamabe et al. (1974b) for their palladium/silica-alumina catalyst. On the other hand, two different behaviours were observed for the used catalyst. A gradual increase in the catalyst activity followed by a constant activity was observed for those catalysts which were kept in a nitrogen atmosphere (Figure 6.1). However, the behaviour of the hydrogen conditioned used catalyst activity was similar to that of the fresh catalyst (Figure 6.2). Here, the constant activity will be called the "steady" activity of the catalyst. The reaction rate for a given condition was always measured at the steady activity of the catalyst.

Test runs were carried out to establish that the catalyst could be used for a longer period under different conditions without losing much of its activity. After an initial loss in activity it was observed that the catalyst tended to lose about 2 to 5% of its activity after using it for more than 10 to 15 experimental runs under different conditions (see Figure 6.3). The loss in the activity was predominant at higher temperatures (> 80°C). A test was designed to check the activity after every series of experiments. If the loss in activity was more than 5% the reactor bed was replaced. Any error
FIGURE 6.1: Nitrogen conditioned catalyst activity

- $P_{C_2H_4} = 29.7\%$, $P_{H_2} = 60.1\%$
- $T_{av} = 365^\circ K$
- $T_{av} = 324^\circ K$

$O$: Fresh Catalyst;  $\square$: Used Catalyst

$W = 1.488 \times 10^{-4}$ kg.
FIGURE 6.2: Hydrogen conditioned catalyst activity

○ Fresh Catalyst; □ Used Catalyst

\[ W = 1.492 \times 10^{-4} \text{ kg.} \]
FIGURE 6.3: Catalyst reproducibility test.
introduced by this small amount of deactivation can be overlooked when compared to the error arising from averaging the reactor temperatures to establish the reaction rate.

For the nitrogen conditioned catalyst, at the maximum hydrogen concentrations, and for the hydrogen conditioned catalyst, at the maximum ethylene concentrations, high axial temperature gradients were observed. As explained later, this was due to the rate dependence being more than first order in hydrogen and nearly first order in ethylene for the nitrogen and hydrogen conditioned catalysts respectively. It was also observed that the maximum temperature rise in the reactor bed occurred during these two situations. Nitrogen gas was therefore used as a diluent in the reaction mixture to avoid these temperature rises. A minimum of 10% nitrogen gas was used as diluent in further studies.

6.2.2 Activation Energy

There is little agreement in the literature on the value of the activation energy of the reaction. The variability of these results could be attributed to the difficulty in estimating the average temperature at which the reaction occurs and in some cases, especially closed systems, the diffusional effects between the bulk gas and the catalyst surface. In the present studies, the value of the activation energy for the reaction was measured over a fairly small temperature range varying from 50\textdegree{} to 90\textdegree{}C. The small temperature range was chosen to avoid any temperature rise in the catalyst bed as the catalytic reaction is exothermic.
Arrhenius plots of experimental data for differently conditioned catalysts, as shown in Figures 6.4 and 6.5, revealed a break occurring around $70^\circ C$. The values of the activation energy obtained using a linear least squares method for different temperature ranges and conditioned catalysts are given in Table 6.1. The change of the slope of the Arrhenius plot has also been reported for this reaction on nickel catalyst at around $150^\circ C$ (Fulton and Crosser (1965), Koh and Hughes (1974)). The explanation given is based on decreased adsorption of hydrogen (Sato and Miyahara (1965)) or decreased adsorption of ethylene (Koh and Hughes (1974)) on the nickel catalyst surface.

<table>
<thead>
<tr>
<th>Catalyst Atmosphere</th>
<th>Temperature between $50^\circ$ to $70^\circ C$ (kcal/mole)</th>
<th>Temperature between $70^\circ$ to $90^\circ C$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>9.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>17.2</td>
<td>7.4</td>
</tr>
</tbody>
</table>

It appears from Table 6.1 that there was an increase in the activation energy for the hydrogen conditioned catalyst. Similar phenomena was also observed by Couper and Eley (1950) and Scholten and Konvalinka (1966) in their studies of the conversion of para-hydrogen on palladium catalysts. Both sets of authors interpreted the increase in the activation energy as being due to the absorption of the hydrogen on
FIGURE 6.4: Temperature dependence of reaction rate for nitrogen conditioned catalyst:

\[ P_{C_2H_4} = (10.95 \pm 0.24)\% \], \[ P_{H_2} = (60.25 \pm 0.25)\% \]

\[ F_0 = (1.765E-06 \pm 8.3E-09) \text{ kg mole/sec} \].

\[ \Delta E = 3.8 \text{ k cal/mole} \]

\[ \Delta E = 9.2 \text{ k cal/mole} \]

(70.5°C)
FIGURE 6.5: Temperature dependence of reaction rate for hydrogen conditioned catalyst;
\[ P_{C_2H_4} = (10.27 \pm 0.10)\%, P_{H_2} = (50.04 \pm 0.04)\% \]
\[ P_0 = (1.76 \times 10^{-6} \pm 7.5 \times 10^{-9}) \text{ kg mole/sec.} \]
the palladium surface and this was attributed to the formation of the 
$\beta$-hydride phase in the Pd-H system.

6.2.3 Rate Equation

An experimental procedure was planned to establish the effect of the average partial pressure of each component while holding the average partial pressures of the other components constant. Nitrogen gas was employed as diluent to make up the total gas flow rate. Figures 6.6 and 6.7 show the results obtained for the experiments with the concentration of ethylene and hydrogen held constant in turn for the differently conditioned catalysts (also see Tables E.6 and E.7 in Appendix E). The empirical dependence of the rate on the component partial pressures under different conditions is given in Table 6.2. A wide spectrum of reaction conditions was used to get an overall picture of the rate dependence.

As the use of the above experimental procedures, which kept one of the component partial pressures and the average temperature of the reaction constant, could bias the apparent effects of the variables on the reaction rate, more experiments were carried out in which partial pressures of ethylene and hydrogen as well as reaction temperature were varied while keeping the total feed flow rate constant. This rate data (see Tables E.8 and E.9 in Appendix E) was first used to determine the empirical dependence of the rate on partial pressures at different temperatures ($T < 70^\circ C$). An empirical rate model such as:

$$
\dot{r} = A_0 \exp\left(\frac{-\Delta E}{RT}\right) \left(\frac{P_{C_2H_4}^{\alpha}}{P} \right) \left(\frac{P_{H_2}^{\beta}}{P} \right)
$$

(6.1)
FIGURE 6.6 : The effect of hydrogen partial pressure on the reaction rate for differently conditioned catalysts

\[ r_{C_2H_6} \] = 1.12 E-04 \( P_{H_2}^{1.23} \)

\[ r_{C_2H_6} \] = 2.47 E-05 \( P_{H_2}^{1.82} \)

- \( \Delta \) : N\(_2\) conditioned, Tav = 332.5°K, \( P_{C_2H_4} = 10.8\% \)

- \( \square \) : H\(_2\) conditioned, Tav = 344.5°K, \( P_{C_2H_4} = 30.2\% \)
FIGURE 6.7: The effect of ethylene partial pressure on the reaction rate for differently conditioned catalysts.

- **N₂ conditioned, Tav = 352.8°K, P₁H₂ = 60.0%**
- **H₂ conditioned, Tav = 343.9°K, P₁H₂ = 50.1%**
Table 6.2: Reaction orders with respect to partial pressures of ethylene and hydrogen under various conditions.

<table>
<thead>
<tr>
<th>Catalyst Atmosphere</th>
<th>Ethylene Dependence</th>
<th>Hydrogen Dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reaction Order</td>
<td>Conditions</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.60</td>
<td>( P_{C_2H_4} = 60.0% )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temp=79.6°C</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.97</td>
<td>( P_{C_2H_4} = 50.1% )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temp=70.7°C</td>
</tr>
</tbody>
</table>
was fitted, after utilizing the reparameterization technique (see Section 3.2.4) and the non-linear least squares method discussed in Chapter 4. This gave the following results (also see Tables E.10 and E.11 for statistical analysis of the parameter estimates):

\[
\left( \frac{r_{N_2}}{C_6H_6} \right)_N = 5.84E+02 \exp\left( -\frac{1.07E+04}{RT} \right) \left( P_{C_2H_4} \right)^{0.43} \left( P_{H_2} \right)^{1.81} \quad (6.2)
\]

(Nitrogen conditioned catalyst)

\[
\left( \frac{r_{H_2}}{C_6H_6} \right)_H = 6.31E+05 \exp\left( -\frac{1.47E+04}{RT} \right) \left( P_{C_2H_4} \right)^{0.95} \left( P_{H_2} \right)^{1.10} \quad (6.3)
\]

(Hydrogen conditioned catalyst)

For the nitrogen conditioned catalyst, the reaction orders with respect to the partial pressures of ethylene and hydrogen are in good agreement with Sakellaropoulos and Langer (1981). The reaction order with respect to the ethylene partial pressure for the hydrogen conditioned catalyst is also in good agreement with Nagamoto and Inoue (1981). The fractional order with respect to ethylene and hydrogen suggest a Langmuir type of mechanism with adsorption of hydrogen and/or ethylene on the catalyst surface.

Equations (6.2) and (6.3) also reveal that the reaction order with respect to the partial pressure of ethylene has increased by a factor of two for the hydrogen conditioned catalyst. It could be interpreted that the ethylene and hydrogen molecules had an equal opportunity to adsorb on the nitrogen conditioned catalyst. On the other hand, in the case of the hydrogen conditioned catalyst, the active sites would have been occupied by the hydrogen atoms due to the nature of the
palladium metal. Therefore, the extra adsorption of hydrogen atoms on the palladium would have reduced the possibility of the ethylene molecules adsorbing, or the gaseous ethylene molecules would have reacted with the adsorbed hydrogen atoms. This blocking by hydrogen of ethylene’s access to the surface in the hydrogen conditioned catalyst could be the reason for an increase in the reaction order with respect to ethylene partial pressure. A similar explanation could be true for the decrease in the reaction order with respect to the hydrogen partial pressure for the hydrogen conditioned catalyst. A nearly second order dependence with respect to the hydrogen partial pressure in the case of the reaction rate for the nitrogen conditioned catalyst could be explained by an addition of a second hydrogen molecule in the reaction mechanism. Similar explanations were also given by Sakellaropoulos and Langer (1981). In summary, it appears there are two different reaction mechanisms taking place, depending upon the pre-conditioning of the catalyst.

6.2.4 Reaction Mechanism and Kinetic Model:

The purpose of the present studies was to establish a reaction mechanism based on the following kinetic observations:

i. Palladium has a strong affinity for hydrogen. Hydrogen is absorbed on its surface and also permeates through it.

ii. The apparent orders of the reaction with respect to ethylene and hydrogen for the nitrogen conditioned catalyst are:
\[ 0.4 < \alpha < 0.6 \quad \text{for ethylene} \]
\[ 1.2 < \beta < 2.0 \quad \text{for hydrogen} \]

iii. The apparent orders of the reaction with respect to ethylene and hydrogen for the hydrogen conditioned catalyst are:

\[ 0.8 < \alpha < 1.0 \quad \text{for ethylene} \]
\[ \beta > 1.0 \quad \text{for hydrogen} \]

iv. The ethylene is adsorbed as \( \pi \)-adsorbed ethylene and reacts instantly as it comes in contact with hydrogen (Soma (1979)).

Based on the observations, the following mechanistic steps are proposed to explain the kinetics of the ethylene hydrogenation reaction on palladium catalyst:

Step (I) \[ \text{H}_2(g) + M \rightarrow H \ldots M + H' \] (6.4)

Step (II) \[ \text{H}_2(g) + 2M \rightarrow 2H \ldots M \] (6.5)

Step (III) \[ \text{C}_2\text{H}_4(g) + M \rightarrow \text{C}_2\text{H}_4 \ldots M \] (6.6)

Step (IV) \[ \text{C}_2\text{H}_4 \ldots M + H \ldots M \rightarrow \text{C}_2\text{B}_5 \ldots M + M \] (6.7)

Step (IV') \[ \text{C}_2\text{H}_4 \ldots M + H' \rightarrow \text{C}_2\text{B}_5 \ldots M \] (6.8)

Step (V) \[ \text{C}_2\text{H}_4(g) + H \ldots M \rightarrow \text{C}_2\text{B}_5 \ldots M \] (6.9)

Step (VI) \[ \text{C}_2\text{B}_5 \ldots M + \text{H}_2(g) \rightarrow \text{C}_2\text{B}_6 \ldots M + H' \] (6.10)

Step (VII) \[ \text{C}_2\text{B}_5 \ldots M + \text{H}_2(g) \rightarrow \text{C}_2\text{B}_6(g) + H \ldots M \] (6.11)

Step (VIII) \[ \text{C}_2\text{B}_6 \ldots M \rightarrow \text{C}_2\text{B}_6(g) + M \] (6.12)

Step (IX) \[ H \ldots M \rightarrow \text{HM} \rightarrow M \] (6.13)

Step (X) \[ \text{HM} \rightarrow H' + M \] (6.14)

Step (XI) \[ H' + H' \rightarrow \text{H}_2(g) \] (6.15)

When the reaction mixture is exposed to the nitrogen
conditioned catalyst, both reactants, ethylene and hydrogen, would be competing for the active sites (M). This may occur via Steps (I) and (III). The adsorption of the ethylene molecule \( \text{C}_2\text{H}_4 \text{...M} \) is assumed to be \( \pi \)-adsorbed ethylene (see Chapter 2). These two steps could be called initiation steps for this reaction. In the case of the hydrogen conditioned catalyst, the catalyst surface would be blanketted by hydrogen atoms (H...M) (Step (II)). Therefore, the gaseous ethylene molecule would react with adsorbed or absorbed hydrogen atoms (Step (V)). Hence Step (II) would be the only initiating step of the reaction for the hydrogen conditioned catalyst.

The reaction could propagate via Steps (IV) or (IV') and Step (VI) for the nitrogen conditioned catalyst. The occurrence of Step (IV) or (IV') is debatable. For Step (IV), both the adsorbed species \( \text{C}_2\text{H}_4 \text{...M} \) and H...M) should be adjacent to each other to react. This situation could occur, but would be a slow step. Since the formation of the adsorbed ethyl radical \( \text{C}_2\text{H}_5 \text{...M} \) is not the slow step based on the kinetic model (to be discussed later), Step (IV) could be discarded. Hence, Steps (IV') and (VI) would be the propagating steps for the nitrogen conditioned catalyst. Steps (V) and (VII) would be the propagating steps for the hydrogen conditioned catalyst.

Steps (IX),(X) and (XI) could be considered as terminating steps. Step (IX) indicates that the adsorbed hydrogen dissolves in the palladium metal (HM). Here it is assumed that the dissolved hydrogen site is still active for the adsorption of the hydrogen atoms. By the nature of the palladium metal, the excess dissolved hydrogen diffuses as atomic hydrogen (H') (Step (X)). Step (XI) is taken as the overall
reaction step for the recombination of atomic hydrogen.

On the basis of the above discussion, the kinetic steps for the ethylene hydrogenation on differently conditioned palladium catalyst could be written in the following ways:

**Reaction mechanism for the nitrogen conditioned palladium catalyst**

Initiation:

\[
\begin{align*}
K_{H_2} & \quad H_2(g) + M \xleftrightarrow{\text{\( K_{H_2} \)}} \quad H \ldots M + H' \\
K_{C_2H_4} & \quad C_2H_4(g) + M \xleftrightarrow{\text{\( K_{C_2H_4} \)}} \quad C_2H_4 \ldots M
\end{align*}
\] (6.4)

Propagation:

\[
\begin{align*}
C_2H_4 \ldots M + H' & \xleftrightarrow{\text{\( K_1 \)}} \quad C_2H_5 \ldots M \\
C_2H_5 \ldots M + H_2(g) & \quad \longrightarrow \quad C_2H_6 \ldots M + H'
\end{align*}
\] (6.8)

Termination:

\[
\begin{align*}
K_{C_2H_6} & \quad C_2H_6 \ldots M \xleftrightarrow{\text{\( K_{C_2H_6} \)}} \quad C_2H_6(g) + M \\
K_2 & \quad H \ldots M \xleftrightarrow{\text{\( K_2 \)}} \quad HM = M \\
K_3 & \quad HM \xleftrightarrow{\text{\( K_3 \)}} \quad H' + M \\
K_4 & \quad H' + H' \xleftrightarrow{\text{\( K_4 \)}} \quad H_2(g)
\end{align*}
\] (6.12)
Reaction mechanism for the hydrogen conditioned palladium catalyst

Initiation:

\[ \text{H}_2(g) + 2 \text{M} \xrightleftharpoons{K_{E_2}^{'}} 2 \text{H}...\text{M} \]  \hspace{1cm} (6.5)

Propagation:

\[ \text{C}_2\text{H}_4(g) + \text{H}...\text{M} \xrightleftharpoons{K_1^{'}} \text{C}_2\text{H}_5...\text{M} \]  \hspace{1cm} (6.9)
\[ \text{C}_2\text{H}_5...\text{M} + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) + \text{H}...\text{M} \]  \hspace{1cm} (6.11)

Termination:

\[ \text{H}...\text{M} \xleftarrow{K_2^{'}} \text{HM} \xrightarrow{K_3^{'}} \text{H} + \text{M} \]  \hspace{1cm} (6.13)
\[ \text{H} + \text{H} \xrightarrow{K_4^{'}} \text{H}_2(g) \]  \hspace{1cm} (6.15)

It is evident from sub-Section 6.2.3 that the reaction order with respect to the hydrogen partial pressure is more than one. Therefore, this shows that there is a second addition of the hydrogen molecule in the reaction scheme. Hence, it is assumed that the step in which the second hydrogen addition takes place would be the rate determining step. Based on the rate determining step, Equation (6.10) and (6.11) for nitrogen and hydrogen conditioned catalysed reactions respectively, the rate models are given as follows (see Appendix F for the detailed derivations):
The least squares fit of the rate data used for finding the empirical dependence in the last sub-section, gave the following results (also see Tables E.12 and E.13 for statistical analysis of the parameter estimates):

\[
\left( \frac{r_{C_2H_6}}{N_2} \right) \propto \frac{\kappa P_{C_2H_4} (P_B)^2}{1 + K_{C_2H_4} P_{C_2H_4} + K_{B_2} (P_B)^{0.5}}
\]  \hspace{1cm} (6.16)

\[
\left( \frac{r_{C_2H_6}}{H_2} \right) \propto \frac{\kappa' P_{C_2H_4} (P_B)^{1.5}}{1 + K_{B_2} (P_B)^{0.5}}
\]  \hspace{1cm} (6.17)

Figures 6.8 and 6.9 show both the observed reaction rate and the predicted rate by Equations (6.18) and (6.19). Good correlation is found between the observed rates and the proposed kinetic models.

The present kinetic model for the reaction is completely different to that proposed for the nickel catalyst (see Chapter 2). The main difference is the second addition of the hydrogen in the
FIGURE 6.8: Rate data correlation for the nitrogen conditioned catalysed reaction kinetic model (Equation (6.18)).
FIGURE 6.9: Rate data correlation for the hydrogen conditioned catalysed reaction kinetic model (Equation (6.19)).
reaction scheme. The second addition of the hydrogen molecule could be considered as being due to the palladium metal's nature. In the present studies, however, no change in the activity was observed during the reaction, hence the proposed reaction mechanism could be applied directly.

To understand the fall in the activation energy above a temperature of 70°C a few more experiments were carried out using the nitrogen conditioned catalyst. These data (see Table E.14 in Appendix E) were used to fit the model defined by Equation (6.16). The least squares fit of the data gave the following results (also see Table E.15 of Appendix E for statistical analysis of the parameter estimates):

\[
\frac{(\text{I}_2\text{H}_6)_2}{2} = \frac{0.11 \exp\left(\frac{-3.64E+03}{RT}\right) \text{P}_{\text{C}_2\text{H}_4}(\text{P}_\text{H}_2)^2}{1 + 4.27 \text{P}_{\text{C}_2\text{H}_4} + 0.19 (\text{P}_\text{H}_2)^{0.5}} \quad (6.20)
\]

Figure 6.10 shows that there is also a good correlation between the observed reaction rates and the proposed kinetic model (Equation (6.16)) beyond the 70°C temperature at which the Arrhenius plots (Figures 6.4 and 6.5) show a break.

It is evident from Equations (6.18) and (6.20) that the values of the equilibrium constants for ethylene and hydrogen are lower in the higher temperature region (T > 70°C). Koh and Hughes (1974) have also observed a similar phenomenon for ethylene adsorption on the nickel supported catalyst. They suggested that the decrease in the equilibrium constant of the ethylene could be the reason for the drop in the
FIGURE 6.10: Rate data correlation for the nitrogen conditioned catalysed reaction kinetic model (Equation (6.20)).
activation energy above 135°C. Therefore, a similar interpretation can be put forward to explain the drop in the activation energy for differently conditioned palladium catalysts above 70°C.

The apparent activation energy ($E_{\text{obs}}$) is related to the heat of adsorption or the enthalpy change due to chemisorption ($\Delta H$) in the heterogeneous catalysis by the following expression:

$$E_{\text{obs}} = E_{\text{true}} + \Sigma (\Delta H)$$  \hspace{1cm} (6.21)

where $E_{\text{true}}$ is the true activation energy of the reaction and $\Sigma (\Delta H)$ is the total heat of adsorption of different chemisorbed species on the catalyst surface during the reaction.

Generally, the heat of adsorption is a function of the surface coverage of the catalyst by chemisorbed species. As a consequence, the temperature variation not only affects the surface coverage but also, by extension, the heat of adsorption. Thus, as it has been observed, in the high reaction temperature region ($T > 70^\circ C$) where the surface coverage is low the apparent activation energy is low. The high apparent activation energy for the hydrogen conditioned catalysed reaction may be explained similarly.

