KINETIC STUDY OF THE HYDROGENOLYSIS
OF n-BUTANE ON NICKEL CATALYST

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by

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ABSTRACT

The catalytic hydrogenolysis of propane and n-butane have been investigated in an integral packed bed reactor (0.70 cm. I.D. by 25. cm. long). The catalyst was 10.% nickel on silica gel. A blocked factorial set of experiments were performed at hydrogen to butane feed ratios of 4. to 9., temperatures of 240.°C. to 282.°C. and feed flowrates of 1.0 to 1.8 ml./sec. Kinetic rate expressions were developed to predict the product distribution, taking into account increasing catalytic activity. A proposed parameter estimation strategy, applying non-linear regression theory, was used to obtain the ten kinetic parameters. Error analysis of the parameters using likelihood ratios is included. Models were developed to describe the catalyst activity changes observed during experimentation. The kinetic models predict the experimental observations very accurately over all conversions and show considerable deviation only at the combination of high temperature and low feed ratio.

The butane kinetic model was incorporated into proposed fluidized bed reactor models and sensitivity analyses were performed on catalyst activity and the interchange parameter.

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A	cross sectional area of packed bed reactor (cm.^{2})
A_i	area under chromatogram for component i
c	concentration of reacting component (moles/cm.^{3})
c	conversion of butane
c_o	initial concentration of reacting component (moles/cm.^{3})
c_o	reference conversion of butane
C_m	maximum relative frequency factor
C_p	heat capacity (cal./gm. °C.)
C_i	chromatograph calibration factor for component i (mm. Hg./area)
D_{eff}	effective diffusivity (cm.^{2}/sec.)
$\mathcal{D}$	Knudson Diffusion coefficient (cm.^{2}/sec.)
d_p	diameter of particle (cm.)
d_B	effective bubble diameter
d_c	diameter of cloud region
D	binary diffusion coefficient of butane and hydrogen (cm.^{2}/sec.)
E	Expectation Operator
E_{DA}	eddy diffusivity (cm.^{2}/sec.)
F	Fraction of C_4* that cracks to C_3* and C_1*
F	Flowrate (cm.^{3}/sec.)
f	probability density function

F_o	effective bubble emulsion interchange factor
F_i	mole fraction of component i
G	superficial mass velocity (gm./sec. cm.^{2})
h	heat transfer coefficient (cal./sec. cm.^{2} °C.)
k	Arrhenius rate constant
k_B	frequency factor for butane (moles/sec. vol. reactor atm.$^{-(m+n)}$)
K_{P1}	pre-exponential factor in propane rate expression in butane model (moles/sec. vol. reactor atm.$^{(m'+n')}$)
K_{P2}	pre-exponential factor in propane rate expression in butane model (dimensionless)
k_r, k_d	frequency factors
K_E	ratio of rates of reaction on the surface of the catalyst to rate of desorption
k_E	pre-exponential factor in ethane rate expression (dimensionless)
k_P	pre-exponential factor for rate of cracking of propane (moles/sec. vol. of reactor atm.$^{-(m+n)}$)
k_n	pre-exponential factor for rate constant in model for catalyst activity change, assuming constant maximum catalyst activity
k_v	pre-exponential factor for rate constant in model for catalyst change, assuming maximum activity a function of temperature
k_v	pseudo-first order rate constant for cracking of butane based on gross volume of catalyst particle (moles/sec. vol.)
k_B	butane pre-exponential factor (moles/sec. cm.^{3} atm.$^{-(m+n)}$)
k_o	frequency factor at standard operating conditions
k_G	mass transfer coefficient (moles/sec. cm.^{2})

K_{CE}	interchange coefficient between cloud and emulsion
k_g	mass transfer coefficient (gm. moles/sec. cm.^{2} atm.)
L	likelihood function
L	length of reactor (cm.)
m	exponent on butane partial pressure
m′	exponent on propane partial pressure
n	exponent of hydrogen partial pressure in butane rate expression
n′	exponent of hydrogen partial pressure in propane rate expression
n	number of experimental runs
N	number of bubbles per unit volume of fluidized bed reactor (1./cm.^{3})
N_{Re}	Reynolds number ($G \cdot d_p/\mu$)
N_{Pr}	Prandtl number ($C_p \cdot \mu/k$)
N_{Sc}	Schmidt number ($\mu/\rho \cdot \mathcal{D}$)
$P_{H.C.}$	partial pressure of hydrocarbon (atm.)
P_{H_2}	partial pressure of hydrogen (atm.)
P_{C_4}	partial pressure of butane (atm.)
P_{C_3}	partial pressure of propane (atm.)
P_i	partial pressure of component i (atm.)
P	prior probability
P_B	partial pressure of butane (atm.)