Equation (6.18) also reveals that the equilibrium constant for the ethylene adsorption is significantly greater than the equilibrium constant for the hydrogen adsorption. This emphasises that the adsorption of the ethylene molecules on the active sites is stronger than the hydrogen molecule adsorption. Therefore, at high concentration of the ethylene and low reaction temperature
and under these conditions Equation (6.16) yields

\[
\frac{\text{d}[\text{C}_2\text{H}_4]_{\text{Pc B}_2}}{\text{d}t} = \frac{1}{1 + K_B (P_B)^{0.5}} \quad \text{(6.22)}
\]

Hence, the reaction is zero order in ethylene and second order in hydrogen at high ethylene concentration and low reaction temperature. Similar observations were made by Sakellaropoulos and Langer (1981). The zero order in ethylene was also observed by Nagamoto and Inoue (1981) for ethylene fractions greater than 20%.

6.2.5 Kinetic Model for Sequential Experimental Design Studies:

Two types of kinetic models, the empirical model (also known as the power law rate model) and the mechanistic model have been proposed for the present kinetic study. The mechanistic kinetic model gave the actual picture of the reaction while the power law rate model shows the overall reaction dependence. The sequential experimental design strategy can be applied to both types of kinetic models for estimating their parameters. Correlations and confidence limits in the parameter estimates were two factors taken into consideration for the selection of the kinetic model for the sequential experimental design studies. It is apparent from Tables E.12, E.13 and E.15 of Appendix E that the parameter estimates for the mechanistic model not only have large confidence limits but also are very highly correlated. However, Tables E.10 and E.11 of Appendix E show that the confidence limits and
correlation coefficients for the parameter estimates of the empirical model are not seriously significant. It is therefore evident that the mechanistic model as such would not be useful for parameter estimation using sequential experimental design. As explained earlier in Chapters 3 and 4, high correlation among the parameter estimates not only complicates the mechanistic interpretation but also complicates the parameter estimation. It is also shown in Chapter 4 that the reparameterized form of the power law rate model gave satisfactory estimates even under high experimental noise. It was also observed that the initial estimates were not critical to start the experimental design for the reparameterized power law rate model.

It is apparent from the above discussions that the power law rate model would be appropriate to use to estimate the parameters by the sequential experimental design strategy for the present reaction kinetic studies.
CHAPTER 7

AN APPLICATION OF SEQUENTIAL EXPERIMENTAL DESIGN
TO
A KINETIC STUDY

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7.1 Introduction

In this chapter the practical application of, and the importance of sequential experimental design to a laboratory experimental study of the kinetics of ethylene hydrogenation are discussed. This is done in the light of the experience gained from the simulation studies of Chapter 4.

7.2 Kinetic Model

Conventional kinetic studies of the ethylene hydrogenation reaction are reported in Chapter 6. Two types of kinetic models, empirical and mechanistic, were proposed. The following empirical model was found satisfactory for the present sequential experimental design (see Section 6.2.5):

\[
\frac{dC_{2H_6}}{dt} = A_0 \exp\left(\frac{-E}{RT}\right) (P_{C_2H_4})^\alpha (P_{H_2})^\beta
\]

Parameters \(A_0\), \(E\), \(\alpha\), and \(\beta\) have been obtained by conventional methods and their values are discussed in Chapter 6. These values were used as the initial estimates in the parameter estimation for the first block of experiments at the start of the sequential experimental design.

The importance and influence of reparameterization on sequential experimental design have been discussed in Chapter 4. It has been established that the reparameterized (RP) model leads to better parameter estimates and more economical experimentation; tolerates noisy data better; and allows an experimental programme to converge. Also
with the RP model, a sudden increase in the number of function evaluations for the optimal design appeared a useful criterion for terminating the experimental programme.

Based on the earlier RP model, Equation (7.1) is reparameterized for Arrhenius rate constants (Equation (3.18)) and yields

$$r_{C_2H_6} = \exp(\theta) \exp[-T \exp(\rho)] \left( P_{C_2H_4} \right)^{\alpha} \left( P_{H_2} \right)^{\beta} \quad (7.2)$$

Equation (7.2) was used for the sequential design in the kinetic studies of ethylene hydrogenation reactions catalysed by differently conditioned palladium catalysts. The MVD criterion (Section 4.5) was used in the sequential experimental design strategy. Three sequential experimental designs were planned covering two main aspects. Firstly, to improve the precision of the parameter estimates for two differently conditioned (nitrogen and hydrogen) palladium catalysts in the temperature range of 50° to 70°C; that is, the temperature just before the fall in activation energy as observed earlier in the conventional kinetic studies (Chapter 6). Secondly, to study the effect of the overall temperature range (that is, 50° to 90°C) on the precision of the parameter estimates in the situation when no prior kinetic information about the reaction is assumed.

The continuous operating region was defined by $P_{C_2H_4}$ from 10 to 30% of the total pressure, $P_{H_2}$ from 50 to 80% and $T$ from 323° to 343°K for the first and second sequential design and 323° to 363°K for the third sequential design. The mole fractions of gas were restricted by $X_{C_2H_4} + X_{H_2} < 0.9$, with nitrogen gas used as diluent.
The data from each set of experiments consisted of one set of independent variables (mole fraction of ethylene and hydrogen and temperature) together with the dependent variable obtained from Equation (5.2) as the observed reaction rate.

7.3 First Sequential Experimental Design (SD-1)

The sequential experimental design strategy was performed to obtain precise parameter estimates for the empirical kinetic model (Equation (6.2)) of the nitrogen conditioned catalysed palladium reaction in the temperature range of 50° to 70°C. That is, the temperature range just before the fall in the activation energy, as observed earlier (Chapter 6) in the conventional kinetic studies.

It has been observed from the simulation studies (Chapter 4) that all the designed experiments lay at the boundaries of the operability region. Therefore, an initial block of six experiments was performed at the boundaries of the operability region in a fairly arbitrary way so as to span the range of variables. The data from this block of six experiments was subject to a least squares fit to obtain the parameter estimates to be used in initiating the subsequent sequential design. The initial parameter estimates used in this least squares fitting were those given in Equation (6.2).

7.3.1 Results and Discussion

The initial block of six experiments and subsequent designed experiments are shown in Figure 7.1 Table 7.1 shows the actual
FIGURE 7.1: Experimental conditions for initial block and subsequent designed experiments (SD-1).
Table 7.1: Experimental data * for the nitrogen conditioned catalyst (SD-1).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Average Temperature (°C)</th>
<th>$P_{C_2H_4}$ (%)</th>
<th>$P_B$ (%)</th>
<th>Rate (kg mole/kg cat/sec) ($E+05$)</th>
<th>No Function Evaluations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD1-1</td>
<td>50.8</td>
<td>29.87</td>
<td>50.06</td>
<td>0.9588</td>
<td></td>
</tr>
<tr>
<td>SD1-2</td>
<td>70.2</td>
<td>30.08</td>
<td>49.87</td>
<td>2.5176</td>
<td></td>
</tr>
<tr>
<td>SD1-3</td>
<td>70.1</td>
<td>10.16</td>
<td>79.85</td>
<td>3.3875</td>
<td></td>
</tr>
<tr>
<td>SD1-4</td>
<td>69.9</td>
<td>10.25</td>
<td>50.13</td>
<td>1.4468</td>
<td></td>
</tr>
<tr>
<td>SD1-5</td>
<td>50.3</td>
<td>10.45</td>
<td>79.65</td>
<td>1.1936</td>
<td></td>
</tr>
<tr>
<td>SD1-6</td>
<td>70.4</td>
<td>29.96</td>
<td>60.18</td>
<td>3.5643</td>
<td></td>
</tr>
<tr>
<td>-7(D)a</td>
<td>70.0</td>
<td>10.00</td>
<td>80.00</td>
<td>-</td>
<td>155</td>
</tr>
<tr>
<td>(E)b</td>
<td>70.5</td>
<td>10.56</td>
<td>79.47</td>
<td>3.4086</td>
<td></td>
</tr>
<tr>
<td>-8(D)</td>
<td>52.34</td>
<td>22.07</td>
<td>67.93</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>(E)</td>
<td>52.5</td>
<td>22.56</td>
<td>68.05</td>
<td>1.5715</td>
<td></td>
</tr>
<tr>
<td>-9(D)</td>
<td>70.0</td>
<td>30.00</td>
<td>60.00</td>
<td>-</td>
<td>167</td>
</tr>
<tr>
<td>(E)</td>
<td>70.3</td>
<td>29.73</td>
<td>60.54</td>
<td>3.5112</td>
<td></td>
</tr>
<tr>
<td>-10(D)</td>
<td>70.0</td>
<td>30.0</td>
<td>50.0</td>
<td>-</td>
<td>126</td>
</tr>
<tr>
<td>(E)</td>
<td>70.5</td>
<td>30.14</td>
<td>49.76</td>
<td>2.4918</td>
<td></td>
</tr>
<tr>
<td>-11(D)</td>
<td>51.3</td>
<td>21.12</td>
<td>68.78</td>
<td>-</td>
<td>1269</td>
</tr>
</tbody>
</table>

* Nitrogen gas is used as diluent.

a D: Designed experiment; b E: Actual experiment performed
experiments performed for the sequential design. As observed earlier (Chapter 4), the designed experiments also lay at the boundaries of the operability region.

It is apparent from the Table 7.1 that after the fourth designed experiment there is a sharp increase in the number of function evaluations for obtaining the fifth optimal design. The sudden increase in the number of function evaluations for the optimal design could be due to a flat surface in the design criterion as a function of experimental conditions. This flatness in the response surface has been discussed in Chapter 4. It was observed in the simulation studies (Chapter 4) that after the point of apparent flatness in the response surface the sequential design was insensitive to variation in the choice of experimental conditions with respect to improvement in the precision of the parameter estimates. It was proposed that the observation of flatness in the response surface could be used as the stopping criterion for sequentially designed experiments. Therefore, the present sequence of the designed experiments was terminated after the fifth designed experiment.

Table 7.2 gives the parameter estimates with their approximate 95% confidence intervals obtained at each stage of the sequential experimental design (also see Table G.1 in Appendix G for the calculated values of parameters for the empirical model, Equation (7.1)). It is apparent from Table 7.2 that the parameters estimated after the fourth designed experiment (experiment number 10), are not significantly different from the parameters estimated by the sixteen experiments of the conventional studies. It is also apparent from Table 7.2 that the
Table 7.2: Estimates at each stage of the sequential experimental design (SD-1) for the nitrogen conditioned catalyst (Equation (7.1)).

<table>
<thead>
<tr>
<th>Run No</th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD1-6</td>
<td>-9.644(±0.204)</td>
<td>8.651(±0.085)</td>
<td>0.518(±0.093)</td>
<td>1.773(±0.242)</td>
</tr>
<tr>
<td></td>
<td>(±12.1%)</td>
<td>(±1.0%)</td>
<td>(±18.0%)</td>
<td>(±13.7%)</td>
</tr>
<tr>
<td>SD1-7</td>
<td>-9.646(±0.123)</td>
<td>8.649(±0.049)</td>
<td>0.518(±0.057)</td>
<td>1.768(±0.138)</td>
</tr>
<tr>
<td></td>
<td>(±1.3%)</td>
<td>(±0.6%)</td>
<td>(±11.0%)</td>
<td>(±7.8%)</td>
</tr>
<tr>
<td>SD1-8</td>
<td>-9.644(±0.096)</td>
<td>8.645(±0.039)</td>
<td>0.523(±0.046)</td>
<td>1.778(±0.113)</td>
</tr>
<tr>
<td></td>
<td>(±1.0%)</td>
<td>(±0.5%)</td>
<td>(±8.8%)</td>
<td>(±6.6%)</td>
</tr>
<tr>
<td>SD1-9</td>
<td>-9.648(±0.081)</td>
<td>8.640(±0.035)</td>
<td>0.516(±0.039)</td>
<td>1.768(±0.102)</td>
</tr>
<tr>
<td></td>
<td>(±0.8%)</td>
<td>(±0.4%)</td>
<td>(±7.6%)</td>
<td>(±5.8%)</td>
</tr>
<tr>
<td>SD1-10</td>
<td>-9.651(±0.082)</td>
<td>8.636(±0.035)</td>
<td>0.513(±0.039)</td>
<td>1.778(±0.102)</td>
</tr>
<tr>
<td></td>
<td>(±0.9%)</td>
<td>(±0.4%)</td>
<td>(±7.6%)</td>
<td>(±5.7%)</td>
</tr>
<tr>
<td>From</td>
<td>-9.724(±0.153)</td>
<td>8.587(±0.084)</td>
<td>0.434(±0.070)</td>
<td>1.805(±0.200)</td>
</tr>
<tr>
<td>studies</td>
<td>(±1.6%)</td>
<td>(±1.0%)</td>
<td>(±16.1%)</td>
<td>(±11.1%)</td>
</tr>
</tbody>
</table>

* Quantities in parantheses are the approximate 95% confidence interval for the parameter estimates.
parameters estimated from sequential experimental design have smaller confidence intervals compared to the conventional studies. Since the precision of the parameter estimates is measured by the confidence intervals (see Section 3.2.2), it is demonstrated that the sequential experimental design leads to a better precision in the parameter estimates with a fewer number of experiments.

It is also apparent from Table 7.2 that the estimated values of $\alpha$ and $\beta$ have comparatively bigger confidence intervals compared to $\theta$ and $\rho$. This could be due to high correlations (see Table 7.3). It may also be due to the deviations of the experimental conditions from those specified by the design criterion (see Table 7.1). Mezaki (1969) has indicated that slight deviations of the experimental conditions from those specified by the design criterion could lead to an increase in the confidence region of the parameter estimates. As $\alpha$ and $\beta$ are highly correlated with $\theta$ (due to the model form), slight deviations of the experimental conditions from those of the design could be the reason behind the bigger confidence intervals for $\alpha$ and $\beta$. However, similar observations were also made with the conventional studies.

The joint confidence regions (JCR) of the sequential design obtained from Equation (3.13) (Figures 7.2 to 7.4) are much smaller than those of the conventional studies, indicating that more precise parameter estimates were obtained by sequential design experimentation. The smaller confidence region is attributed to the experimental approach which resulted from the improved design of experiments.

The sequentially designed experimentation has, therefore, demonstrated that the parameter estimates obtained were more precise and
Table 7.3: Correlation coefficients between parameter estimates.

<table>
<thead>
<tr>
<th></th>
<th>$\theta$</th>
<th>$\rho$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conventional Method</strong></td>
<td>1</td>
<td>-0.2509</td>
<td>0.9541</td>
<td>0.8065</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>-0.2167</td>
<td>0.0611</td>
</tr>
<tr>
<td><strong>Sequential Design Method</strong></td>
<td>1</td>
<td>-0.1913</td>
<td>0.9415</td>
<td>0.8709</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>0.0434</td>
<td>0.0832</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>0.8125</td>
<td>1</td>
</tr>
</tbody>
</table>
FIGURE 7.2: The joint approximate 95% confidence region for $\theta$ and $\varphi$ at constant $\alpha$ and $\beta$ (SD-1).
Figure 7.3: The joint approximate 95% confidence region for $\beta$ and $\alpha$ at constant $\phi$ and $\beta$ (SD-1).
FIGURE 7.4 : The joint approximate 95% confidence region for $\theta$ and $\beta$ at constant $\phi$ and $\alpha$ (SD-1).
also required fewer experiments compared to the conventional kinetic studies.

7.4 Second Sequential Experimental Design (SD-2)

Similar to the first sequential experimental design, this design was also performed to obtain precise parameter estimates for the hydrogen conditioned palladium catalysed reaction's empirical kinetic model (Equation (6.3)) in the temperature range of 50°C to 70°C. An initial set of six experiments was also performed at the boundaries of the operability region in a fairly arbitrary way so as to span the range of variables. The parameter values given in Equation (6.3) were used as the initial estimates in the least squares fit to obtain the parameter estimates from the initial block of experiments. The parameters estimated then were used to initiate the subsequent sequential experimental design.

7.4.1 Results and Discussion

Table 7.4 shows the initial block of six experiments and subsequent designed and actual experiments performed for the hydrogen conditioned palladium catalysed reaction. The designed experiments also lay at the boundaries of the operability region.

It is apparent from the Table 7.4 that a sharp increase in the number of function evaluations is observed for the fifth experimental design. As before, the sharp increase in the number of function evaluations could also be interpreted as being due to the flat surface
Table 7.4: Experimental data* for the hydrogen conditioned catalyst (SD-2).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (°C)</th>
<th>( P_{C_2H_4} ) (%)</th>
<th>( P_{H_2} ) (%)</th>
<th>Rate (kg mole/kg cat/sec) ( \times 10^5 )</th>
<th>No. Function Evaluations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD2-1</td>
<td>50.2</td>
<td>30.18</td>
<td>59.92</td>
<td>1.8537</td>
<td></td>
</tr>
<tr>
<td>SD2-2</td>
<td>70.5</td>
<td>30.21</td>
<td>59.98</td>
<td>7.0935</td>
<td></td>
</tr>
<tr>
<td>SD2-3</td>
<td>70.3</td>
<td>29.83</td>
<td>50.37</td>
<td>5.8494</td>
<td></td>
</tr>
<tr>
<td>SD2-4</td>
<td>69.8</td>
<td>10.07</td>
<td>50.35</td>
<td>1.7648</td>
<td></td>
</tr>
<tr>
<td>SD2-5</td>
<td>70.8</td>
<td>10.16</td>
<td>79.56</td>
<td>3.5182</td>
<td></td>
</tr>
<tr>
<td>SD2-6</td>
<td>50.6</td>
<td>29.95</td>
<td>50.18</td>
<td>1.4884</td>
<td></td>
</tr>
</tbody>
</table>

-7(D)\(^a\) (E) 70.0 15.58 74.42 - 156
-8(D) (E) 71.4 30.33 59.51 7.3604 -
-9(D) (E) 70.0 10.00 80.00 - 131
-10(D) (E) 70.6 29.87 50.56 5.7707 -
-11(D) 56.3 30.00 60.00 - 1230

* Nitrogen gas is used as diluent.

\(^a\) D: Designed experiment; \(^b\) E: Actual experiment performed
in the design criterion as a function of experimental conditions. Similarly, as explained earlier for the first sequential design, the sequence of the designed experiments was terminated after the fifth designed experiment.

Table 7.5 compares the parameter estimates obtained after the fourth designed experiment with the sixteen experiments performed by the conventional studies (Chapter 6). It is apparent from Table 7.5 that the parameter estimate confidence intervals obtained by the sequential design are smaller than those obtained by conventional studies. This also demonstrates that the sequential experimental design leads to better precision in the parameter estimates with a fewer number of experiments; that is, a rapid convergence.

Table 7.6 compares the correlation coefficients of the parameter estimates obtained after the fourth designed experiment performed with those from the conventional studies. It is apparent from Table 7.6 that the sequential design has reduced most of the correlation coefficients except for correlations between \( \theta \) and \( \beta \) and \( \alpha \) and \( \beta \). The increase in the correlation coefficients for \( \beta \) with \( \theta \) and \( \alpha \) could be interpreted as due to variations in the hydrogen conditioning of the palladium catalyst. This demonstrates that the sequential experimental design could be quite sensitive to the experimental conditions, as noted earlier.

The JCR of the sequential design is also smaller than that for the conventional studies for \( \rho \) and \( \beta \) at constant \( \theta \) and \( \alpha \) (Figure 7.5). This also demonstrates that more precise parameters were obtained by the sequential design method.
Table 7.5: A comparison of the parameter estimates

<table>
<thead>
<tr>
<th>Parameter Value</th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Method</td>
<td>$-8.872(\pm 0.143)^a$</td>
<td>$8.910(\pm 0.063)$</td>
<td>$0.954(\pm 0.069)$</td>
<td>$1.104(\pm 0.176)$</td>
</tr>
<tr>
<td>Sequential Method (after 4th designed experiment)</td>
<td>$-8.738(\pm 0.126)$</td>
<td>$8.917(\pm 0.049)$</td>
<td>$1.018(\pm 0.062)$</td>
<td>$1.334(\pm 0.166)$</td>
</tr>
</tbody>
</table>

* Quantities in parantheses are the approximate 95% confidence interval for the parameter estimates;
* See Tables G.2 and G.3 of Appendix G for parameter estimates at each stage of sequential experimental design.

Table 7.6: Correlation coefficients between parameter estimates.

<table>
<thead>
<tr>
<th>Correlation Coefficients</th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Method</td>
<td>1</td>
<td>0.5998</td>
<td>0.9204</td>
<td>0.8082</td>
</tr>
<tr>
<td>Sequential Design Method</td>
<td>1</td>
<td>0.6436</td>
<td>0.5726</td>
<td>1</td>
</tr>
<tr>
<td>Sequential Design Method</td>
<td>1</td>
<td>-0.4051</td>
<td>0.8854</td>
<td>0.8669</td>
</tr>
<tr>
<td>Sequential Design Method</td>
<td>1</td>
<td>-0.0329</td>
<td>-0.0862</td>
<td>0.7772</td>
</tr>
<tr>
<td>Sequential Design Method</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 7.5: The joint approximate 95% confidence region for $\theta$ and $\beta$ at constant $\phi$ and $\alpha$ (SD-2).
It is apparent from the Figure 7.5 that the increase in the correlation coefficient between \( \theta \) and \( \beta \) by sequential design (Table 7.6) did not reduce the precision of the parameter estimates.

7.5 Third Sequential Experimental Design (SD-3)

The sequential design was performed to study the effect of the fall in the activation energy in the temperature region greater than 70°C on the precision of the parameter estimates for the nitrogen conditioned palladium catalysed ethylene hydrogenation reaction kinetics. For this design it was assumed that the previous kinetic information was not known.

An initial set of six experiments was planned so as to span the range of variables in a fairly arbitrary way. As discussed earlier (Chapter 4), the initial estimates of parameters were not critical for the RP model in the sequential experimental design. Therefore the average values of the parameter estimates determined in the two temperature ranges by conventional studies (Chapter 6) were taken as the initial estimates for the least squares fit for the initial block of experiments. The estimated parameter values were then used to initiate the sequential design programme.

7.5.1 Results and Discussion

Table 7.7 shows the initial block of six experiments and subsequent designed and actual experiments performed for the sequential design using nitrogen conditioned palladium catalyst. The designed
Table 7.7: Experimental data* for the nitrogen conditioned catalyst (SD-3).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Average Temperature (°C)</th>
<th>( P_{C_2H_4} ) (%)</th>
<th>( P_{H_2} ) (%)</th>
<th>Rate (kg mole/kg cat/sec ( \times 10^5 ))</th>
<th>No Function Evaluations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD3-1</td>
<td>49.2</td>
<td>10.09</td>
<td>80.10</td>
<td>1.1103</td>
<td></td>
</tr>
<tr>
<td>SD3-2</td>
<td>59.2</td>
<td>19.86</td>
<td>70.26</td>
<td>2.2561</td>
<td></td>
</tr>
<tr>
<td>SD3-3</td>
<td>80.8</td>
<td>30.18</td>
<td>59.88</td>
<td>7.0605</td>
<td></td>
</tr>
<tr>
<td>SD3-4</td>
<td>68.3</td>
<td>10.00</td>
<td>60.10</td>
<td>2.0033</td>
<td></td>
</tr>
<tr>
<td>SD3-5</td>
<td>69.2</td>
<td>10.12</td>
<td>80.17</td>
<td>3.2546</td>
<td></td>
</tr>
<tr>
<td>SD3-6</td>
<td>88.2</td>
<td>10.15</td>
<td>50.09</td>
<td>2.6847</td>
<td></td>
</tr>
<tr>
<td>-7(D)</td>
<td>74.68</td>
<td>30.00</td>
<td>50.00</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td>(E)</td>
<td>74.3</td>
<td>30.25</td>
<td>49.77</td>
<td>2.2297</td>
<td></td>
</tr>
<tr>
<td>-8(D)</td>
<td>90.0</td>
<td>10.00</td>
<td>80.00</td>
<td>-</td>
<td>138</td>
</tr>
<tr>
<td>(E)</td>
<td>90.8</td>
<td>10.06</td>
<td>79.77</td>
<td>5.0118</td>
<td></td>
</tr>
<tr>
<td>-9(D)</td>
<td>90.0</td>
<td>30.00</td>
<td>60.00</td>
<td>-</td>
<td>85</td>
</tr>
<tr>
<td>(E)</td>
<td>92.5</td>
<td>30.37</td>
<td>59.49</td>
<td>8.7181</td>
<td></td>
</tr>
<tr>
<td>-10(D)</td>
<td>90.0</td>
<td>10.00</td>
<td>80.00</td>
<td>-</td>
<td>81</td>
</tr>
<tr>
<td>(E)</td>
<td>90.1</td>
<td>10.07</td>
<td>79.89</td>
<td>5.2347</td>
<td></td>
</tr>
<tr>
<td>-11(D)</td>
<td>90.0</td>
<td>30.00</td>
<td>50.00</td>
<td>-</td>
<td>133</td>
</tr>
<tr>
<td>(E)</td>
<td>89.0</td>
<td>30.29</td>
<td>49.81</td>
<td>5.7940</td>
<td></td>
</tr>
<tr>
<td>-12(D)</td>
<td>90.0</td>
<td>30.00</td>
<td>60.00</td>
<td>-</td>
<td>198</td>
</tr>
<tr>
<td>(E)</td>
<td>90.3</td>
<td>30.15</td>
<td>59.87</td>
<td>8.5327</td>
<td></td>
</tr>
<tr>
<td>-13(D)</td>
<td>90.0</td>
<td>10.00</td>
<td>80.00</td>
<td>-</td>
<td>121</td>
</tr>
<tr>
<td>(E)</td>
<td>89.5</td>
<td>10.17</td>
<td>79.87</td>
<td>4.9897</td>
<td></td>
</tr>
<tr>
<td>-14(D)</td>
<td>90.0</td>
<td>30.00</td>
<td>60.00</td>
<td>-</td>
<td>164</td>
</tr>
<tr>
<td>(E)</td>
<td>90.2</td>
<td>30.07</td>
<td>60.02</td>
<td>8.5187</td>
<td></td>
</tr>
<tr>
<td>-15(D)</td>
<td>90.0</td>
<td>10.00</td>
<td>80.00</td>
<td>-</td>
<td>120</td>
</tr>
<tr>
<td>(E)</td>
<td>89.9</td>
<td>10.03</td>
<td>80.17</td>
<td>5.1927</td>
<td></td>
</tr>
<tr>
<td>-16(D)</td>
<td>90.0</td>
<td>12.18</td>
<td>50.00</td>
<td>-</td>
<td>191</td>
</tr>
</tbody>
</table>

* Nitrogen gas is used as diluent.

a D: Designed experiment; b E: Actual experiment performed
experimental conditions also lay on the boundaries of the operability region.

The parameters $\alpha$, $\beta$ and the calculated values of $E$ estimated after each stage of the designed experiment in sequence are shown in Figure 7.6 (also see Table G.4 of the Appendix G). It is evident from Figure 7.6 that the first few designed experiments showed instability in the parameter estimates. Such observations were not made in earlier sequential design studies, nor in the simulation studies (Chapter 4) even at high noise level for the RP model. It is also evident from the Table 7.8 that the estimated values of $\alpha$ and $\beta$ have large confidence intervals, but comparatively small confidence intervals for $\theta$ and $\rho$. However, these confidence intervals are significantly bigger than those of the first sequential design for the nitrogen conditioned catalyst in the temperature range of $50^\circ$C to $70^\circ$C (see Table 7.1). The instability and high confidence limits could be interpreted as due to the fall in the apparent activation energy in the higher temperature region ($T > 343^\circ$K). This demonstrates that the parameter estimates would not be too precise if there is a change in the apparent activation energy within the experimental temperature range. Also, this instability in the parameter estimates points towards the fact that the variable ranges are too great for a single set of parameters.

The earlier sequential design studies and the simulation studies (Chapter 4) showed a distinct point at which a flat surface in the MVD criterion occurred by observing the sharp change in the number of function evaluations for the optimal experimental design. In the present sequential design a similar phenomenon was also observed after the
FIGURE 7.6: Estimated parameters vs experiment number.
Table 7.8: Parameter estimates at each stage of the sequential experimental design (SD-3) for nitrogen conditioned catalyst (Equation (7.2)).

<table>
<thead>
<tr>
<th>Run No</th>
<th>$\theta$</th>
<th>$\rho$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD3-1</td>
<td>$-8.681(\pm1.304)$</td>
<td>$8.657(\pm0.699)$</td>
<td>$0.726(\pm0.605)$</td>
<td>$2.106(\pm2.622)$</td>
</tr>
<tr>
<td></td>
<td>($\pm15.0%$)</td>
<td>($\pm8.1%$)</td>
<td>($\pm83.4%$)</td>
<td>($\pm124.5%$)</td>
</tr>
<tr>
<td>SD3-7</td>
<td>$-8.825(\pm1.334)$</td>
<td>$8.767(\pm0.539)$</td>
<td>$0.590(\pm0.550)$</td>
<td>$2.674(\pm2.009)$</td>
</tr>
<tr>
<td></td>
<td>($\pm15.1%$)</td>
<td>($\pm6.2%$)</td>
<td>($\pm93.2%$)</td>
<td>($\pm75.1%$)</td>
</tr>
<tr>
<td>SD3-8</td>
<td>$-9.369(\pm1.503)$</td>
<td>$8.387(\pm0.530)$</td>
<td>$0.492(\pm0.660)$</td>
<td>$1.553(\pm1.679)$</td>
</tr>
<tr>
<td></td>
<td>($\pm16.0%$)</td>
<td>($\pm6.3%$)</td>
<td>($\pm138.8%$)</td>
<td>($\pm108.1%$)</td>
</tr>
<tr>
<td>SD3-9</td>
<td>$-9.168(\pm1.143)$</td>
<td>$8.440(\pm0.398)$</td>
<td>$0.581(\pm0.523)$</td>
<td>$1.692(\pm1.403)$</td>
</tr>
<tr>
<td></td>
<td>($\pm12.5%$)</td>
<td>($\pm4.7%$)</td>
<td>($\pm90.0%$)</td>
<td>($\pm82.9%$)</td>
</tr>
<tr>
<td>SD3-10</td>
<td>$-9.193(\pm1.019)$</td>
<td>$8.411(\pm0.335)$</td>
<td>$0.583(\pm0.466)$</td>
<td>$1.615(\pm1.191)$</td>
</tr>
<tr>
<td></td>
<td>($\pm11.1%$)</td>
<td>($\pm4.0%$)</td>
<td>($\pm80.3%$)</td>
<td>($\pm73.8%$)</td>
</tr>
<tr>
<td>SD3-11</td>
<td>$-9.152(\pm0.993)$</td>
<td>$8.427(\pm0.324)$</td>
<td>$0.606(\pm0.453)$</td>
<td>$1.587(\pm1.167)$</td>
</tr>
<tr>
<td></td>
<td>($\pm10.9%$)</td>
<td>($\pm3.8%$)</td>
<td>($\pm74.8%$)</td>
<td>($\pm73.5%$)</td>
</tr>
<tr>
<td>SD3-12</td>
<td>$-9.052(\pm0.863)$</td>
<td>$8.447(\pm0.285)$</td>
<td>$0.651(\pm0.394)$</td>
<td>$1.660(\pm1.059)$</td>
</tr>
<tr>
<td></td>
<td>($\pm9.5%$)</td>
<td>($\pm3.36%$)</td>
<td>($\pm60.5%$)</td>
<td>($\pm63.8%$)</td>
</tr>
<tr>
<td>SD3-13</td>
<td>$-9.063(\pm0.810)$</td>
<td>$8.429(\pm0.261)$</td>
<td>$0.657(\pm0.369)$</td>
<td>$1.606(\pm0.970)$</td>
</tr>
<tr>
<td></td>
<td>($\pm8.9%$)</td>
<td>($\pm3.1%$)</td>
<td>($\pm56.2%$)</td>
<td>($\pm60.4%$)</td>
</tr>
<tr>
<td>SD3-14</td>
<td>$-8.992(\pm0.735)$</td>
<td>$8.441(\pm0.240)$</td>
<td>$0.690(\pm0.335)$</td>
<td>$1.657(\pm0.910)$</td>
</tr>
<tr>
<td></td>
<td>($\pm8.2%$)</td>
<td>($\pm2.8%$)</td>
<td>($\pm48.6%$)</td>
<td>($\pm54.9%$)</td>
</tr>
<tr>
<td>SD3-15</td>
<td>$-8.993(\pm0.694)$</td>
<td>$8.432(\pm0.222)$</td>
<td>$0.695(\pm0.315)$</td>
<td>$1.635(\pm0.847)$</td>
</tr>
<tr>
<td></td>
<td>($\pm7.7%$)</td>
<td>($\pm2.6%$)</td>
<td>($\pm45.3%$)</td>
<td>($\pm51.8%$)</td>
</tr>
</tbody>
</table>

* Quantities in parantheses are the approximate 95% confidence interval of the parameter estimates.
fourth designed experiment (experiment number 10) but it is not as distinct as observed in earlier studies (see Figure 7.7). A few more experiments were designed and performed, but it is evident from Table 7.8 that no significant improvement was obtained in the parameter estimates values. This demonstrates that the proposed stopping criterion for sequential experimental design is also valid even in this case where a single set of parameters gives a poor representation of reality.

FIGURE 7.7: Number of function evaluations vs experimental number (SD-3).
CHAPTER 8

CONCLUSIONS

CONTENTS

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  8.2.1 Conventional Studies . . . . . . . . . . . . . . 156
  8.2.2 Application of Sequential Design . . . . . . . 157
The major aim of this work was experimentally to demonstrate the advantage of sequential experimental design in the catalyst kinetic studies. Thus, the work had two aspects; firstly, the study of the sequential experimental design strategy and secondly, its application in the kinetic studies of the selected reaction; namely ethylene hydrogenation over supported palladium catalyst.

8.1 Sequential Experimental Design Studies

The effect of reparameterization on sequential experimental design, and comparison of design criteria for their performance in the parameter estimation were examined through simulation studies. A common, empirical rate model was used and the following points were noted:

i. The minimum volume design (MVD) criterion proposed by Box et al. (1959, 1965) gave satisfactory parameter estimation at all levels of noise studied.

ii. Sequential experimental design using the MVD criterion and the reparameterized (RP) model led to economical experimentation, with saving in computational time; and demonstrated potential for achieving equivalent parameter precision with fewer experiments. It was also observed that the RP model could tolerate noisy data.

iii. A sudden increase in the number of function evaluations when estimating the optimal design, using the RP model and the MVD criterion, appeared as a useful criterion for terminating the sequential experimental programme.
8.2 Kinetic Studies

A significant portion of the total effort was devoted to the development of the laboratory reactor, and to the kinetic studies of the ethylene hydrogenation reaction. The reaction kinetics over a supported palladium catalyst were measured for the first time in a flow system.

8.2.1 Conventional Studies

As no detailed kinetic studies of the ethylene hydrogenation reaction were reported in the literature, conventional studies were performed and the following conclusions were drawn:

i. The catalyst was reproducible and showed no significant sign of deactivation, except for the initial decline in its activity.

ii. Different activities were observed for differently conditioned palladium catalysts. The hydrogen conditioned catalyst was more active than the nitrogen conditioned catalyst.

iii. A change in the activation energy was observed around 70°C. The hydrogen conditioned catalyst had higher apparent activation energy compared to the nitrogen conditioned catalyst.

iv. Two reaction mechanisms were proposed for the two differently conditioned catalysts. The kinetic models were derived on the basis of the reaction between an adsorbed ethyl radical and gaseous hydrogen as the rate determining step. A good correlation between the observed reaction rate and the proposed kinetic models was
obtained.

8.2.2 Application of Sequential Design

Sequential experimental design strategy was applied to the ethylene hydrogenation reaction. The following points demonstrated its value over the conventional studies:

i. The usefulness of the proposed criterion for terminating the sequential experimental design programme.

ii. Sequential experimental design achieved better precision with a fewer number of experiments.
APPENDIX - A

MASS BALANCE RELATIONSHIP
The stoichiometry of the ethylene hydrogenation reaction is

\[ \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 \]  \hspace{1cm} (A.1)

Let \( F \) be the molar gas flow rate at a point in the reactor and \( X_i \) be the mole fraction of species \( i \). Also it is assumed that no ethane and inert are present in the reactor feed. Then, at steady state, the hydrogen balance:

\[
F_0 (X_{\text{B}_2})_0 = F X_{\text{H}_2} + F X_{\text{C}_2\text{H}_6}
\]

or \( F_0 (X_{\text{B}_2})_0 = F (1 - X_{\text{C}_2\text{H}_4}) \) as \( X_{\text{C}_2\text{H}_4} + X_{\text{C}_2\text{H}_6} + X_{\text{B}_2} = 1 \)

which may be rearranged as

\[
X_{\text{C}_2\text{H}_4} = 1 - \frac{F_0 (X_{\text{B}_2})_0}{F}
\]  \hspace{1cm} (A.2)

The subscript \( o \) refers to the inlet conditions. The ethylene balance:

\[
F_0 (X_{\text{C}_2\text{H}_4})_0 = F X_{\text{C}_2\text{H}_4} + F X_{\text{C}_2\text{H}_6}
\]

or \( F_0 (X_{\text{C}_2\text{H}_4})_0 = F (1 - X_{\text{B}_2}) \)

which may be rearranged as

\[
X_{\text{B}_2} = 1 - \frac{F_0 (X_{\text{C}_2\text{H}_4})_0}{F}
\]  \hspace{1cm} (A.3)

and, the overall mass balance
The conversion is defined as

\[ X = \frac{\frac{F_0 (X_{C_2H_4})_o - F X_{C_2H_4}}{F_0 (X_{C_2H_2})_o}}{(X_{C_2H_4})_o (1 + X_{C_2H_2})} \]  

(A.5)

By substituting Equations (A.2) and (A.4) and \((X_{C_2H_2})_o + (X_{B_2})_o = 1\) in Equation (A.5), it yields

\[ X = \frac{X_{C_2H_6}}{(X_{C_2H_4})_o (1 + X_{C_2H_2})} \]  

(A.6)

Equation (A.6) is used to calculate the conversion from the analytical results.

Calculations of Reaction Data

Consider a differential element of catalyst of mass \(dW\) as shown in the following figure

\[ F \quad \xrightarrow{dW} \quad F + dF \]

\[ X_{C_2H_6} \quad X_{C_2H_6} + dX_{C_2H_6} \]
At steady state, the ethane balance is given by

\[ F X_{C_2H_6} + r_{C_2H_6} \, dW = (F + dF) (X_{C_2H_6} + dX_{C_2H_6}) \]  \hspace{1cm} (A.7)

By neglecting the terms involving a second-order differential, Equation (A.7) becomes:

\[ r_{C_2H_6} \, dW = d(F X_{C_2H_6}) \]  \hspace{1cm} (A.8)

substituting the \( F \) from Equation (A.4) and expanding the differential, it yields

\[ r_{C_2H_6} = \frac{F_0}{(1 + X_{C_2H_6})^2} \cdot \frac{dX_{C_2H_6}}{dW} \]  \hspace{1cm} (A.9)

Equation (A.9) applies to a truly differential reactor, that is one in which the change in mole fraction of ethane through the reactor and the mass of catalyst are both infinitesimal. For the actual reactor, approaching differential operation, this expression (Equation (A.9)) can be integrated. If there is no ethane present in the reactor feed, Equation (A.9) becomes

\[ r_{C_2H_6} = \frac{F_0}{W} \cdot \frac{(X_{C_2H_6})_f}{(1 + (X_{C_2H_6})_f)} \]  \hspace{1cm} (A.10)

where \( (X_{C_2H_6})_f \) is the measured mole fraction of ethane in the product gas. Equation (A.10) is used to calculate the reaction rate for the present studies.
APPENDIX - B

ELEMENTS OF THE \((X^TX)^{-1}\) MATRIX
The \((X^TX)^{-1}\) matrix appeared frequently in all discussions relating to least squares estimation (Chapter 3). It is therefore necessary to know its physical meaning and picture for linear and non-linear models.

**Linear Model**

Consider a linear model involving two independent variables

\[ y_u = k_0 x_0 + k_1 x_1 + k_2 x_2 \]  \hspace{1cm} (B.1)

and assume three experiments were carried out. The conditions of these experiments are

<table>
<thead>
<tr>
<th>Expt No</th>
<th>(x_0)</th>
<th>(x_1)</th>
<th>(x_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>(x_{1,1})</td>
<td>(x_{2,1})</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>(x_{1,2})</td>
<td>(x_{2,2})</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>(x_{1,3})</td>
<td>(x_{2,3})</td>
</tr>
</tbody>
</table>

Now,

\[
X = \begin{bmatrix}
1 & x_{1,1} & x_{2,1} \\
1 & x_{1,2} & x_{2,2} \\
1 & x_{1,3} & x_{2,3}
\end{bmatrix}
\]  \hspace{1cm} (B.2)

then, the \((X^TX)\) matrix is
\[
\begin{pmatrix}
3 & 0 & 0 \\
0 & \Sigma(x_{1,i})^2 & \Sigma(x_{1,i}x_{2,i}) \\
0 & \Sigma(x_{1,i}x_{2,i}) & \Sigma(x_{2,i})^2
\end{pmatrix}
\]  

(B.3)

and from the rules of matrix inversion

\[
\begin{pmatrix}
1/3 & 0 & 0 \\
0 & \Sigma(x_{2,i})^2/D - \Sigma(x_{1,i}x_{2,i})/D \\
0 & -\Sigma(x_{1,i}x_{2,i})/D & \Sigma(x_{1,i})^2/D
\end{pmatrix}
\]  

(B.4)

where, \( D \) is the determinant of the \((X^TX)\) matrix:

\[
D = 3 [\Sigma(x_{2,i})^2 \Sigma(x_{1,i})^2 - \Sigma(x_{1,i}x_{2,i})^2]
\]  

(B.5)

\( \Sigma \) refers to the sum over all values of \( i \) from 1 to 3. The elements of \((X^TX)^{-1}\) show how the values of the independent variables for a designed experiment affect the accuracy of the predicted parameters. Also, the determinant \( D \) should increase to reduce the variance of the parameter estimates. Therefore, to reduce the confidence limits of parameters, experiments should be chosen to maximise the determinant (\( D \)) of the \((X^TX)\) matrix (Equation (B.5)) or minimise \( 1/D \).