P_H	partial pressure of hydrogen (atm.)
q	volume flowrate in and out of a bubble (cm.^{3}/sec.)
Q	volume flowrate in and out of bubble including bulk and diffusive transfer (cm.^{3}/sec.)
$r_{C_4}, r_{C_3}, r_{C_2}$ r_{C_1}, r_{H_2}	rates of disappearance of butane, propane, ethane, methane and hydrogen respectively (gm. moles/sec. vol. of packed bed)
r_a, r_d	rates of adsorption and desorption of propane (gm. moles/sec. cm.^{3})
r_r, r_1	rates of cracking of propane and ethane on the surface of the catalyst (gm. moles/sec. cm.^{3})
$-r_{Vi}$	rate of disappearance of component i (moles/sec. cm.^{3})
r	number of responses
R	universal gas law constant (atm. cm.^{3}/gm. moles °K.)
r_B	rate of cracking of butane (gm. moles/sec. cm.^{3})
Re_c	cloud Reynolds number
S_i	selectivity of component i (moles of component i produced/moles of butane or propane reactant reacted)
$S(\underline{\theta})$	weighted sum of squares objective function
SSQ_{ij}	weighted difference between calculated and observed response for the ith run and the jth response
Sh_c	Sherwood number for transfer from a sphere of uniform surface composition
t	time (min.)
T_o	temperature below which reduction of catalyst is assumed not to occur (°K.)
T	reacting temperature (°K.)

u	superficial gas velocity (cm./sec.)
u_o, $u_{m.f.}$	minimum fluidization velocity (cm./sec.)
U_A	bubble rise velocity (cm./sec.)
$\overline{u}$	average superficial gas velocity (cm./sec.)
V	volumetric flow through packed bed reactor (cm.^{3}/sec.)
V_i	pen, temperature, flowrate and feed ratio variables
w_{ui}	weighting factor for ith response of the uth experiment
$\underline{x}_u$	vector of constants for the uth experiment
x	distance along packed bed reactor (cm.)
X	fluidized bed model interchange parameter
$\underline{X}$	matrix of operating variables such as temperature or pressure
$\underline{X}_i$	Jacobian matrix of partial derivatives with respect to parameters (using model i)
$\underline{y}$	vector of observations
y_{ui}	observed variable for ith response of uth experiment
z	Roth criterion objective function

Greek Letters

$\underline{\alpha}$	vector of initial parameter estimates
ε_{ui}	error in the ith response of the uth experiment
η_{ui}	dependent variable or value predicted for the ith response of the uth experiment
θ_i^*	fraction of active catalyst surface sites covered by species i
$\underline{\theta}$	column vector of unknown parameters
$\underline{\theta}\,^*$	column vector of best estimate parameter values for $\underline{\theta}$
σ^2	error variance
σ_i^2	error variance under model i
$\Delta E_a'$	activation energy for adsorption process (cal./gm. mole)
ΔE_B	activation energy for rate of butane cracking
$\Delta E_d'$	activation energy for desorption
ΔE_E	ethane activation energy
ΔE_{P1}, ΔE_{P2}	activation energies in propane rate expressions in butane cracking model
ΔE_P	activation energy for rate of propane cracking
$\Delta E'_r$	activation energy for reaction
ΔE_n, ΔE_v	activation energies for models to describe rate of increasing catalyst activity
ΔH	heat of reaction (cal./gm. mole of butane reacted)
Δ_p	partial pressure driving force for mass transfer to and from surface of catalyst pellet. (atm.)
ΔT	temperature driving force for heat transfer to and from surface of catalyst pellet (°C.)
ΔT_{max}	widest temperature variation observed in packed bed reactor (C.°)