The elements of the \((X^TX)^{-1}\) matrix also indicate the magnitude of the correlation of the parameter estimates i.e. the lower the off-diagonal elements, the lower the correlation.
Non-Linear Model

Consider the non-linear model

\[ y_u = f(X_u, K) \] (B.6)

and linearise it about the initial estimates of the parameters to utilize the least squares analysis. If the initial estimates of all the parameters \((k_1, k_2, \ldots, k_p)\) are \((k_1^0, k_2^0, \ldots, k_p^0)\) then the Taylor series expansion of Equation (B.6), truncated with the linear terms, can be written as

\[ y_u = f(X_u, K^0) + \sum_{i=1}^{P} \frac{\partial f(X_u, K)}{\partial k_i} (k_i - k_i^0) \] (B.7)

Let,

\[ f_u^0 = f(X_u, K^0) \] (B.8)

\[ \beta_i^0 = k_i - k_i^0 \] (B.9)

\[ d_{iu} = \frac{\partial f(X_u, K)}{\partial k_i} \bigg|_{K=K^0} \] (B.10)

Thus, the equation can be written as

\[ y_u - f_u^0 = \sum_{i=1}^{P} \beta_i^0 d_{iu} \] (B.11)

Equation (B.11) is linear with respect to the parameters \(\beta^0\). Thus, the estimates \(\hat{\beta}^0\), of the parameters \(\beta^0\), may be obtained from the least
squares solution of the equations \( D_0^0 = Y - f_0 \). That is,

\[
 b_0^0 = (D_0^T D_0)^{-1} D_0^T (Y - f_0) 
\]  

(B.12)

where subscript or superscript zero refers to the evaluation of the matrices at the initial estimates, \( X_0 \). These parameters, \( b_0^0 \), exactly minimise the sum of squares of residuals:

\[
 S_0(X) = \sum_{u=1}^{n} (y_u - f_0^0 - \sum_{i=1}^{p} \beta_i^0 d_{iu})^2 
\]  

(B.13)

and thus approximately minimise Equation (3.2) to the extent that the Taylor expansion is valid.

Note that in place of \( K \), we have the deviation from a good estimation, \( \beta \), and in place of \( x_i \) values, the value of \( \frac{\partial f}{\partial k_i} \). The matrix \( X \) for the linear model can be compared with the matrix \( D \) for the non-linear model as

\[
 X = \begin{bmatrix} x_{1,1} & x_{1,2} \\ x_{2,1} & x_{2,2} \end{bmatrix} \\
 D = \begin{bmatrix} \frac{\partial f_1}{\partial k_1} & \frac{\partial f_1}{\partial k_2} \\ \frac{\partial f_2}{\partial k_1} & \frac{\partial f_2}{\partial k_2} \end{bmatrix}
\]

The derivatives in the \( D \) matrix are complex functions of \( K \). Therefore, the correlation and the parameter confidence limits of non-linear models not only depend on experimental conditions as with the linear least squares, but also depend on the model form and the initial estimates of the parameters.

The kinetic model discussed in Section 4.2 can be taken as an example to show the complexity of the elements of the \( D \) matrix. The
kinetic model is:

\[ r_{C_2B_6} = A_o \exp(-E/RT) (X_{C_2B_4})^\alpha (X_{B_2})^\beta \]  \hspace{1cm} (B.14)

where \(A_o, E, \alpha,\) and \(\beta\) are the four parameters. The elements of the D matrix are:

\[ \frac{\partial r_{C_2B_6}}{\partial A_o} = \exp(-E/RT) (X_{C_2B_4})^\alpha (X_{B_2})^\beta \]  \hspace{1cm} (B.15)

\[ \frac{\partial r_{C_2B_6}}{\partial E} = - \frac{r_{C_2B_6}}{RT} \]  \hspace{1cm} (B.16)

\[ \frac{\partial r_{C_2B_6}}{\partial \alpha} = r_{C_2B_6} \ln(X_{C_2B_4}) \]  \hspace{1cm} (B.17)

\[ \frac{\partial r_{C_2B_6}}{\partial \beta} = r_{C_2B_6} \ln(X_{B_2}) \]  \hspace{1cm} (B.18)
APPENDIX - C

COMPUTER PROGRAM
A computer program EXPDES was developed to design the optimal experimental conditions and estimate the kinetic parameters sequentially. A Quasi-Newton method was employed to minimise the objective functions. The code which perform the Quasi-Newton minimisation was subroutine E04JBF from the 8th release of the NAG library. Figure C.1 shows the flow diagram of EXPDES program. A listing of the EXPDES program along with its subroutines are given in Appendix H.
FIGURE C.1: Flow diagram of EXPDES program.
APPENDIX - D

Calculation of External Mass- and Heat- Transfer Gradient in the Reactor
This appendix is devoted to calculation and to prove that the investigation of the kinetic study was free from any mass- and heat-transfer effects by utilizing some of the available correlations. These can very broadly be considered as interparticle and intraparticle effects. The intraparticle effects were assumed to be negligible as the impregnated catalyst was prepared by using a non-porous alumina support of negligible internal surface area.

Interparticle Transfer Effect

Consider a single catalyst pellet surface to which reactant molecules from the bulk gas phase diffuse and react. The heat is generated due to the chemical reaction at the surface and removed only by transfer to the bulk gas phase by convection. It is assumed that the dynamics of these transfer processes are sufficiently fast to enable the steady state assumption to be made. The mass balance is then:

\[ k \frac{A}{g} \Delta C = r \frac{W}{g} \]  \hspace{1cm} (D.1)

where:

- \( k \) is the mass transfer coefficient;
- \( A \) is the external surface area of catalyst;
- \( \Delta C \) is the concentration difference between the catalyst surface and the bulk gas;
- \( r \) is the reaction rate;
- \( W \) is the mass of the catalyst.

With a similar assumption, the heat balance is then:
\[ h A \Delta T = (-\Delta H) r W \] 

where:

\( h \) is the heat transfer coefficient;

\( \Delta T \) is the temperature difference between the catalyst surface and the bulk gas;

\( (-\Delta H) \) is the heat of reaction.

A number of correlations exist to calculate the heat and mass transfer effects for such systems. For the present calculations those given by Carberry (1960) have been used as it appears that these are the most applicable to the present system (see also Smith (1970) and Satterfield (1970) for further details). These correlations are:

\[ St = 1.15 \ Re^{-0.5} \ Pr^{-0.67} \] 
\[ k_g = 1.15 \ U_s \ Re^{-0.5} \ Sc^{-0.67} \]

where:

\( St \) is the Stanton number;

\( Re \) is the Reynolds number based upon the flow around a sphere of external surface area the same as the catalyst pettet;

\( Pr \) is Prandtl number;

\( U_s \) is the superficial velocity of the gas over the catalyst particles based upon the cross sectional area available for flow;

\( Sc \) is the Schmidt number.

As the gas mixture used in the studies contained a minimum of
50% hydrogen, the physical properties of hydrogen have been used to determine the necessary values of the dimensionless numbers.

The bulk of experiments performed in the present study lay with in the temperature range 50°C to 90°C. As reaction rate and hence likely magnitude of gradient effects, increases with temperature, a case at about 100°C and 1 atm pressure is considered.

The physical properties of hydrogen are (Perry and Chilton (1973)):

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prandtl number, Pr</td>
<td>0.73</td>
</tr>
<tr>
<td>Specific heat, ( c_p )</td>
<td>3.5 kcal kg(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>Viscosity, ( \mu )</td>
<td>1.04E-05 kg m(^{-1}) sec(^{-1})</td>
</tr>
<tr>
<td>Density, ( \rho )</td>
<td>6.53e-02 kg m(^{-3})</td>
</tr>
</tbody>
</table>

The average mass of a single pellet = 4.26E-06 kg

- The average diameter of pellet = 1.27E-03 m
- External area of pellet = 1.189 m\(^2\) kg\(^{-1}\)
- Volume of pellet = 2.52E-04 m\(^3\) kg\(^{-1}\)
- The average mass of the catalyst = 1.5E-04 kg
- The average mass of the inert = 9.0e-04 kg
- The cross sectional area of the reactor = 1.39E-05 m\(^2\)
- The height of pellets in reactor = 4.0E-02 m
- Total volume occupied by pellets = 2.64E-07 m\(^3\)
- Volume of the reactor = 5.56E-07 m\(^3\)
- Hence, the bed voidage = 0.525
The average volumetric flow rate is 4.2E-05 m³ sec⁻¹.

Therefore, the superficial velocity is 5.755 m sec⁻¹.

\[
Re = \frac{\nu_s d \rho_{B_2}}{\mu_{B_2}} = 45.89
\]

\[
St = \frac{h}{\rho_{B_2} \nu_s C_{p_{B_2}}} = 0.21
\]

which gives:

\[
h = 0.276 \text{ KCal m}^{-2} \text{ sec}^{-1} \text{ K}^{-1}
\]

The enthalpy of reaction at 100°C is about 33.1E+03 KCal (kg mole)⁻¹.

If the max reaction rate is 1.0E-04 kg mole (Kg Cat)⁻¹ sec⁻¹.

Hence,

\[
\Delta T = \frac{(-\Delta H)}{h} = 10^\circ K
\]

Hence by assuming that ΔT=0, it is expected to introduce a maximum error of about 2.7% in the determination of temperature. In most of the cases it is expected that a lower value for ΔT than that calculated.

To calculate the Schmidt group an estimate of the molecular diffusivity of the multi-component mixture is required. Smith (1970) suggested that by considering the binary case a reasonable estimate of the molecular diffusivity may be made. This is calculated using the Chapman-Enskog equation:
\[
D_{AB} = 1.8583 \times 10^{-7} \left( \frac{T^{3/2}}{p (\sigma_{AB})^2 \Omega_{AB}} \right) \text{ m}^2 \text{ sec}^{-1}
\]  

where:

- \( M_A, M_B \) are the molecular weights of the gases;
- \( p \) is the total pressure of the system, atm;
- \( \sigma_{AB} \) is the Lennard Jones constant for the binary;
- \( \Omega_{AB} \) is the collision integral for the binary.

Smith (1970) gave the necessary data for calculating \( \sigma_{C_2H_4/H_2} \) and \( \Omega_{C_2H_4/H_2} \):

\[
\sigma_{C_2H_4/H_2} = 3.574 \text{ Å}^0
\]
\[
\epsilon_{C_2H_4/H_2} = 88.261 \text{ k_B} \text{°K}
\]

where, \( \text{k_B} \) is Boltzmann's constant.

Hence, at 100°C,

\[
\frac{\text{k_B} T}{\epsilon_{C_2H_4/H_2}} = 3.67
\]

and so

\[
\Omega_{C_2H_4/H_2} = 0.901 \text{ sec}
\]

Hence,

\[
\frac{D_{C_2H_4/H_2}}{} = 5.748 \times 10^{-5} \text{ m}^2 \text{ sec}^{-1}
\]
\[
\begin{align*}
\text{sc} &= \frac{\mu_{B_2}}{D_{C_2H_4/H_2} \rho_{H_2}} = 2.76 \\
\text{and} \\
\kappa_g &= 0.495 \text{ m sec}^{-1}
\end{align*}
\]

Therefore,
\[
\Delta C = \frac{\pi W}{\kappa_g A} = 2.0E-04 \text{ kg mol m}^{-3}
\]

at 100°C and 1 atm pressure the total concentration is
\[
C_T = \frac{P}{RT} = 3.266E-02 \text{ kg mol m}^{-3}
\]

Hence, the maximum value of \(\Delta C\) represents about 0.61%. Therefore, the experimental studies presented in Chapter 6 and 7 indicate that the experiments carried out were free from any interparticle effect.
APPENDIX E

EXPERIMENTAL DATA AND ANALYSIS OF CONVENTIONAL KINETIC STUDIES
Table E.1(a): Fresh nitrogen conditioned catalyst activity

Conditions: \( P_{C_2H_4} = 29.70\% \); \( P_2 = 60.14\% \)

\[ F = 1.759 \times 10^{-6} \text{ kg mole sec}^{-1} \]

\[ W = 1.488 \times 10^{-4} \text{ kg}; \ T_{av} = (324.4 \pm 0.6) \text{ K} \]

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate ( \times 10^5 ) kg mole/kg cat/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.978</td>
<td>3.4341</td>
</tr>
<tr>
<td>27</td>
<td>0.799</td>
<td>2.8034</td>
</tr>
<tr>
<td>44</td>
<td>0.734</td>
<td>2.5779</td>
</tr>
<tr>
<td>60</td>
<td>0.662</td>
<td>2.3231</td>
</tr>
<tr>
<td>77</td>
<td>0.638</td>
<td>2.2390</td>
</tr>
<tr>
<td>89</td>
<td>0.625</td>
<td>2.1936</td>
</tr>
<tr>
<td>102</td>
<td>0.604</td>
<td>2.1209</td>
</tr>
<tr>
<td>115</td>
<td>0.602</td>
<td>2.1121</td>
</tr>
<tr>
<td>128</td>
<td>0.578</td>
<td>2.0301</td>
</tr>
<tr>
<td>144</td>
<td>0.573</td>
<td>2.0104</td>
</tr>
<tr>
<td>159</td>
<td>0.570</td>
<td>1.9996</td>
</tr>
<tr>
<td>185</td>
<td>0.558</td>
<td>1.9601</td>
</tr>
</tbody>
</table>

Average reaction rate = \( (2.0001 \times 10^{-5} \pm 2.95 \times 10^{-7}) \)
kg mole/kg cat/sec
Table E.1(b) : Used nitrogen conditioned catalyst activity

Conditions : $P_{C_2H_4} = 29.75\%$; $P_{H_2} = 60.14\%$

$F = 1.75 \times 10^{-6}$ kg mole sec$^{-1}$

$W = 1.488 \times 10^{-4}$ kg; $T_{av} = (364.9 \pm 1.68)^0K$

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate kg mole/kg cat/sec $(\times 10^5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1.700</td>
<td>5.9512</td>
</tr>
<tr>
<td>20</td>
<td>1.761</td>
<td>6.1637</td>
</tr>
<tr>
<td>48</td>
<td>1.781</td>
<td>6.2352</td>
</tr>
<tr>
<td>60</td>
<td>1.795</td>
<td>6.2829</td>
</tr>
<tr>
<td>72</td>
<td>1.785</td>
<td>6.2494</td>
</tr>
<tr>
<td>86</td>
<td>1.798</td>
<td>6.2928</td>
</tr>
<tr>
<td>105</td>
<td>1.792</td>
<td>6.2714</td>
</tr>
</tbody>
</table>

Average reaction rate $= (6.2663 \times 10^{-5} \pm 2.38 \times 10^{-7})$ kg mole/kg cat/sec
Table E.2(a): Fresh hydrogen conditioned catalyst activity

Conditions: $P_{C_2H_4} = 10.15\%$, $P_{H_2} = 50.07\%$

$P = 1.753E-06$ kg mole/sec

$W = 1.494E-04$ kg; $T_{av} = (362.9 \pm 1.0)^{\circ}$K

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate kg mole/kg cat/sec $(X \times E+05)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.439</td>
<td>2.9058</td>
</tr>
<tr>
<td>18</td>
<td>2.377</td>
<td>2.8316</td>
</tr>
<tr>
<td>43</td>
<td>2.321</td>
<td>2.7641</td>
</tr>
<tr>
<td>55</td>
<td>2.282</td>
<td>2.7179</td>
</tr>
<tr>
<td>78</td>
<td>2.266</td>
<td>2.6996</td>
</tr>
<tr>
<td>99</td>
<td>2.261</td>
<td>2.6929</td>
</tr>
<tr>
<td>120</td>
<td>2.249</td>
<td>2.6786</td>
</tr>
</tbody>
</table>

Average reaction rate = $(2.6904E-05 \pm 1.07E-07)$ kg mole/kg cat/sec
Table E.2(b): Used hydrogen conditioned catalyst activity

Conditions: $p_{C_2H_4} = 10.29\%; p_{H_2} = 50.06\%$

$F = 1.762E-06 \text{ kg mole/sec}$

$W = 1.494E-04 \text{ kg, } T_{av} = (332.3 \pm 0.3)^0K$

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate kg mole/kg cat/sec $(X E+05)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.757</td>
<td>0.9185</td>
</tr>
<tr>
<td>22</td>
<td>0.684</td>
<td>0.8297</td>
</tr>
<tr>
<td>49</td>
<td>0.701</td>
<td>0.8506</td>
</tr>
<tr>
<td>65</td>
<td>0.636</td>
<td>0.7713</td>
</tr>
<tr>
<td>78</td>
<td>0.636</td>
<td>0.7718</td>
</tr>
<tr>
<td>94</td>
<td>0.640</td>
<td>0.7768</td>
</tr>
<tr>
<td>115</td>
<td>0.644</td>
<td>0.7811</td>
</tr>
</tbody>
</table>

Average reaction rate = $(7.753E-06 \pm 4.6E-08)$ kg mole/kg cat/sec
Table E.3(a) : Run NC-6

Conditions: \( P_{C_2H_4} = 30.22\% \); \( P_{H_2} = 49.81\% \)

\[ P = 1.749 \times 10^{-6} \text{ kg mole/sec} \]

\[ W = 1.436 \times 10^{-4} \text{ kg}; \ T_{av} = (363.1 \pm 1.35)^{\circ} \text{K} \]

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate kg mole/kg cat/sec (X 10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.873</td>
<td>3.2121</td>
</tr>
<tr>
<td>18</td>
<td>0.910</td>
<td>3.3477</td>
</tr>
<tr>
<td>30</td>
<td>0.910</td>
<td>3.3499</td>
</tr>
<tr>
<td>42</td>
<td>0.892</td>
<td>3.2835</td>
</tr>
<tr>
<td>56</td>
<td>0.888</td>
<td>3.2676</td>
</tr>
<tr>
<td>70</td>
<td>0.891</td>
<td>3.2778</td>
</tr>
<tr>
<td>82</td>
<td>0.881</td>
<td>3.2419</td>
</tr>
<tr>
<td>96</td>
<td>0.887</td>
<td>3.2643</td>
</tr>
<tr>
<td>112</td>
<td>0.890</td>
<td>3.2754</td>
</tr>
</tbody>
</table>

Average reaction rate = 
\( (3.2654 \times 10^{-5} \pm 1.45 \times 10^{-7}) \) kg mole/kg cat/sec.
Table E.3(b) : Run NC-8

Conditions : $P_{C_2H_4} = 29.95\%$; $P_{H_2} = 50.72\%$
$P = 1.744E-06$ kg mole/sec
$W = 1.436E-04$ kg; $T_{av} = (363.0 \pm 1.13)^{\circ}K$

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate kg mole/kg cat/sec ($X \times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.916</td>
<td>3.3306</td>
</tr>
<tr>
<td>20</td>
<td>0.927</td>
<td>3.3711</td>
</tr>
<tr>
<td>33</td>
<td>0.927</td>
<td>3.3731</td>
</tr>
<tr>
<td>45</td>
<td>0.929</td>
<td>3.3808</td>
</tr>
<tr>
<td>57</td>
<td>0.937</td>
<td>3.4085</td>
</tr>
<tr>
<td>70</td>
<td>0.932</td>
<td>3.3921</td>
</tr>
<tr>
<td>85</td>
<td>0.911</td>
<td>3.3123</td>
</tr>
<tr>
<td>109</td>
<td>0.921</td>
<td>3.3488</td>
</tr>
<tr>
<td>121</td>
<td>0.916</td>
<td>3.3322</td>
</tr>
</tbody>
</table>

Average reaction rate = $(3.331E-05 \pm 1.83E-07)$ kg mole/kg cat/sec
Table E.3(c) : Run NC-19

Conditions : \( P_{C_2H_4} = 10.55\% \); \( P_B = 59.66\% \)

\( P = 1.759E-06 \) kg mole/sec

\( W = 1.436E-04 \) kg; \( T_{av} = (347.6 \pm 0.52)^\circ K \)

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate kg mole/kg cat/sec ((X E+05))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.798</td>
<td>1.0316</td>
</tr>
<tr>
<td>36</td>
<td>0.794</td>
<td>1.0262</td>
</tr>
<tr>
<td>48</td>
<td>0.823</td>
<td>1.0632</td>
</tr>
<tr>
<td>60</td>
<td>0.806</td>
<td>1.0412</td>
</tr>
<tr>
<td>73</td>
<td>0.857</td>
<td>1.1076</td>
</tr>
<tr>
<td>85</td>
<td>0.821</td>
<td>1.0605</td>
</tr>
<tr>
<td>96</td>
<td>0.846</td>
<td>1.0929</td>
</tr>
</tbody>
</table>

Average reaction rate = \((1.0731E-05 \pm 2.67E-07)\)
kg mole/kg cat/sec
Table E.3(d): Run NC-23

Conditions: $P_{C_2H_4} = 10.20\%$; $P_H_2 = 59.78\%

$F = 1.758E-06 \text{ kg mole/sec}$

$W = 1.436E-04 \text{ kg}; T_{av} = (347.3 \pm 0.38)\text{°K}$

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Conversion (%)</th>
<th>Reaction rate kg mole/kg cat/sec (X E+05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.712</td>
<td>0.8890</td>
</tr>
<tr>
<td>26</td>
<td>0.778</td>
<td>0.9718</td>
</tr>
<tr>
<td>37</td>
<td>0.835</td>
<td>1.0422</td>
</tr>
<tr>
<td>49</td>
<td>0.802</td>
<td>1.0017</td>
</tr>
<tr>
<td>65</td>
<td>0.800</td>
<td>0.9984</td>
</tr>
<tr>
<td>77</td>
<td>0.810</td>
<td>1.0116</td>
</tr>
<tr>
<td>90</td>
<td>0.795</td>
<td>0.9927</td>
</tr>
</tbody>
</table>

Average reaction rate = $(1.001E-05 \pm 7.9E-08)\text{ kg mole/kg cat/sec}$
Table E.4: Activation Energy data* for the nitrogen conditioned catalyst.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Average Temperature</th>
<th>Rate (kg mole/kg cat/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(X E+05)</td>
</tr>
<tr>
<td>NC-25</td>
<td>53.4</td>
<td>1.1805</td>
</tr>
<tr>
<td>NC-26</td>
<td>57.9</td>
<td>1.4717</td>
</tr>
<tr>
<td>NC-27</td>
<td>63.8</td>
<td>1.8664</td>
</tr>
<tr>
<td>NC-28</td>
<td>73.1</td>
<td>2.6615</td>
</tr>
<tr>
<td>NC-29</td>
<td>79.8</td>
<td>2.9257</td>
</tr>
<tr>
<td>NC-30</td>
<td>85.2</td>
<td>3.1973</td>
</tr>
<tr>
<td>NC-31</td>
<td>89.7</td>
<td>3.4192</td>
</tr>
</tbody>
</table>

* $P_{C_2H_4} = (14.95 \pm 0.24)\%$

$P_H_2 = (60.25 \pm 0.14)\%$

$P_0 = (1.8.3E-06 \pm 7.5E-09) \text{ kg mole/sec}$

Nitrogen gas is used as diluent.

Table E.5: Activation Energy data* for the hydrogen conditioned catalyst.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Average Temperature</th>
<th>Rate (kg mole/kg cat/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(X E+05)</td>
</tr>
<tr>
<td>HC-5</td>
<td>51.0</td>
<td>0.3981</td>
</tr>
<tr>
<td>HC-6</td>
<td>59.3</td>
<td>0.7753</td>
</tr>
<tr>
<td>HC-7</td>
<td>69.3</td>
<td>1.4522</td>
</tr>
<tr>
<td>HC-8</td>
<td>79.6</td>
<td>1.9714</td>
</tr>
<tr>
<td>HC-9</td>
<td>89.9</td>
<td>2.6904</td>
</tr>
</tbody>
</table>

* $P_{C_2H_4} = (10.27 \pm 0/10)\%$

$P_H_2 = (50.04 \pm 0.04)\%$

$P_0 = (1.762E-06 \pm 7.5E-09) \text{ kg mole/sec}$

Nitrogen gas is used as diluent.
Table E.6: Effect of ethylene partial pressure on the reaction rate.

A: Experimental data for the nitrogen conditioned catalyst.

<table>
<thead>
<tr>
<th>Run No</th>
<th>( P_2 \text{C}_2 \text{H}_4 ) (%)</th>
<th>Rate (kg mole/kg cat/sec) (X E+05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-33</td>
<td>10.53</td>
<td>1.7259</td>
</tr>
<tr>
<td>NC-34</td>
<td>19.85</td>
<td>2.5273</td>
</tr>
<tr>
<td>NC-35</td>
<td>30.21</td>
<td>3.2568</td>
</tr>
</tbody>
</table>

\( T_{av} = (352.6 \pm 0.51)^0K; \quad P_{H_2} = (59.95 \pm 0.23)^0 \%

\( F_0 = (1.770E-06 \pm 2.14E-08) \text{ kg mole/sec} \)

B: Experimental data for the hydrogen conditioned catalyst.

<table>
<thead>
<tr>
<th>Run No</th>
<th>( P_2 \text{C}_2 \text{H}_4 ) (%)</th>
<th>Rate (kg mole/kg cat/sec) (X E+05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-10</td>
<td>10.50</td>
<td>2.1351</td>
</tr>
<tr>
<td>HC-11</td>
<td>15.17</td>
<td>3.0372</td>
</tr>
<tr>
<td>HC-12</td>
<td>20.13</td>
<td>4.0752</td>
</tr>
<tr>
<td>HC-13</td>
<td>24.87</td>
<td>4.8936</td>
</tr>
</tbody>
</table>

\( T_{av} = (343.6 \pm 0.13)^0K; \quad P_{H_2} = (50.05 \pm 0.09)^0 \%

\( F_0 = (1.757E-06 \pm 4.6E-09) \text{ kg} \)
Table E.7: Effect of hydrogen partial pressure on the reaction rate.

A: Experimental data* for the nitrogen conditioned catalyst.

<table>
<thead>
<tr>
<th>Run No</th>
<th>$P_{H_2}$ (%)</th>
<th>Rate (kg mole/kg cat/sec) ($\times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-36</td>
<td>79.44</td>
<td>2.2571</td>
</tr>
<tr>
<td>NC-37</td>
<td>69.46</td>
<td>1.7501</td>
</tr>
<tr>
<td>NC-38</td>
<td>59.41</td>
<td>1.3432</td>
</tr>
<tr>
<td>NC-39</td>
<td>49.57</td>
<td>0.9523</td>
</tr>
<tr>
<td>NC-40</td>
<td>64.79</td>
<td>1.5609</td>
</tr>
</tbody>
</table>

* $T_{av} = (332.5 \pm 0.15)\,^\circ K$; $P_{C_2H_4} = (10.78 \pm 0.12)\%$

$P_o = (1.766E-06 \pm 6.5E-09) \, \text{kg mole/sec}$

B: Experimental data* for the hydrogen conditioned catalyst.

<table>
<thead>
<tr>
<th>Run No</th>
<th>$P_{H_2}$ (%)</th>
<th>Rate (kg mole/kg cat/sec) ($\times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-15</td>
<td>59.51</td>
<td>7.3604</td>
</tr>
<tr>
<td>HC-16</td>
<td>55.07</td>
<td>6.7355</td>
</tr>
<tr>
<td>HC-17</td>
<td>50.06</td>
<td>5.9551</td>
</tr>
</tbody>
</table>

* $T_{av} = (344.5 \pm 0.13)\,^\circ K$; $P_{C_2H_4} = (30.19 \pm 0.11)\%$

$P_o = (1.748E-06 \pm 3.2E-09) \, \text{kg mole/sec}$
### Table E.8: Experimental data for rate
Equations (6.2) and (6.18)

<table>
<thead>
<tr>
<th>Run No</th>
<th>Average Temperature (°C)</th>
<th>( P_{\text{CeH}_4} ) (%)</th>
<th>( P_{\text{H}_2} ) (%)</th>
<th>Rate (kg mole/kg cat/sec) (( \times 10^5 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-36</td>
<td>59.7</td>
<td>10.68</td>
<td>79.44</td>
<td>2.2571</td>
</tr>
<tr>
<td>NC-37</td>
<td>59.5</td>
<td>10.89</td>
<td>69.46</td>
<td>1.7501</td>
</tr>
<tr>
<td>NC-38</td>
<td>59.4</td>
<td>10.91</td>
<td>59.41</td>
<td>1.3432</td>
</tr>
<tr>
<td>NC-39</td>
<td>59.4</td>
<td>10.79</td>
<td>49.57</td>
<td>0.9523</td>
</tr>
<tr>
<td>NC-40</td>
<td>59.1</td>
<td>10.63</td>
<td>64.79</td>
<td>1.5609</td>
</tr>
<tr>
<td>NC-41</td>
<td>51.5</td>
<td>30.15</td>
<td>50.03</td>
<td>0.9553</td>
</tr>
<tr>
<td>NC-42</td>
<td>50.5</td>
<td>30.17</td>
<td>59.68</td>
<td>1.3121</td>
</tr>
<tr>
<td>NC-43</td>
<td>70.7</td>
<td>30.34</td>
<td>59.47</td>
<td>3.6589</td>
</tr>
<tr>
<td>NC-44</td>
<td>70.8</td>
<td>30.31</td>
<td>49.92</td>
<td>2.5283</td>
</tr>
<tr>
<td>NC-45</td>
<td>69.8</td>
<td>10.17</td>
<td>49.87</td>
<td>1.4328</td>
</tr>
<tr>
<td>NC-46</td>
<td>70.5</td>
<td>30.29</td>
<td>59.70</td>
<td>3.3738</td>
</tr>
<tr>
<td>NC-47</td>
<td>49.6</td>
<td>10.53</td>
<td>79.55</td>
<td>1.2794</td>
</tr>
<tr>
<td>NC-48</td>
<td>70.2</td>
<td>10.70</td>
<td>79.40</td>
<td>3.4045</td>
</tr>
<tr>
<td>NC-49</td>
<td>55.3</td>
<td>15.25</td>
<td>70.08</td>
<td>1.9031</td>
</tr>
<tr>
<td>NC-50</td>
<td>53.6</td>
<td>22.08</td>
<td>67.93</td>
<td>1.6046</td>
</tr>
<tr>
<td>NC-51</td>
<td>52.0</td>
<td>10.41</td>
<td>79.53</td>
<td>1.4735</td>
</tr>
</tbody>
</table>

* Nitrogen gas is used as diluent.
Table E.9: Experimental data* for rate Equations (6.3) and (6.19)

<table>
<thead>
<tr>
<th>Run No</th>
<th>Average Temperature (°C)</th>
<th>$P_{C_2H_4}$ (%)</th>
<th>$P_{H_2}$ (%)</th>
<th>Rate (kg mole/kg cat/sec) (X E+05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-10</td>
<td>70.4</td>
<td>10.50</td>
<td>49.93</td>
<td>2.1351</td>
</tr>
<tr>
<td>HC-11</td>
<td>70.7</td>
<td>15.17</td>
<td>50.03</td>
<td>3.0372</td>
</tr>
<tr>
<td>HC-12</td>
<td>70.5</td>
<td>20.13</td>
<td>50.12</td>
<td>4.0752</td>
</tr>
<tr>
<td>HC-13</td>
<td>70.6</td>
<td>24.87</td>
<td>50.10</td>
<td>4.8936</td>
</tr>
<tr>
<td>HC-14</td>
<td>50.3</td>
<td>30.27</td>
<td>59.85</td>
<td>1.9454</td>
</tr>
<tr>
<td>HC-15</td>
<td>50.3</td>
<td>30.05</td>
<td>49.94</td>
<td>1.5656</td>
</tr>
<tr>
<td>HC-16</td>
<td>69.2</td>
<td>9.93</td>
<td>79.62</td>
<td>3.0873</td>
</tr>
<tr>
<td>HC-17</td>
<td>60.8</td>
<td>29.73</td>
<td>60.31</td>
<td>4.0064</td>
</tr>
<tr>
<td>HC-18</td>
<td>60.7</td>
<td>24.88</td>
<td>60.35</td>
<td>3.1793</td>
</tr>
<tr>
<td>HC-19</td>
<td>60.0</td>
<td>9.96</td>
<td>60.12</td>
<td>1.3002</td>
</tr>
<tr>
<td>HC-20</td>
<td>70.5</td>
<td>10.29</td>
<td>60.20</td>
<td>2.2217</td>
</tr>
<tr>
<td>HC-21</td>
<td>55.2</td>
<td>10.13</td>
<td>79.85</td>
<td>1.2365</td>
</tr>
<tr>
<td>HC-22</td>
<td>65.1</td>
<td>15.08</td>
<td>50.17</td>
<td>2.1220</td>
</tr>
<tr>
<td>HC-23</td>
<td>58.5</td>
<td>29.87</td>
<td>55.08</td>
<td>3.1635</td>
</tr>
<tr>
<td>HC-24</td>
<td>53.8</td>
<td>25.03</td>
<td>64.89</td>
<td>2.0879</td>
</tr>
<tr>
<td>HC-25</td>
<td>62.5</td>
<td>20.11</td>
<td>70.03</td>
<td>3.3498</td>
</tr>
</tbody>
</table>

* Nitrogen gas is used as diluent.
Table E.10: Statistical analysis of the parameter estimates for Equation (6.2).

A. The reparameterized parameters with approximate 95% confidence intervals

\[ \frac{r_{C,H}}{N_2} = \exp(\theta) \exp\left[- \frac{1}{T} \left( \frac{1}{T} - \frac{1}{T^*} \right) \exp(\rho) \right] \left( \frac{p_{C,H}}{p_{H}_2} \right)^\alpha \left( \frac{p_{H}_2}{p_{C,H}} \right)^\beta \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
</table>
| \( \theta \) | \(-9.7240 (\pm 0.1532) \)  
| \( \rho \)   | \(8.5871 (\pm 0.0836)\)  
| \( \alpha \) | \(0.4338 (\pm 0.0702)\)  
| \( \beta \)  | \(1.8053 (\pm 0.1998)\)  

a Quantities in parentheses are estimates of confidence intervals

\( T^* = 333^\circ K \)

B. The parameter estimates correlation matrix

<table>
<thead>
<tr>
<th></th>
<th>( \theta )</th>
<th>( \rho )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>1</td>
<td>-0.2509</td>
<td>0.9541</td>
<td>0.8065</td>
</tr>
<tr>
<td>( \rho )</td>
<td>1</td>
<td>1.0000</td>
<td>0.0611</td>
<td>0.6691</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1</td>
<td>0.9541</td>
<td>1.0000</td>
<td>0.6691</td>
</tr>
<tr>
<td>( \beta )</td>
<td>1</td>
<td>0.8065</td>
<td>0.0611</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

C. Eigenvalues to define the JCR of the parameter estimates:

\[ \lambda_1 = 2.545E-08 \quad \lambda_2 = 1.233E-10 \]
\[ \lambda_3 = 4.341E-10 \quad \lambda_4 = 6.415E-11 \]

D. The volume of the JCR of the parameter estimates = \( 1.070E+18 \)
Table E.11: Statistical analysis of the parameter estimates for Equation (6.3).

A. The reparameterized parameters with approximate 95% confidence intervals

\[ (\frac{r_{C_2H_6}}{H_2}) = \exp(\theta) \exp[- \left( \frac{1}{T} - \frac{1}{T^*} \right) \exp(\phi)] \left( p_{C_2H_4} \right)^\alpha \left( p_B \right)^\beta \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>-8.8716 (± 0.1434) (^a)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>8.9099 (± 0.0625)</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.9543 (± 0.0689)</td>
</tr>
<tr>
<td>( \beta )</td>
<td>1.1036 (± 0.1762)</td>
</tr>
</tbody>
</table>

\(^a\) Quantities in parentheses are estimates of confidence intervals

\[ T^* = 333^\circ K \]

B. The parameter estimates correlation matrix

<table>
<thead>
<tr>
<th></th>
<th>( \theta )</th>
<th>( \rho )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>1</td>
<td>0.5998</td>
<td>0.9204</td>
<td>0.8081</td>
</tr>
<tr>
<td>( \rho )</td>
<td>0.5998</td>
<td>1</td>
<td>0.6435</td>
<td>0.5923</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.9204</td>
<td>0.6435</td>
<td>1</td>
<td>0.5725</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.8081</td>
<td>0.5923</td>
<td>0.5725</td>
<td>1</td>
</tr>
</tbody>
</table>

C. Eigenvalues to define the JCR of the parameter estimates:

\[ \lambda_1 = 4.701E-08 \quad \lambda_2 = 1.954E-09 \]
\[ \lambda_3 = 8.308E-10 \quad \lambda_4 = 1.092E-10 \]

D. The volume of the JCR of the parameter estimates = 3.463E+17
Table E.12: Statistical analysis of the parameter estimates for Equation (6.18).

A. The reparameterized parameters with approximate 95% confidence intervals

\[
\left( \frac{v_{C_2H_6}}{v_{N_2}} \right) = \frac{\exp(\theta) \exp\left( -\left( \frac{1}{T} - \frac{1}{T^*} \right) \exp(\rho) \right) \left( P_{C_2H_4} \right)^2 \left( P_B \right)^2}{1 + \exp(\eta) \left( P_{C_2H_4} \right)^2 + \exp(\xi) \left( P_B \right)^{0.5}}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\theta)</td>
<td>(-6.3426 (\pm 3.6985))^a</td>
</tr>
<tr>
<td>(\rho)</td>
<td>(8.5929 (\pm 0.0785))</td>
</tr>
<tr>
<td>(\eta)</td>
<td>(3.3901 (\pm 3.7527))</td>
</tr>
<tr>
<td>(\xi)</td>
<td>(1.4980 (\pm 4.5667))</td>
</tr>
</tbody>
</table>

^a Quantities in parentheses are estimates of confidence intervals

\(T^* = 333^\circ K\)

B. The parameter estimates correlation matrix

\[
\begin{array}{cccc}
\theta & \rho & \eta & \xi \\
1 & 0.0717 & 0.9998 & 0.9997 \\
1 & 0.0179 & 0.0027 & 1 \\
1 & 0.9990 & 1 &
\end{array}
\]

C. Eigenvalues to define the JCR of the parameter estimates:

\[
\begin{align*}
\lambda_1 &= 1.059E-08 \\
\lambda_2 &= 8.302E-10 \\
\lambda_3 &= 1.726E-10 \\
\lambda_4 &= 6.117E-14
\end{align*}
\]

D. The volume of the JCR of the parameter estimates = 1.038E+20
Table E.13: Statistical analysis of the parameter estimates for Equation (6.19).

A. The reparameterized parameters with approximate 95\% confidence intervals

\[
\exp(\theta) \exp\left(-\frac{1}{T^*} - \frac{1}{T}\right) \exp(\psi) \left[ \frac{C_{26}H_4}{(P_H)^{1.5}} \right] = \frac{1 + \exp(\eta) (P_H^{0.5})}{1 + \exp(\eta) (P_H^{1.5})}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\theta)</td>
<td>(-7.5622 (\pm 0.9662)^a)</td>
</tr>
<tr>
<td>(\rho)</td>
<td>(8.9350 (\pm 0.0506))</td>
</tr>
<tr>
<td>(\eta)</td>
<td>(0.8761 (\pm 1.4429))</td>
</tr>
</tbody>
</table>

\(^a\) Quantities in parentheses are estimates of confidence intervals.

\(T^* = 333^\circ K\)

B. The parameter estimates correlation matrix

<table>
<thead>
<tr>
<th></th>
<th>(\theta)</th>
<th>(\rho)</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\theta)</td>
<td>1</td>
<td>-0.3839</td>
<td>0.9996</td>
</tr>
<tr>
<td>(\rho)</td>
<td>1</td>
<td>0.3679</td>
<td>1</td>
</tr>
<tr>
<td>(\eta)</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

C. Eigenvalues to define the JCR of the parameter estimates:

\(\lambda_1 = 2.202E-08\) \hspace{1cm} \(\lambda_2 = 2.156E-09\)

\(\lambda_3 = 2.250E-12\)

D. The volume of the JCR of the parameter estimates = 9.674E+13
Table E.14: Experimental data for rate
Equation (6.20).

<table>
<thead>
<tr>
<th>Run No</th>
<th>Average Temperature (°C)</th>
<th>$P_{C_2H_4}$ (%)</th>
<th>$P_{H_2}$ (%)</th>
<th>Rate (kg mole/kg cat/sec) $(X \times 10^5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-52</td>
<td>73.1</td>
<td>14.77</td>
<td>60.37</td>
<td>2.6615</td>
</tr>
<tr>
<td>NC-53</td>
<td>85.2</td>
<td>14.70</td>
<td>60.55</td>
<td>3.1973</td>
</tr>
<tr>
<td>NC-54</td>
<td>89.7</td>
<td>15.35</td>
<td>59.90</td>
<td>3.4192</td>
</tr>
<tr>
<td>NC-55</td>
<td>79.8</td>
<td>15.13</td>
<td>60.05</td>
<td>2.9257</td>
</tr>
<tr>
<td>NC-56</td>
<td>79.7</td>
<td>10.37</td>
<td>60.13</td>
<td>2.2623</td>
</tr>
<tr>
<td>NC-57</td>
<td>79.8</td>
<td>10.02</td>
<td>79.13</td>
<td>3.7986</td>
</tr>
<tr>
<td>NC-58</td>
<td>85.1</td>
<td>15.01</td>
<td>50.13</td>
<td>2.1643</td>
</tr>
<tr>
<td>NC-59</td>
<td>76.5</td>
<td>14.85</td>
<td>56.87</td>
<td>3.0594</td>
</tr>
<tr>
<td>NC-60</td>
<td>79.6</td>
<td>10.13</td>
<td>70.17</td>
<td>3.0887</td>
</tr>
<tr>
<td>NC-61</td>
<td>90.1</td>
<td>10.08</td>
<td>70.15</td>
<td>3.6848</td>
</tr>
<tr>
<td>NC-62</td>
<td>90.1</td>
<td>20.15</td>
<td>69.87</td>
<td>5.3909</td>
</tr>
<tr>
<td>NC-63</td>
<td>90.2</td>
<td>15.67</td>
<td>70.08</td>
<td>4.7542</td>
</tr>
<tr>
<td>NC-64</td>
<td>76.5</td>
<td>25.15</td>
<td>65.37</td>
<td>4.3094</td>
</tr>
<tr>
<td>NC-65</td>
<td>80.3</td>
<td>13.17</td>
<td>75.37</td>
<td>4.2153</td>
</tr>
<tr>
<td>NC-66</td>
<td>85.3</td>
<td>20.17</td>
<td>65.38</td>
<td>4.5444</td>
</tr>
<tr>
<td>NC-67</td>
<td>75.2</td>
<td>19.87</td>
<td>65.17</td>
<td>3.7596</td>
</tr>
</tbody>
</table>

* Nitrogen gas is used as diluent.
Table E.15: Statistical analysis of the parameter estimates for Equation (6.20).

### A. The reparameterized parameters with approximate 95% confidence intervals

\[
\frac{\exp(\theta) \exp[-(1/T - 1/T^*) \exp(\rho)] P_{CH}^2 (P_{H_2})^2}{1 + \exp(\eta) P_{C_2H_4} + \exp(\xi) (P_{H_2})^{0.5}}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>(-7.3967 (\pm 0.6715) ) (^a)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>7.5120 (\pm 0.2251)</td>
</tr>
<tr>
<td>( \eta )</td>
<td>1.4510 (\pm 0.7634)</td>
</tr>
<tr>
<td>( \xi )</td>
<td>-1.6653 (\pm 4.4141)</td>
</tr>
</tbody>
</table>

\(^a\) Quantities in parentheses are estimates of confidence intervals

\( T^* = 353^0K \)

### B. The parameter estimates correlation matrix

<table>
<thead>
<tr>
<th></th>
<th>( \theta )</th>
<th>( \rho )</th>
<th>( \eta )</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>1</td>
<td>0.0665</td>
<td>0.9857</td>
<td>0.9904</td>
</tr>
<tr>
<td>( \rho )</td>
<td>0.0665</td>
<td>1</td>
<td>0.0716</td>
<td>0.0840</td>
</tr>
<tr>
<td>( \eta )</td>
<td>0.9857</td>
<td>0.0716</td>
<td>1</td>
<td>0.9541</td>
</tr>
<tr>
<td>( \xi )</td>
<td>0.9904</td>
<td>0.0840</td>
<td>0.9541</td>
<td>1</td>
</tr>
</tbody>
</table>

### C. Eigenvalues to define the JCR of the parameter estimates:

\[
\begin{align*}
\lambda_1 &= 2.55E-08 \\
\lambda_2 &= 1.50E-10 \\
\lambda_3 &= 8.68E-11 \\
\lambda_4 &= 2.40E-13
\end{align*}
\]

### D. The volume of the JCR of the parameter estimates = 1.120E+18
APPENDIX F

DERIVATION OF KINETIC MODEL
This appendix is devoted to the derivation of the kinetic expression for the reaction mechanism of ethylene hydrogenation on two differently conditioned palladium catalysts. From the conventional kinetic studies (Chapter 6), it was observed that the reaction order with respect to the hydrogen partial pressure is more than or equal to one. Therefore, this clearly indicate that there is a second addition of the hydrogen in the reaction scheme. Hence, it is assumed that the step in which the second hydrogen addition takes place is a rate controlling step.

**Derivation of the Kinetic Expression**

A. Nitrogen Conditioned Catalyst

Mechanism steps:

1. \[ \text{H}_2(g) + M \rightleftharpoons \text{H}_2M + \text{H} \] (F.1)
2. \[ \text{C}_2\text{H}_4 + M \rightleftharpoons \text{C}_2\text{H}_4M \] (F.2)
3. \[ \text{C}_2\text{H}_4M + \text{H} \rightleftharpoons \text{C}_2\text{H}_5M \] (F.3)
4. \[ \text{C}_2\text{H}_5M + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6M + \text{H} \] (F.4)
5. \[ \text{C}_2\text{H}_6M \rightleftharpoons \text{C}_2\text{H}_6(g) + M \] (F.5)
6. \[ \text{H}_2M \rightleftharpoons \text{HM} = M \] (F.6)
\[ H^+ + H^+ \xleftrightarrow{K_4} H_2(g) \]

Assumed steps (F.1), (F.2), (F.3), (F.5), (F.6), (F.7), and (F.8) are under equilibrium, therefore

\[ [H\ldots M] = \frac{K_{H_2} P_{H_2} [M]}{[H']} \]

\[ [C_2H_4\ldots M] = K_{C_2H_4} P_{C_2H_4} [M] \]

\[ [C_2H_5\ldots M] = K_1 [C_2H_4\ldots M] [H'] \]

\[ [C_2H_6\ldots M] = (1 / K_{C_2H_6}) P_{C_2H_6} [M] \]

\[ [H\ldots M] = [M] / K_2 \]

\[ [H'] = (P_{H_2})^{0.5} / (K_4)^{0.5} \]

Equations (F.9) and (F.13) yield

\[ [H'] = K_2 K_{H_2} P_{H_2} \]

Equations (F.9) and (F.14) yield

\[ [H\ldots M] = K_{H_2} (K_4)^{0.5} (P_{H_2})^{0.5} [M] \]

From Equations (F.10), (F.11), and (F.15) it yield

\[ [C_2H_5\ldots M] = K_1 K_2 K_{H_2} K_{C_2H_4} P_{C_2H_4} (P_{H_2})^2 \]
Since at equilibrium

$$[B...M] + [C_2H_4...M] + [C_2H_5...M] + [C_2H_6...M] + [M] = 1 \quad (F.18)$$

As the production of ethane is small due to the differential operation of the reactor; therefore, the surface concentrations of $[C_2H_5...M]$ and $[C_2H_6...M]$ can be assumed to be negligible. Therefore, Equations (F.10), (F.16), and (F.18) yield

$$[M] = \left(1 + K_B (K_4)^{0.5} (P_{H_2})^{0.5} + K_{C_2H_4} (P_{C_2H_4}) \right)^{-1} \quad (F.19)$$

The rate determining step, Equation (F.4) yields the following rate expression for the formation of ethane

$$\langle r_{C_2H_6} \rangle_{N_2} = k [C_2H_5...M] (P_{H_2})^2 \quad (F.20)$$

which, from Equation (F.17) and (F.19) becomes

$$\langle r_{C_2H_6} \rangle_{N_2} = \frac{k K_1 K_2 K_{C_2H_4} K_B P_{C_2H_4} (P_{H_2})^2}{1 + (K_4)^{0.5} K_B (P_{H_2})^{0.5} + K_{C_2H_4} (P_{C_2H_4})} \quad (F.21)$$

or

$$\langle r_{C_2H_6} \rangle_{N_2} = \frac{k' P_{C_2H_4} (P_{H_2})^2}{1 + K_{C_2H_4} P_{C_2H_4} + K_B (P_{H_2})^{0.5}} \quad (F.22)$$

where

$$k' = k K_1 K_2 K_B K_{C_2H_4} \quad (F.23)$$
Equation (F.22) represents the kinetic model proposed for the ethylene hydrogenation reaction on the nitrogen conditioned palladium catalyst.

B. Hydrogen Conditioned Catalyst

Reaction mechanism steps:

\[
K'_{H_2} = K_{H_2} (K_4)^{0.5} \quad (F.24)
\]

Assumed steps (F.25) and (F.26) are also under equilibrium, therefore

\[
[H...M] = (K'_{H_2} P_{H_2})^{0.5} [M] \quad (F.28)
\]

\[
[C_2H_5...M] = K_1 P_{C_2H_4} [H...M] \quad (F.29)
\]

which, from Equation (F.28), becomes
\[ [C_2H_5...M] = K_1 (K'' P_H)_{0.5} P_{C_2H_4} [M] \]  \hspace{1cm} (F.30)

Since at equilibrium

\[ [H...M] + [C_2H_5...M] + [M] = 1 \]  \hspace{1cm} (F.31)

Since the production of ethane is small due to differential behaviour of the reactor, therefore the concentration of \([C_2H_5...M]\) on the catalyst surface could be assumed negligible. Equation (F.31) yields

\[ [H...M] + [M] = 1 \]  \hspace{1cm} (F.32)

Now, Equations (F.29) and (F.32) yield

\[ [M] = \left( 1 + (K'' P_H)_{0.5} \right)^{-1} \]  \hspace{1cm} (F.33)

The rate determining step, Equation (F.27), yields the following rate expression for the formation of ethane

\[ \left( \frac{X_{C_2H_6}}{H_2} \right) H_2 = K'' [C_2H_5...M] P_H \]  \hspace{1cm} (F.34)

which, from Equations (F.30) and (F.33), becomes

\[ \left( \frac{X_{C_2H_6}}{H_2} \right) H_2 = \frac{k'' K_1 (K'')^{0.5} P_{C_2H_4} (P_H)^{1.5}}{1 + K'' (P_H)^{0.5}} \]  \hspace{1cm} (F.35)

\[ \left( \frac{X_{C_2H_6}}{H_2} \right) H_2 = \frac{k'' P_{C_2H_4} (P_H)^{1.5}}{1 + K'' (P_H)^{0.5}} \]  \hspace{1cm} (F.36)
where

\[ \kappa'' = \kappa K_i (K_{B_2}^*)^{0.5} \]  
\[ K_{B_2}^- = (K_{B_2}^*)^{0.5} \]  

Equation (F.36) represents the kinetic model proposed for the ethylene hydrogenation reaction on the hydrogen conditioned palladium catalyst.
APPENDIX - G

CALCULATED VALUES OF PARAMETERS
(SEQUENTIAL DESIGN STUDIES)
Table G.1: Calculated parameter estimates at each stage of sequential experimental design (SD-1).

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>$A_0$ (X E-03)</th>
<th>$E$ (X E-04)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD1-1</td>
<td>1.828</td>
<td>1.136</td>
<td>0.518</td>
<td>1.773</td>
</tr>
<tr>
<td>SD1-7</td>
<td>1.780</td>
<td>1.134</td>
<td>0.518</td>
<td>1.768</td>
</tr>
<tr>
<td>SD1-8</td>
<td>1.658</td>
<td>1.129</td>
<td>0.523</td>
<td>1.778</td>
</tr>
<tr>
<td>SD1-9</td>
<td>1.503</td>
<td>1.123</td>
<td>0.516</td>
<td>1.768</td>
</tr>
<tr>
<td>SD1-10</td>
<td>1.414</td>
<td>1.119</td>
<td>0.513</td>
<td>1.778</td>
</tr>
</tbody>
</table>

Table G.2: Estimates at each stage of the sequential experimental design (SD-2).

<table>
<thead>
<tr>
<th>Run No</th>
<th>$\theta$</th>
<th>$\rho$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD2-1</td>
<td>-8.725(±0.315) *</td>
<td>8.929(±0.122)</td>
<td>1.039(±0.159)</td>
<td>1.296(±0.447)</td>
</tr>
<tr>
<td></td>
<td>(±3.6%)</td>
<td>(±1.4%)</td>
<td>(±15.3%)</td>
<td>(±34.5%)</td>
</tr>
<tr>
<td>SD2-7</td>
<td>-8.710(±0.195)</td>
<td>8.931(±0.079)</td>
<td>1.041(±0.105)</td>
<td>1.326(±0.236)</td>
</tr>
<tr>
<td></td>
<td>(±2.2%)</td>
<td>(±0.9%)</td>
<td>(±10.9%)</td>
<td>(±19.8%)</td>
</tr>
<tr>
<td>SD2-8</td>
<td>-8.740(±0.170)</td>
<td>8.917(±0.069)</td>
<td>1.022(±0.088)</td>
<td>1.320(±0.240)</td>
</tr>
<tr>
<td></td>
<td>(±2.0%)</td>
<td>(±0.8%)</td>
<td>(±8.6%)</td>
<td>(±18.8%)</td>
</tr>
<tr>
<td>SD2-9</td>
<td>-8.738(±0.145)</td>
<td>8.916(±0.059)</td>
<td>1.017(±0.073)</td>
<td>1.337(±0.198)</td>
</tr>
<tr>
<td></td>
<td>(±1.7%)</td>
<td>(±0.7%)</td>
<td>(±7.2%)</td>
<td>(±14.8%)</td>
</tr>
<tr>
<td>SD2-10</td>
<td>-8.738(±0.126)</td>
<td>8.917(±0.049)</td>
<td>1.018(±0.062)</td>
<td>1.334(±0.166)</td>
</tr>
<tr>
<td></td>
<td>(±1.4%)</td>
<td>(±0.6%)</td>
<td>(±6.1%)</td>
<td>(±12.4%)</td>
</tr>
</tbody>
</table>

* Quantities in parantheses are the approximate 95% confidence interval for the parameter estimates.
Table G.3: Calculated parameter estimates at each stage of sequential experimental design (SD-2).

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>$A_0$</th>
<th>$E$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X E-05)</td>
<td>(X E-04)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 - 6</td>
<td>11.194</td>
<td>1.500</td>
<td>1.039</td>
<td>1.296</td>
</tr>
<tr>
<td>SD2-7</td>
<td>12.031</td>
<td>1.504</td>
<td>1.041</td>
<td>1.326</td>
</tr>
<tr>
<td>SD2-8</td>
<td>8.509</td>
<td>1.483</td>
<td>1.022</td>
<td>1.320</td>
</tr>
<tr>
<td>SD2-9</td>
<td>8.281</td>
<td>1.481</td>
<td>1.017</td>
<td>1.337</td>
</tr>
<tr>
<td>SD2-10</td>
<td>8.498</td>
<td>1.482</td>
<td>1.018</td>
<td>1.334</td>
</tr>
</tbody>
</table>

Table G.4: Calculated parameter estimates at each stage of sequential experimental design (SD-3).

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>$A_0$</th>
<th>$E$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X E-03)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 - 6</td>
<td>3.243E+03</td>
<td>11.432</td>
<td>0.726</td>
<td>2.106</td>
</tr>
<tr>
<td>SD3-7</td>
<td>1.938E+04</td>
<td>12.750</td>
<td>0.590</td>
<td>2.674</td>
</tr>
<tr>
<td>SD3-8</td>
<td>30.559</td>
<td>8.721</td>
<td>0.492</td>
<td>1.553</td>
</tr>
<tr>
<td>SD3-9</td>
<td>74.704</td>
<td>9.194</td>
<td>0.581</td>
<td>1.692</td>
</tr>
<tr>
<td>SD3-10</td>
<td>49.680</td>
<td>8.932</td>
<td>0.583</td>
<td>1.615</td>
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<tr>
<td>SD3-11</td>
<td>64.326</td>
<td>9.081</td>
<td>0.606</td>
<td>1.587</td>
</tr>
<tr>
<td>SD3-12</td>
<td>92.854</td>
<td>9.263</td>
<td>0.651</td>
<td>1.660</td>
</tr>
<tr>
<td>SD3-13</td>
<td>70.810</td>
<td>9.085</td>
<td>0.657</td>
<td>1.606</td>
</tr>
<tr>
<td>SD3-14</td>
<td>90.397</td>
<td>9.203</td>
<td>0.690</td>
<td>1.657</td>
</tr>
<tr>
<td>SD3-15</td>
<td>80.465</td>
<td>9.125</td>
<td>0.695</td>
<td>1.635</td>
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APPENDIX - H

LISTING OF EXPEDES PROGRAM
PROGRAM EXPDES(INPUT,OUTPUT,T.APES•IKPUT,~E6-QDTPOT)

C THIS PROGRAM ESTIMATES THE PARAMETER AND
C SEQUENTIALLY DESIGNS EXPERIMENT FOR SIMULATION
C STUDIES AND AS WELL AS FOR THE ACTUAL LABORATORY
C EXPERIMENTAL STUDIES.
C
C THIS PROGRAM CAN ALSO BE USED FOR:
C I. PARAMETER ESTIMATION ONLY; AND
C II. DESIGN OF AN EXPERIMENT FOR SEQUENTIAL DESIGN ONLY.
C
C THE EMPIRICAL KINETIC MODEL IS USED.
C
C IT USES E04JBF AND E04UAF NAG LIBRARY SUBROUTINES
C TO MINIMIZE THE FITTING AND DESIGN FUNCTIONS RESPECTIVELY.
C QUASI-NEWTON METHOD IS USED IN THESE SUBROUTINES.
C
C AO - PRE-EXPOI!N'l'IAL FACTOR
C E - ACTIVATION ENERGY (CAL/mole).
C A - REACTION ORDER WITH RESPECT TO ETHYLENE.
C B - REACTION ORDER WITH RESPECT TO HYDROGEN.
C RAO - REPARAMETERIZED AO.
C REO - RPARAMETERIZED EO.
C AVTC - AVERAGE REACTION TEMPERATURE
C GCOM - IDEAL GAS CONSTANT.
C DER - DERIVATIVE MATRIX (ARRAY)
C NOISE - % NOISE INTRODUCED IN SIMULATED EXPERIMENTS.
C SFP - SCALING FACTORS OF PARAMETERS (ARRAY).
C IFIT - FUNCTION EVOLUTION COUNTER.

COMMON/PAR/AO,EO,A,B
COMMON/ACTEXP/ACTEXP
COMMON/ERROR/ERROR
COMMON/VL/VT,VTU
COMMON/XP/ARAO,AE0,AA',AB,ARAO,ARAO
COMMON/VAR/VT,XXZ,XXH
COMMON/PR/PRESS
COMMON/ARAO/ARAO,EOB,END
COMMON/MULTF/FIFTY,FIFTY
COMMON/MULT/FDEPT,DESPTS
COMMON/FLAG/DETAIL,MODEL
COMMON/DCR1/DCR1
COMMON/VAR/EMOISE
COMMON/CON/AVT,GCOM
COMMON/RATE/RBS,RPRED
COMMON/EPAR/RAO,EO
COMMON/FIV/IFIT
COMMON/ON/DER
COMMON/E04JBP, E04UAF
COMMON/E04WA1'
INTEGER OITER,DETAIL,ISTATP(6),1WP(10),1FITE(50),1FITD(50)
LOGICAL LOCSCH,LHSET

CALL NAGLIB
WRITE(6,9999)

INITIAL PARAMETER GUESSES

READ(5,*)(AO,EO,A,B)
FLAG(60!)
READ(5,*)(AO,EO,A,B)
READ(5,*) T,EMF,HMF
READ(5,*) TL,TU
READ(S,*)(EMFL,EMFO)
READ(S,*)(UHFL,HMFU)

ACTUAL PARAMETERS AND AVERAGE TEMP
READ(5,*)(AO,EO,A,B)
READ(5,*)(AVTC)

LIMITS ON VARIABLES
T - TEMPERATURE (C)
EMF - ETHYLENE MOLE FRACTION
HMF - HYDROGEN MOLE FRACTION
L - LOWER LIMIT U - UPPER LIMIT
PRESS - REACTION PRESSURE

READ(5,*)(TL,TT)
READ(5,*)(EMFL,EMFO)
READ(5,*)(TAO,AE0,AA',AB)

REAL XC2(50),XXZ(50),XXH(50),TT(50),AXC2(50),AXXZ(50)
REAL BLP(6),BUP(6),0ELTAP(6) 1 GP(6),PARAM(6),HESOP(6) 1
+HESLP(20),wP(54)
REAL XAO(50),XEO(50),PAL(50),PE(50),PRAO(50),PREO(50),
+SP(6)
REAL ROBS(50),AROBS(50),ROBX(50),ERD(50),REPRED(50),Z(50),
+RESD(50),PCL(4),CONV(50),DETCM(50),EIGI(4),EIGR(4)
REAL EX(1),BL(3),BU(3),IWG(50),CI(1),CH(1),ELAM(2),C(2),
+W(200)
DOUBLE PRECISION DERT(4,50),DETCM,VAR,REL(4,4),CSDF,
+DUXD,CH(4,4),WP(50,50),TM(4,50),CNV(4,4),PSN(4,4),
+CQENT(4,50),DER(50,4),CR(4,4),CSD(50),DETM
EXTERNAL E04JBF, FUNCT, MOEN, E04WAY
INTEGER DITER,DETAIL,ISTATP(6),IW(30),IFITE(50),IFITD(50)
LOGICAL LOCSCH, LHSET

...
READ(5,*) PRESS
C
C EXPERIMENTAL NOISE LEVEL FOR SIMULATION STUDIES
C
READ(5,*) ENOISE
C
NUMBER OF VARIABLES (NVAR) AND PARAMETERS (NPAR)
C
READ(5,*) NVAR,NPAR
C
MAXIMUM NUMBER OF EXPERIMENTS
C
READ(5,*) NEXPTS
C
NUMBER OF EXPERIMENTS FOR 1ST BLOCK
C
READ(5,*) IAEXP
C
PSEUDO RANDOM REAL NUMBER FROM NORMAL (GAUSSIAN)
C DISTRIBUTION WITH 0.0 MEAN AND STANDARD DEVIATION 0.5.
C
READ(5,*) NOISE
IF( IAEXP .EQ. 1 ) GO TO 37
IF( ENOISE .EQ. 0.0 ) GO TO 37
CALL GOSCBF( NOISE)
DO 30 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
CONTINUE
C
DO 10 I=1,NEXPTS
T(I),XC(I),XH(I)
IF( MODEL .EQ. 1 ) WRITE(6,9956) AO,EO,A,B
IF( MODEL .EQ. 2 ) WRITE(6,9959) AO,EO,A,B,RAO,RE0

C
C ECHO THE INPUT VALUES
C
IF( IDCRI .EQ. 1 ) WRITE(6,9919)
IF( IDCRI .EQ. 2 ) WRITE(6,9918)
IF( IDCRI .EQ. 3 ) WRITE(6,9917)
IF( DETAIL .EQ. 0 ) GO TO 550
WRITE(6,9949) TL,TU,TU,EMF,EMF,EMF,EMF
WRITE(6,9948) NVAR,NVAR,INEXP,NEXPTS
WRITE(6,9936) DEFP,FITFT
WRITE(6,9947)
DO 551 I=1,NEXP
WRITE(6,9976) I,T(I),XC2(I),XB2(I),(1.0-XC2(I)-XB2(I))

C
C ESTIMATION OF PARAMETERS FROM FIRST BLOCK OF EXPERIMENTAL
C DESIGN
C VARIABLES FOR OPTIMIZATION ROUTINE EO4JBF

C
LWP = 54
LWP = 26
LWP = 30
LOCSCH = .TRUE.
XTOL = 1.0E-05
STEPMX = 1.0E+05
MAXP = 3000
PESTP = 0.0
ETA = 0.01
INBOUND = 0

C
520 CONTINUE
IF( JOB .EQ. 0 ) GO TO 152
IF( NEXP .EQ. 1 ) AND. NEXPTS .GE. 100000 ) GO TO 177
IF( DETAIL .EQ. 1 ) WRITE(6,9905)
IF( DETAIL .EQ. 1 ) WRITE(6,9924)

C
C STARTING POINTS FOR FITTING
C
IF( MODEL .EQ. 2 ) GO TO 510
PARAM(1) = AO
PARAM(2) = EO
PARAM(3) = A
PARAM(4) = B
GO TO 511
510 CONTINUE
PARAM(1) = RAO
PARAM(2) = RE0
PARAM(3) = A

C
PARAM(4) = B
C
C SCALE PARAMETERS
C
DO 710 I=1,NPAR
WRITE(6,9919) SPF(I),ET(I)
DO 705 I=1,NPAR
IF( PARAM(I) .EQ. 0 ) GO TO 704
WRITE(6,9918) SPF(I),ETF(I),ET(I)
GO TO 702
IF( DETAIL .EQ. 0 ) WRITE(6,9932)
IF( DETAIL .EQ. 1 ) WRITE(6,9906)
IF( DETAIL .EQ. 1 ) WRITE(6,9924)

C
CALL EO4MSF AT STARTING POINT TO FIND SUITABLE
C DIFFERENCING INTERVALS
C
IFAIL = 0
IPIT = 0
WRITE(6,9932) SPF(I),ET(I),ETF(I),ET(I)
GO TO 512

C
CALL EO4JBF(NPAR,FUNCI',MONIT,IPRIE,UXSCB,INTYPE)
EO PARAM(2)/SFP(2)
INTYPE = 1
IFAIL = 1
CALL EO4JBF(NPAR,FUNCI',MONIT,IPRIE,UXSCB,INTYPE)
EO PARAM(3)/SFP(3)
IFAIL = 0
CALL EO4JBF(NPAR,FUNCI',MONIT,IPRIE,UXSCB)
EO PARAM(4)/SFP(4)

C
C UPDATE THE PARAMETERS
C
IF( MODEL .EQ. 2 ) GO TO 512
AO = PARAM(1)/SFP(1)
EO = PARAM(2)/SFP(2)
A = PARAM(3)/SFP(3)
B = PARAM(4)/SFP(4)

C
STORE THE ESTIMATED PARAMETERS
C
PARAM(NEXPTS) = AO
PARAM(NEXPTS) = EO
PARAM(NEXPTS) = A
PARAM(NEXPTS) = B
GO TO 513
RAO = PARAM(1)/SFP(1)
REO = PARAM(2)/SFP(2)
A = PARAM(3)/SFP(3)
B = PARAM(4)/SFP(4)
PAO(NEXPTS) = RAO
PBO(NEXPTS) = REO
PAL(NEXPTS) = A
PVE(NEXPTS) = B
PAO(NEXPTS) = EXP(REO)
REO( NEXPTS) • RAO
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PAO( NEXPTS) • RE0
C VARIANCE
C
0264 VAR = OPTP/DFLOAT(NEXPTS-NPAR)
0265 WRITE(6,9990) VAR
C
C STANDARD DEVIATION
C
0266 DO 54 I=1,NPAR
0267 DO 54 J=1,NPAR
0268 PSD(I,J) = VAR*CINV(I,J)
0269 WRITE(6,9906)
0270 WRITE(6,9906) ((PSD(I,J),J=1,NPAR),I=1,NPAR)
C
C READ THE T-DISTRIBUTION
C
0271 READ(5,*) TD
0272 TD = TD
C
C PARAMETER CONFIDENCE INTERVALS
C
0273 DO 56 I=1,NPAR
0274 56 PCl(I) = DTD*DSQR(PSD(I,I))
C
C ECHO PARAMETERS WITH CONFIDENCE INTERVALS
C
0275 WRITE(6,9900)
0276 DO 57 I=1,NPAR
0277 PARAM(I) = PARAM(I)/STP(I)
0278 57 WRITE(6,9900) PARAM(I),PCI(I)
C
C CORRELATION MATRIX AND THE PARAMETER ESTIMATES
C
C JOINT CONFIDENCE REGION
C
0279 DO 60 I=1,NPAR
0280 DO 60 J=1,NEXPTS
0281 60 DEP(I,J) = DEP(J,I)
0282 DO 61 J=1,NPAR
0283 DO 61 I=1,NPAR
0284 CRH(I,J) = 0.000
0285 DO 62 K=1,NEXPTS
0286 62 CRH(I,J) = CRH(I,J)+DEP(I,K)*DEP(K,J)
0287 CALL CSDCRI(NPAR,CRH,CSDV,REL,DETIM)
0288 DETIM(NEXPTS) = DETIM
0289 CONV(NEXPTS) = 1.0/SQR(DETIM(NEXPTS))
0290 IF( DETAIL .EQ. 1 ) WRITE(6,9958) NEXPTS,CONV(NEXPTS)
0292 WRITE(6,9941) NEXPTS
0293 WRITE(6,9941) ((REL(I,J),J=1,NPAR),I=1,NPAR)
0294 CSD(NEXPTS) = CSDV
0295 IF( DETAIL .EQ. 1 ) WRITE(6,9939) CSD(NEXPTS)
C
C Eigenvalues of criterion matrix
C
0297 CALL CSDCRI(NPAR,CRH,CSD,EIGR,EIGI)
0298 WRITE(6,9920)

C DESIGN OF SUCCESSIVE SINGLE EXPERIMENTS
C
C SET EXPERIMENT NUMBER
C
0304 IF( NEXPTS .GE. NEXPTS ) GO TO 177
0306 NEXPTS = NEXPTS+1
0307 IF( DETAIL .EQ. 0 ) GO TO 540
0309 WRITE(6,9982)
0310 WRITE(6,9982)
0312 560 CONTINUE
C
C LIMITS ON VARIABLES
C
0313 IF( MODEL .EQ. 2 ) B1(1) = 77.7/TTU
0315 IF( MODEL .EQ. 1 ) B1(1) = TH/TTU
0317 B1(1) = 1.0
0318 B1(2) = XMPB
0319 B1(3) = XMPB
0320 B1(3) = XMPB
0321 B1(3) = XMPB
C
C GUESS DESIGN VARIABLES
C
0322 READ(5,*) TGC, XCZG, XBZG
0323 TGC = TGC+273.16
0324 IF( NEXPTS .GE. NEXPTS ) EX(1) = (AVTC-TGC)/AVT/TTU
0326 IF( MODEL .EQ. 1 ) EX(1) = TGC/TTU
0328 EX(3) = XCIG
0329 EX(3) = XB2G
0330 IF( UT ) = 0
0331 DIF = 0
0332 151 CONTINUE
C
C EQUAL VARIABLES
C
0333 RHO = 1.0
0334 RHO = 0
0335 MINEQ = 1
0336 IF( IAEXP .EQ. 0 ) MINEQ = 2
0338 HRANGE = 0
0339 M = MINEQ+HRANGE
0340 LAMSET = .FALSE.
0341 MAXCALL = 3000
0342 ETAD = 0.01
0343 LCIG = 1
0344 IBOUND = 0
0345 LWD = 700
0346 LWD = 50
```fortran
IPAIL = 1
CALL EDUAPF(MVAR, MEQ, NLINF, NLNOL, N, EQNAM, IFPRINT, XNCALL, 
+ XSTAD, XTO, XERROR, C, C, CLQ, XBOUND, BL, BJ, XAMST, EX, RX, XAM, 
+ FD, C, XM, LD, W, XM, IPAIL)

DITER = DITER+1

C STORE THE SUCCESSIVE EXPERIMENTAL DESIGN
C
0350 IF( MODEL .EQ. 1 ) GO TO 521
0352 T(I) = EX(I)*T
0353 T(NEP) = AVT/(T(NEP)*AVT+1.0)-273.16
0354 GO TO 522
0355 521 CONTINUE
0356 T(NEP) = EX(I)*T
0357 522 CONTINUE
0358 X2(NEP) = EX(2)
0359 X22(NEP) = EX(3)
0360 XM2(NEP) = 1.0-EX(2)-EX(3)
0361 DX(NEP) = X(NEP)
0362 DXC2(NEP) = XC2(NEP)
0363 DXR2(NEP) = XR2(NEP)

C PRINT THE LOCATION OF SUCCESSIVE EXPERIMENTS
C
0364 IF( DETAIL .EQ. 0 ) GO TO 542
0366 WRITE(6, 9980) NEPTS
0367 WRITE(6, 9979) T(NEP), XC2(NEP), XR2(NEP), XM2(NEP)
0368 WRITE(6, 9926) IPIT
0369 WRITE(6, 9932) IPAIL
0370 WRITE(6, 9910) RX((1),I=1,M)
0371 WRITE(6, 9916) FD
0372 542 CONTINUE

C CHECK THE DESIGN FUNCTION FOR REAL OPTIMUM
C
0373 IF( FD .LT. SQRTN ) GO TO 150
0375 WRITE(6, 9908)
0376 IF( DITER .EQ. 4 ) STOP
0378 GO TO 153
0379 150 CONTINUE
0380 IF(TD(NEP) .LT. IPIT)
0381 IF( JOB .EQ. 0 ) STOP

C READ THE ACTUAL DESIGN AND STORE
C
0383 IF( IAEKP .EQ. 0 ) GO TO 544
0385 IF( NEP .EQ. NEP ) GO TO 543
0387 READ(*, *) T(NEP), XC2(NEP), XR2(NEP)
0388 IF( MODEL .EQ. 2 ) T(T(NEP)) = (AVT-T(NEP))/AVT/
+ (T(NEP)+273.16)
0390 AX(T(NEP)) = T(NEP)
0391 DXC2(NEP) = XC2(NEP)
0392 DXR2(NEP) = XR2(NEP)
0393 IF( DETAIL .EQ. 3 ) WRITE(6, 9942)
0395 IF( DETAIL .EQ. 1 ) WRITE(6, 9979) AT(NEP)
+ AXC2(NEP), AXR2(NEP), (1.0-AXC2(NEP))**AXR2(NEP)
0397 543 CONTINUE
0398 GO TO 154
0399 153 CONTINUE
0400 TN = (T+TN)/2.0
0401 IF( DITER .EQ. 2 ) TN = TN+T
0403 IF( DITER .EQ. 3 ) TN = TN-4.0
0405 IF( MODEL .EQ. 1 ) EX(I) = (AVT-T)/AVT/(T+273.16)/T
0407 IF( MODEL .EQ. 2 ) EX(I) = (AVT-T)/AVT/(T+273.16)/T
0409 GO TO 151
0410 154 CONTINUE
0411 C ESTIMATİON OF PARAMETERS FROM SUCCESSIVE EXPERIMENT
C
0412 520 CONTINUE
C PRINT THE FINAL RESULTS IN TABULATED FORM
C
0413 WRITE(6, 9978) NEP
0414 WRITE(6, 9977)
0415 DO 22 I=1,NEP
0416 WRITE(6, 9976) I,DT(I),DXC2(I),DXR2(I),(1.0-DC2(I)-DXR2(I))
0417 IF( IAEXP .EQ. 0 ) GO TO 544
0418 WRITE(6, 9943)
0419 IF(IlDEL .EQ. 2) WRITE(6, 9916)
0420 IF(IlDEL .EQ. 3) WRITE(6, 9926)
0421 DO 24 I=1,M
0422 WRITE(6, 9976) I,AT(I),AXC2(I),AXR2(I),(1.0-AXC2(I)-AXR2(I))
0423 544 CONTINUE
0424 IF( IAEXP .EQ. 1 ) NEP = NEP-1
0426 IF( IAEXP .EQ. 0 .AND. EX .EQ. 0.0 ) WRITE(6, 9975)
0428 IF( IAEXP .EQ. 0 .AND. EX .EQ. 0.0 ) WRITE(6, 9974)
+ (AROB(I),I=1,NEP)
0430 WRITE(6, 9973)
0431 WRITE(6, 9974) (ROB(I),I=1,NEP)
0432 WRITE(6, 9972)
0433 WRITE(6, 9974) (RPRED(I),I=1,NEP)
0434 DO 23 I=1,NEP
0435 23 RESD(I) = ROBS(I)-RPRED(I)
0436 WRITE(6, 9971)
0437 WRITE(6, 9978) (RESD(I),I=1,NEP)
0439 DO 21 I=1,NEP
0440 21 Z(I) = 1.0-(RPRED(I)/ROB(I))
0442 IF( IAEKP .EQ. 1 ) GO TO 18
0444 WRITE(6, 9970)
0445 DO 24 I=1,NEP
0446 24 WRITE(6, 9960) I,ROD(I)
0447 30 CONTINUE
C
0448 WRITE(6, 9935) AAO, AAO, AAL, ABB
0449 IF( MODEL .EQ. 2 ) WRITE(6, 9934) AAO, AAO
0451 IF( MODEL .EQ. 1 ) GO TO 517
```
WRITE(6,9949)
DO 25 I=1,INEXP,NEXP
WRITE(6,9968)I,PAEO(I),PAEO(I),PAEO(I),PAEO(I),PAEO(I)
CONTINUE
WRITE(6,9967)
DO 26 I=1,IEXP,NEPTS
WRITE(6,9968)I,PAEO(I),PAEO(I),PAEO(I),PAEO(I),PAEO(I)
WRITE(6,9966)
DO 27 I=1,INEXP,NEPTS
WRITE(6,9965)I,DEVICE(I),COMB(I)
WRITE(6,9939)
WRITE(6,9960)I
WRITE(6,9963)I,IFITE(I),IFITE(I)
STOP
C
C PROGRAM TERMINATES HERE
C
9959 FORMAT(12X, 'SUMMARY OF ERROR INTRODUCED :', +5X, 'EXP NO',6X, 'ERROR')
9960 FORMAT(8X,'SUMMARY OF ESTIMATED PARAMETERS IN ORDER :', +5X, 'EXP NO',6X, 'REP AO',5X, 'THAN EO',5X, 'ALPHA',1X, 'BETA')
9961 FORMAT(8X,'SUMMARY OF ACTUAL ESTIMATED PARAMETERS IN ORDER :', +5X, 'EXP NO',8X, 'AO',1X, 'EO',12X, 'ALPHA',12X, 'BETA')
9962 FORMAT(8X,'SUMMARY OF PARAMETERS CONFIDENCE REGION IN ORDER :', +5X, 'EXP NO',5X, 'CRI DET',1X, 'CONF')
9963 FORMAT(8X,'SUMMARY OF FUNCTION EVALUATIONS IN ORDER :', +5X, 'EXP NO',5X, 'PARAMETER ESTIMATION',5X, 'EXP DESIGN')
9964 FORMAT(8X,'SUMMARY OF INITIAL GUESSES FOR PARAMETERS :', +5X, 'AO =',1PE16.8/, +5X, 'EO =',1PE16.8/, +5X, 'ALPHA =',1PE16.8/, +5X, 'BETA =',1PE16.8/, +5X, 'THETA =',1PE16.8/, +5X, 'ZDR =',1PE16.8/, +5X, 'NIT =',1PE16.8/)
```
SUBROUTINE PUNCT(IFLAG,N,SXC,FC,GC,IW,LIW,W,LW)

THIS SUBROUTINE CALCULATES THE OBJECTIVE FUNCTION
FOR THE LEAST SQUARES FITTING AND IS CALLED BY
OPTIMIZATION SUBROUTINE E04JB.

ROBS - AN ARRAY STORES THE CALCULATED RATE WITH NOISE
IN SIMULATION STUDIES AND ACTUAL EXPERIMENTAL
RATES IN EXPERIMENTAL STUDIES.

AROBS - AN ARRAY STORES THE ACTUAL CALCULATED RATE IN
IN THE SIMULATION STUDIES.

RPRED - AN ARRAY OF PREDICTED RATES.
SUM - SUM OF LEAST SQUARES FITTING.
FC - FITTING OBJECTIVE FUNCTION VALUE.
XC - INTERNAL WORKING ARRAY FOR VARIABLES.
ERO - AN ARRAY STORES THE ERROR ADDED TO THE CALCULATED

FIT - FUNCTION EVALUATION COUNTER

DIMENSION GC(N),W(LW),IW(LIW),SXC(R),
+ROBS(50),RPRED(50),T(50),XB2(50),ROBX(50),AROBS(50),
+ERO(50),XCZ(50),TT(50),XC(6)

INTEGER DETAIL

COMMON/PS/SFP(10)
COMMON/ACTEXP/IAEXP
COMMON/ERROR/ROBEX
COMMON/VRS/ERROR
COMMON/NOISE
COMMON/EREXP/ROBEX,ERO
COMMON/MULT/ROBS,ROBX,AROBS,ERO
COMMON/AKER/AROBS,ERO
COMMON/MULT/FLIT,FITTS
COMMON/FLAG/DATA,MODEL
COMMON/RATE/ROBS,RPRED
COMMON/CON/AVT,GOON
COMMON/T/TFIT
COMMON/VAR/TT,T,T,TC2,X2H
COMMON/P/PRESS
COMMON/EXP/NEXTS,INEXP
COMMON/HV/TVAR,MPAR

OBJECTIVE FUNCTION FOR FITTING

IFLAG = 0
DO 400 I=1,NPAR
X2(I) = SXC(I)/SFP(I)
SUM = 0.0
IF IT(FIT).EQ.0 ) FITTS = FITTS
DO 510 I=1,NEXTS
IF (NEXTS.GT.INEXP) GO TO 320
IF (FIT(UN = 0 ) GO TO 330
```

IF ( IAEXP .EQ. 1 ) REAL(5,*) ROBS(I)
GO TO 330

C OBSERVED RATE FOR FIRST BLOCK OF EXPERIMENTS
C
IF ( MODEL .EQ. 1 ) ROBS(I) = AAO*EXP(-AEO/GCOM/(T(I)+273.16))
+((XC2(I)**AAL)*((XB2(I))**ABE)*PRESS)**(AAL+ABE))
IF ( MODEL .EQ. 2 ) ROBS(I) = EXP(AAAO-T(I)*EXP(AER0))
+((XC2(I)**AAL)*((XB2(I))**ABE)*PRESS)**(AAL+ABE))
AROBS(I) = ROBS(I)

C ADD NOISE TO CALCULATED RATES
C
ROBS(I) = ROBS(I)+ROBS(I)*ENOISE/100.0
END(I) = ROBX(I)*ENOISE
GO TO 330
C
IF ( IPIT .EQ. 0 ) GO TO 330
IF ( I .GT. 1 ) GO TO 330
IF ( IAEXP .EQ. 1 ) REAL(5,*) ROBS(NEXPTS)
IF ( IAEXP .EQ. 1 ) GO TO 330
C
C ADD NOISE TO SUBSEQUENT EXPERIMENTS
C
ROBS(NEXPTS) = ROBS(NEXPTS)+ROBS(NEXPTS)*ROBX(NEXPTS)
+ENOISE/100.0
END(NEXPTS) = ROBX(NEXPTS)*ENOISE
GO TO 330
C
C PREDICTED REACTION RATE FOR SUBSEQUENT EXPERIMENTS
C
IF ( MODEL .EQ. 1 ) RPRED(I) = XC(I)*EXP(-XC(2)/GCOM/
+((T(NEXPTS)+273.16)*((XC2(NEXPTS)**AAL)*((XB2(NEXPTS))**ABE)
+PRESS)**(AAL+ABE))
IF ( MODEL .EQ. 2 ) RPRED(I) = EXP(AAAO-T(NEXPTS)*EXP(AER0))
+((XC2(NEXPTS)**AAL)*((XB2(NEXPTS))**ABE)
+PRESS)**(AAL+ABE))
AROBS(NEXPTS) = ROBS(NEXPTS)
C
C ADD NOISE TO SUBSEQUENT EXPERIMENTS
C
ROBS(NEXPTS) = ROBS(NEXPTS)+ROBS(NEXPTS)*ROBX(NEXPTS)
+ENOISE/100.0
END(NEXPTS) = ROBX(NEXPTS)+ENOISE
GO TO 330
C
C PREDICTED REACTION RATE
C
IF ( MODEL .EQ. 1 ) RPRED(I) = XC(I)*EXP(-XC(2)/GCOM/
+((T(I)+273.16)*((XC2(I)**X(3)))*((XB2(I))**X(4)))
+PRESS)**((X(3)+X(4)))
IF ( MODEL .EQ. 2 ) RPRED(I) = EXP(XC(I)-TT(I)*EXP(XC(2)))
+((XC2(I)**X(3)))*((XB2(I))**X(4))*PRESS)**((X(3)+X(4)))
C
C LEAST SQUARES FUNCTION
C
SUQ = 1.0-22
SUM = SUM+SUQ*SUSQ
VOBJP = SUQ+FITS
GO TO 340
C
C SCALE THE FUNCTION VALUE
C
IF ( VOBJF .GT. 1.0 ) GO TO 341
FITS = FITTS*1.0E+01
VOBJ = VOBJF*1.0E+01
GO TO 342
CONTINUE
IF ( VOBJF .LT. 1.0 ) GO TO 340
FITS = FITTS*1.0E-01
VOBJ = VOBJF*1.0E-01
GO TO 343
CONTINUE
PC = VOBJF
IF ( IFIT .EQ. 0 ) AND. DETAIL .EQ. 1 ) WRITE(6,9999) SUM,PC
IF ( IFIT = IFIT+1
GO TO 343
C
END
SUBROUTINE FUNCT(ln.AG,H,SXC,FC)

THIS SUBROUTINE CALCULATES THE OBJECTIVE FUNCTION FOR THE SUBSEQUENT EXPERIMENTAL DESIGN IN THE SIMULATION AND EXPERIMENTAL STUDIES. THIS SUBROUTINE IS CALLED BY OPTIMIZATION SUBROUTINE E04UAY.

DER - DESIGN MATRIX
CRI - CRITERION MATRIX
FC - OBJECTIVE FUNCTION
DEPS - SCALING FACTOR
ICRIT - FLAG FOR DESIGN CRITERIA
IFIT - FUNCTION EVALUATION COUNTER

REAL SXC(H),EIGR(4),EIGI(4),XC(4),AO,EO,A,B,RAO,REO,DTU,DTTU,rENP,AVT,GCON,PRESS,VOBJFD

DOUBLE PRECISION DER(50,4),DET,CRI(4,4),TDER(4,50),REL(4,4),CSD

INTEGER DETAIL
COMMON/PAR/AO,EO,A,B
COMMON/PR/PRESS
COMMON/RPAR/RAO,REO
COMMON/DRV/DER
COMMON/FLAG/DETAIL,MODEL
COMMON/EXPT/KDPTS,INDCP
COMMON/CON/AVT,GCON
COMMON/SDF/SDF

OBJECTIVE FUNCTION FOR SUBSEQUENT EXPERIMENT DESIGN

DO 370 I=1,NVM
XC(I) = SXC(I)
GO TO 350

IF( MODEL.EQ.1 ) GO TO 350
XC(1) = XC(1)*DTU
TEMP = EXP(-RAO-XC(1)*EXP(REO))*(XC(2)**A)*(XC(3)**B)*
*(PRESS**A)*EXP(-EO/GCON/(XC(1)+273.16)/(XC(2)**A))

DER(NEXPTS,1) = TEMP
DER(NEXPTS,2) = (XC(2)*EXP(REO))/TEMP
DER(NEXPTS,3) = TEMP*ALOG(XC(3))*PRESS*TEMP
DER(NEXPTS,4) = AO*ALOG(XC(3))*PRESS*TEMP
GO TO 360

CONTINUE

CRITERION MATRIX

DO 400 I=1,NPAR
DO 400 J=1,NEXPTS
TDER(I,J) = DER(J,I)
GO TO 410

IF( IDCR1 .EQ. 1 ) GO TO 400
IF( IDCR1 .EQ. 2 ) GO TO 420
IF( IDCR1 .EQ. 3 ) GO TO 430
CONTINUE

MINIMUM VOLUME DESIGN CRITERION

CALL CRIV(NPAR,CRI,DET)
VOBJFD = DABS(DET)
FC = -VOBJFD
GO TO 410

SHAPE DESIGN CRITERION

CALL SDCRl(NPAR,CRI,SDC,EIGR,EIGI)
VOBJFD = -ABS(SDC)
PC = VOBJFD
GO TO 410

CORRELATION-SPECIFIC DESIGN CRITERION

CALL CSDCRI(NPAR,CRI,SDC,EIGR,EIGI)
PC = -ABS(SDC)
GO TO 410

SUBSEQUENT ROW FOR DERIVATIVE MATRIX

IF( MODEL.EQ.1 ) GO TO 350
XC(1) = XC(1)*DTU
TEMP = EXP(-RAO-XC(1)*EXP(REO))*XC(2)**A)*(XC(3)**B)*
*(PRESS**A)*EXP(-EO/GCON/(XC(1)+273.16)/(XC(2)**A))

DER(NEXPTS,1) = TEMP
DER(NEXPTS,2) = (XC(2)*EXP(REO))/TEMP
DER(NEXPTS,3) = TEMP*ALOG(XC(3))*PRESS*TEMP
DER(NEXPTS,4) = AO*ALOG(XC(3))*PRESS*TEMP
GO TO 360

CONTINUE
IF( IPIT .EQ. 0 ) DESPTS = DESPT
IF( IPIT .GT. 0 ) GO TO 700
C SCALE THE DESIGN FUNCTION VALUE
C
IF( ABS(FC) .GT. 1.0 ) GO TO 701
PC = FC*1.0E+01
DESPTS = DESPTS*1.0E+01
GO TO 703
CONTINUE
IF( ABS(FC) .LT. 1.0 ) GO TO 700
PC = FC*1.0E-01
DESPTS = DESPTS*1.0E-01
GO TO 703
CONTINUE
IF( IPIT .EQ. 0 ) WRITE(6,998) FC
IF( IPIT .EQ. 0 ) SUM = FC
IF( IPIT = IPIT+1)
RETURN
C
C
C FORMAT(/5X,"ACTUAL STARTING DES FUN VALUE =",1PE16.8)
C FORMAT(/5X,"STARTING DES FUN VALUE FOR OPTIMIZATION =", +1PE16.8)
C FORMAT(/5X,"INITIAL EIGEN VALUES =", +1PE16.8)
C
C END
C
SUBROUTINE CRINV(N,CRI,DET)
C THIS SUBROUTINE CALCULATES THE FUNCTION VALUE FOR
C MINIMUM VOLUME DESIGN CRITERION.
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION CRI(N,N)
C CALCULATE THE DETERMINANT OF CRITERION MATRIX
CALL DETER(CRI,DET)
C DETERMINANT VALUE OF INVERSE OF CRITERION MATRIX
DET = 1.000/DET
RETURN
END
SUBROUTINE CSOCRI(M, CRI, CINV, CSD, REL, DET)
C THIS SUBROUTINE CALCULATES THE INVERSE OF CRITERION MATRIX,
C CORRELATION MATRIX AND FUNCTION VALUE FOR CORRELATION
C SPECIFIC DESIGN CRITERION IN DOUBLE PRECISION.
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION CRI(N,N),REL(N,N),CINV(M,N)
C INVERSE OF CRITERION MATRIX
CALL INV(N, CRI, CINV, DET)
C CORRELATION MATRIX
DO 10 I=1,N
DO 10 J=1,N
REL(I,J) = 0.000
10 REL(I,J) = REL(I,J)+CINV(I,J)/DSQRT(CINV(I,I)*CINV(J,J))
C CORRELATION SPECIFIC DESIGN CRITERION
XX = FLOAT(M*(M-1))
SCR = 0.000
DO 11 J=1,N
IF( J .EQ. 1 ) GO TO 21
11 SCR = SCR+REL(I,J)*REL(I,J)/XX
10 CONTINUE
21 CONTINUE
C SD = DSQRT(SCR)
RETURN
END
SUBROUTINE DETER4(CRI,DET)

THIS SUBROUTINE CALCULATES THE VALUE OF A 4X4 DETERMINANT.

CRI - 4X4 MATRIX (CRITERION MATRIX)
DET - VALUE OF CRI MATRIX'S DETERMINANT

DOUBLE PRECISION CRI(4,4),DET,SUM1, SUM2, SUM3, SUM4

SUM1 = CRI(1,1)*(CRI(2,2)*CRI(3,3)*CRI(4,4)-CRI(3,4)*CRI(4,3))
  + CRI(2,1)*(CRI(3,2)*CRI(4,4)-CRI(3,4)*CRI(4,2))
  + CRI(3,1)*(CRI(4,3)-CRI(3,2)*CRI(4,1))
  + CRI(4,1)*(CRI(3,3)-CRI(3,2)*CRI(4,1))

SUM2 = CRI(1,2)*(CRI(2,1)*CRI(3,3)*CRI(4,4)-CRI(3,4)*CRI(4,3))
  + CRI(2,2)*(CRI(3,1)*CRI(4,4)-CRI(3,4)*CRI(4,1))
  + CRI(3,2)*(CRI(4,3)-CRI(3,1)*CRI(4,2))
  + CRI(4,2)*(CRI(3,3)-CRI(3,1)*CRI(4,1))

SUM3 = CRI(1,3)*(CRI(2,1)*CRI(3,2)*CRI(4,4)-CRI(3,4)*CRI(4,2))
  + CRI(2,3)*(CRI(3,1)*CRI(4,4)-CRI(3,4)*CRI(4,1))
  + CRI(3,3)*(CRI(4,2)-CRI(3,1)*CRI(4,1))
  + CRI(4,3)*(CRI(3,2)-CRI(3,1)*CRI(4,1))

SUM4 = CRI(1,4)*(CRI(2,1)*CRI(3,2)*CRI(4,3)-CRI(3,4)*CRI(4,2))
  + CRI(2,4)*(CRI(3,1)*CRI(4,3)-CRI(3,4)*CRI(4,1))
  + CRI(3,4)*(CRI(4,2)-CRI(3,1)*CRI(4,1))
  + CRI(4,4)*(CRI(3,3)-CRI(3,1)*CRI(4,1))

DET = SUM1-SUM2+SUM3-SUM4

RETURN
END

SUBROUTINE CON4(IFLAG,N,XC,CC)

THIS SUBROUTINE CALCULATES THE DESIGN VARIABLES
CONSTRAINTS AND CALLED BY 504UAF OPTIMIZATION
SUBROUTINE.

XC - DESIGN VARIABLES(ARRAY)
CC - CONSTRAINTS(ARRAY)

REAL CC(M),XC(N),DXC(4)
INTEGER DETAIL
COMMON (VLTU, EU0)
COMMON (AVT, GVST, GCON)
COMMON (SFC(10))
COMMON (FIT, EXP1, EXP2)

IFLAG = 0
DO 10 I=1,N
   DXC(I) = XC(I)
   IF (IAEXP .EQ. 1 ) GO TO 200
   IF (MODEL .EQ. 1 ) DXC(I) = T+273.16
   IF (MODEL .EQ. 2 ) DXC(I) = T+273.16
   RATE = AAO*EXP(-AEO/GCON/T)*(DXC(2)**AAL)*(DXC(3)**ABE)
   CC(I) = 1.0-(DXC(2)+DXC(3))
   CC(2) = 1.5E-04-RATE
   CC(3) = 1.5E-04-RATE
   CC(4) = 0.9-(DXC(2)+DXC(3))
   CC(I) = CC(I)*1.0E-01
   SFC(I) = SFC(I)*1.0E-01
   GO TO 210
10   CONTINUE
200   CONTINUE
201   CONTINUE

SCALE THE CONSTRAINTS

IF (IFIT .LT. 1 ) GO TO 110
DO 11 I=1,N
   SFC(I) = 1.0
11   CONTINUE

IF (CC(I) .EQ. 0.0 ) GO TO 103
102   CONTINUE

CC(I) = CC(I)*1.0E+01
SFC(I) = SFC(I)*1.0E+01
GO TO 102
104   CONTINUE

END

SUBROUTINE CON1(IFLAG,M,N,XC,CC)

THIS SUBROUTINE CALCULATES THE DESIGN VARIABLES
CONSTRAINTS AND CALLED BY 504UAF OPTIMIZATION
SUBROUTINE.

XC - DESIGN VARIABLES(ARRAY)
CC - CONSTRAINTS(ARRAY)

REAL CC(M),XC(N),DXC(4)
INTEGER DETAIL
COMMON (VLTU, EU0)
COMMON (AVT, GVST, GCON)
COMMON (SFC(10))
COMMON (FIT, EXP1, EXP2)

IFLAG = 0
DO 10 I=1,M
   DXC(I) = XC(I)
   IF (IAEXP .EQ. 1 ) GO TO 200
   IF (MODEL .EQ. 1 ) DXC(I) = T+273.16
   IF (MODEL .EQ. 2 ) DXC(I) = T+273.16
   RATE = AAO*EXP(-AEO/GCON/T)*(DXC(2)**AAL)*(DXC(3)**ABE)
   +PRESS**([AAL+ABE])
   CC(I) = 1.0-(DXC(2)+DXC(3))
   CC(2) = 1.5E-04-RATE
   GO TO 210
10   CONTINUE
200   CONTINUE
201   CONTINUE
202   CONTINUE
203   CONTINUE

SCALE THE CONSTRAINTS

IF (IFIT .LT. 1 ) GO TO 110
DO 11 I=1,M
   SFC(I) = 1.0
11   CONTINUE

IF (CC(I) .EQ. 0.0 ) GO TO 103
102   CONTINUE

CC(I) = CC(I)*1.0E+01
SFC(I) = SFC(I)*1.0E+01
GO TO 102
104   CONTINUE

END
SUBROUTINE INVM(N,AA,A,DETER)

THIS SUBROUTINE CALCULATES THE INVERSE OF AN MATRIX.

THE GAUSS-JORDAN COMPLETE ELIMINATION METHOD IS EMPLOYED
WITH MAXIMUM POINT STRATEGY.

REF: CARNABY, R., LUTHER, S.A., AND WILKES, J.O., APPLIED
NUMERICAL METHODS, P280-91, JOHN WILEY & SONS, 1969.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

DIMENSION IROW(50),JCOL(S0),JORD(50),Y(50),
+A(N,N),AA(N,N)

SAVE THE MATRIX

DO 1 1=1,N
DO 1 J=1,N
A(I,J) = AA(I,J)

BEGIN THE ELIMINATION PROCEDURE

DETER = 1.000
DO 10 K=1,N
X(K) = K-1

SEARCH FOR THE PIVOT ELEMENT

PIVOT = 0.000
DO 20 I=1,N
DO 20 J=1,N
IF( I .EQ. IROW(K) ) GO TO 9
IF( J .EQ. JCOL(J) ) GO TO 10
CONTINUE
CONTINUE

IF( K .EQ. I ) GO TO 9
IF( I .EQ. IROW(I) ) GO TO 12
IF( J .EQ. JCOL(J) ) GO TO 12
CONTINUE

IF( DABS(A(I,J)) .LE. DABS(PIVOT) ) GO TO 12
PIVOT = A(I,J)
IROW(I) = I
JCOL(I) = J
CONTINUE

UPDATE THE DETERMINANT VALUE

DETER = DETER*PIVOT
C
C normalize pivot row elements
C
0012  DO 14 J=1,N
0013 14 A(IRDWIT,J) = A(IRDWIT,J)/PIVOT
C
C carry out elimination and develop inverse
C
0014  A(IRDWIT,JCOLK) = 1.000/PIVOT
0015  DO 18 I=1,N
0016  AJJCK = A(I,JCOLK)
0017  IF( I .EQ. IRDWIT ) GO TO 19
0018  A(I,JCOLK) = -AJJCK/PIVOT
0019  DO 17 J=1,N
0020  IF( J .NE. JCOLK ) A(I,J) = A(I,J)-AJJCK*A(IRDWIT,J)
0021  CONTINUE
0022  CONTINUE
C
C order solution value and create JORD array
C
0023  DO 20 I=1,N
0024  IRWIN = IRWIN(I)
0025  JCOLI = JCOL(I)
0026  JORD(IRWIN) = JCOLI
0027  CONTINUE
C
C adjust sign of determinant
C
0028  INTCB = 0
0029  BM1 = N-1
0030  DO 22 I=1,BM1
0031  IPL = I+1
0032  DO 22 J=IPL,N
0033  IF( JORD(I) .GE. JORD(I) ) GO TO 23
0034  JTEMP = JORD(I)
0035  JORD(I) = JORD(J)
0036  JORD(J) = JTEMP
0037  CONTINUE
0038  CONTINUE
0039  IF( INTCB/2*2 .NE. INTCB ) DETER = -DETER
C
C unscramble the inverse
C
0040  FIRST THE ROW
C
0041  DO 28 J=1,N
0042  IRWIN = IRWIN(I)
0043  JCOLI = JCOL(I)
0044  Y(JCOLI) = A(IRWIN,J)
0045  DO 28 I=1,N
0046  A(I,J) = Y(I)
C
C them by column
SUBROUTINE HONIT(N, XC, PC, GC, ISTATE, GPJNRH, COND, POSDEF, +MTER, RF, IW, LIW, W, LW)

THIS SUBROUTINE MONITORS THE PROGRESS OF E04JBF OPTIMIZATION SUBROUTINE.

LOGICAL POSDEF
REAL GC(N), W(LW), XC(N)
INTEGER ISTATE(N), IW(LIW), DETAIL
COMMON/FLAG/DETAIL, MODEL

IF( DETAIL .EQ. 0 ) RETURN

WRITE(6, 9999) MTER, RF, PC, GPJNRH
WRITE(6, 9998)
DO 100 J = 1, N
ISJ = ISTATE(J)
IF( ISJ .GT. 0 ) GO TO 20
ISJ = -ISJ
IF( ISJ .LT. 0 ) GO TO 40
IF( ISJ .EQ. 0 ) GO TO 60
IF( ISJ .GT. 0 ) GO TO 80
WRITE(6, 9997) J, XC(J), GC(J)
GO TO 100

WRITE(6, 9996) J, XC(J), GC(J)
GO TO 100

WRITE(6, 9995) J, XC(J), GC(J)
GO TO 100

CONTINUE

IF( COND .EQ. 0.0 ) RETURN
IF( COND .LE. 1.0E+06 ) GO TO 120
WRITE(6, 9993)
GO TO 140

WRITE(6, 9992) COND
GO TO 140

IF( .NOT. POSDEF ) WRITE(6, 9991)
RETURN

FORMAT(* WX*, 1X, *W*X*, 16X, *FREE*)
FORMAT(* WX*, 1X, *W*X*, 16X, *UPPER BOUND*)
FORMAT(* WX*, 1X, *W*X*, 16X, *LOWER BOUND*)
FORMAT(* WX*, 1X, *W*X*, 16X, *CONSTANT*)
FORMAT(* ESTIMATED CONDITION NUMBER OF PROJECTED HESSIAN*, +*IS MORE THAN 1.0E+06*),
FORMAT(* ESTIMATED CONDITION NUMBER OF PROJECTED HESSIAN **,
FORMAT(* PROJECTED HESSIAN MATRIX IS NOT POSITIVE DEFINITE*)
SUBROUTINE AHONIT(N,M,X,P,C,NITER,NP,GLNORM,COND,POSDEP,
+RHO,RLall:)

TBIS SUBRDOTINE MONITORS THE PROGRESS OF E04UAF OPTIMIZATION SUBROUTINE.

LOGICAL POSDEP
REAL C(M),RLAI((M). X(N))
INTEGER ETA.IL
COMMON/SPCOH/SFC(10)
COMMON/PINT/IPRINT
COMMON/NORM/FNORM,CNORM

IF( NITER .GE. 0 )
  DUMMY = DUMMY+C(I)**2
  CNORM = SQRT(DUMMY)
  IF( DETAIL .EQ. 0 ) RETURN
  WRITE(6,997) MF
  WRITE(6,996) (XI(I),I=1,N)
  WRITE(6,995) F
  WRITE(6,998) GLNORM,CNORM,(C(I),I=1,M)
  WRITE(6,999) RHO,(RLAI(I),I=1,M)
  CONTINUE
  IF( DETAIL .EQ. 0 ) RETURN
  WRITE(6,997) MF
  WRITE(6,996) (XI(I),I=1,N)
  WRITE(6,995) F,(C(I),I=1,M)
  WRITE(6,998) NITER, GLNORM
  IF( COND .LT. 1.0E+06 ) GO TO 110
  WRITE(6,993) COND
  IF( .NOT. POSDEP ) RETURN
  WRITE(6,991.)
  WRITE(6,990) NITER, GLNORM
  IF( .NOT. POSDEP ) RETURN
  WRITE(6,991.)
  WRITE(6,990) NITER, GLNORM

END
APPENDIX - I

PUBLICATIONS FROM THIS WORK
Following papers have been accepted for publication:

- A K Agarwal and M L Brisk,
  "Sequential Experimental Design for Precise Parameter Estimation:
   1. Use of Reparameterization",

- A K Agarwal and M L Brisk,
  "Sequential Experimental Design for Precise Parameter Estimation:
   2. Design Criteria",
REFERENCES
Box, G E P and Hill, W J, Technometrics, 9, 57 (1967).
Box, G E P and Draper, N R, Biometrika, 52, 355 (1965).
Carberry, J J, AICHE J, 6, 460 (1960).


Toyama, O, Rev Phys Chem Japan, 12, 115 (1938).


APPENDIX

Sample Calculations

Flowrates:

The ethylene, hydrogen and nitrogen flowmeters were calibrated at a mixing pressure of 100 kPa(g) using a wet-test meter and/or a soap bubble meter. The flowrates were measured against the voltage across the precise resistance (see Section 5.3.2) and the volumetric flowrates were fitted to a second order polynomial equation after they were corrected to STP. The polynomial equations were:

\[ v_{C_2H_4} = -9.743 + 12.272V - 1.297V^2 \]  
(Correlation Coefficient = 0.999)

\[ v_{H_2} = -11.007 + 12.894V - 0.507V^2 \]  
(Correlation Coefficient = 0.999)

\[ v_N_2 = -6.429 + 7.920V - 0.547V^2 \]  
(Correlation Coefficient = 0.999)

where,

\[ V \]  - digital voltmeter reading; volts

\[ v_{C_2H_4} \]  - volumetric flowrate of ethylene; ml/sec

\[ v_{H_2} \]  - volumetric flowrate of hydrogen; ml/sec

\[ v_N_2 \]  - volumetric flowrate of nitrogen; ml/sec
Gas Analysis:

Gas analysis was carried out by using a gas chromatograph as discussed in Section 5.3.4. The gas chromatograph was calibrated every time at the start of the day. A typical linear regression (for the Run NC-19) was:

\[
\text{C}_2\text{H}_6 \text{ mole \%} = 2.074E-05 \text{ (Peak Area)} + 1.56E-05 \\
\text{(Correlation Coefficient} = 0.999\text{)}
\]

The initial concentration of ethylene was calculated from the reactant flowrate measurements.

Sample Calculations for Run NC-19

Feed:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Voltmeter Reading (volts)</th>
<th>Flowrate (ml/sec)</th>
<th>Composition (mole%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>1.39</td>
<td>4.62</td>
<td>10.55</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.31</td>
<td>26.12</td>
<td>59.66</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.14</td>
<td>13.04</td>
<td>29.80</td>
</tr>
</tbody>
</table>

Total volumetric flowrate = 43.78 ml/sec

Feed sample flowrate = 1.47 ml/sec

Therefore, total flowrate through reactor = 43.78 - 1.47

= 42.31 ml/sec

\[
F_0 = \frac{(1 \text{ atm}) (42.31 \text{ ml/sec})}{(82.06 \text{ ml atm/mole/K}) (293.16 \text{ K})}
\]

= 1.76E-03 mole/sec

= 1.76E-06 kg mole/sec

Catalyst weight \((W) = 1.436E-04 \text{ kg}\)
APPENDIX

Sample Calculations

Flowrates:

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\[ v_{H_2} = -11.007 + 12.894v - 0.507v^2 \]
\[ \text{(Correlation Coefficient} = 0.999) \]

\[ v_{N_2} = -6.429 + 7.920v - 0.547v^2 \]
\[ \text{(Correlation Coefficient} = 0.999) \]

where,

\[ v \] - digital voltmeter reading, volts

\[ v_{C_2H_4}, v_{H_2}, v_{N_2} \] - volumetric flowrate of ethylene, hydrogen, and nitrogen, ml/sec