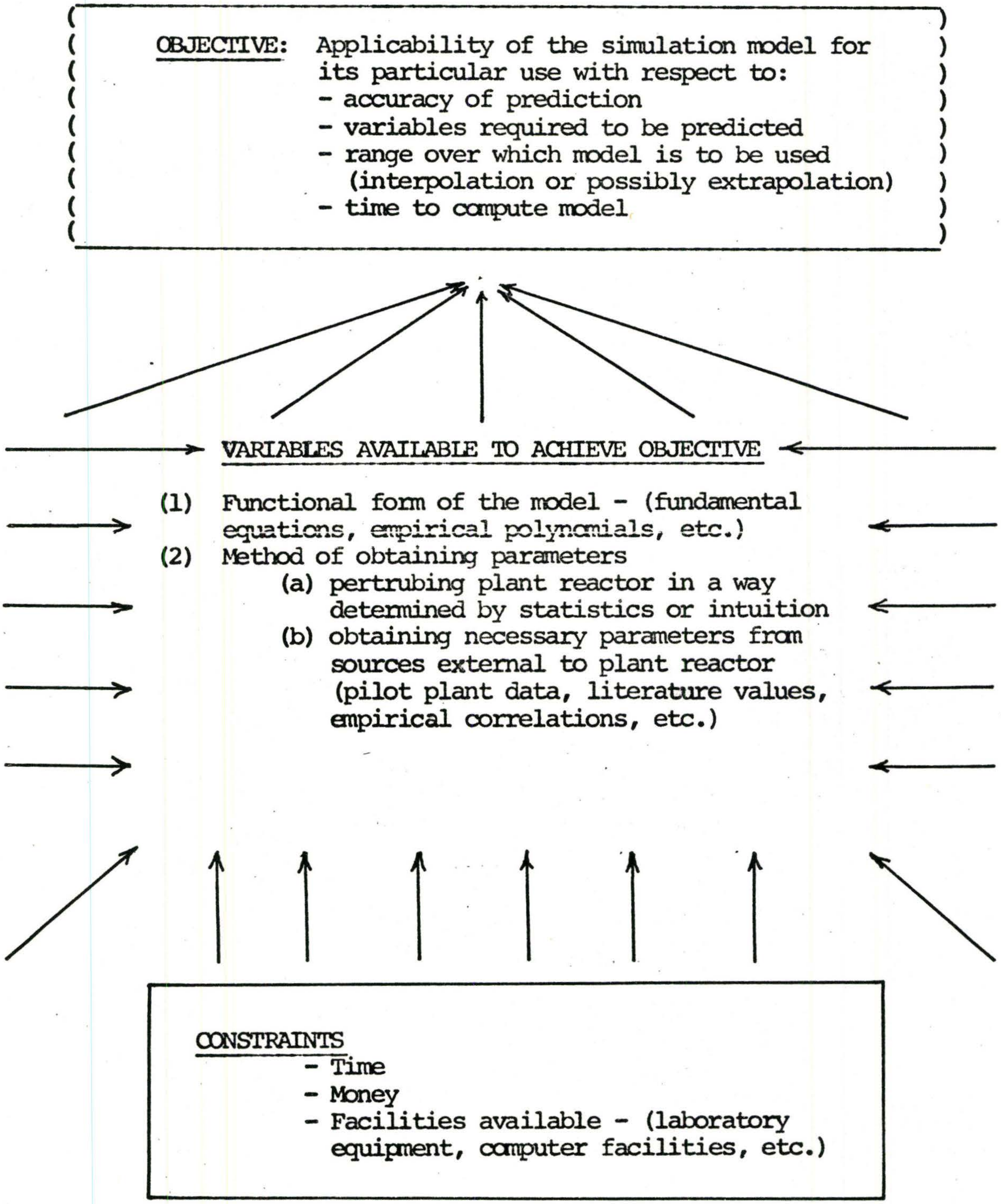
1. INTRODUCTION

For the past five years the faculty and students in the Chemical Engineering Department at McMaster University have been gaining experience in the simulation of chemical processes. These have included C.I.L.'s sulfuric acid plant, Shell's alkylation unit, Alcan's Bayer process, British Petroleum's waste-water treatment plant, Polymer's light-end recovery unit, Hercules' polymer reactor train, Atomic Energy's heavy water process and a number of other processes upon which the faculty have been consulted. The almost universal experience has been that sufficient data have not been available to adequately describe the chemical reactors, although these units are usually the most important in determining the plant operation and economics. The problem is usually one of describing the chemical reactions taking place, both with respect to the mechanism and kinetic rate constants. In most instances there is a great reluctance to carry out fundamental bench or pilot scale studies. On the other hand, the plant reactor may be used for limited testing. It then becomes important to learn how to use this data to estimate parameters in the proposed models. New techniques may have to be developed; application of known techniques will have to be tested; and it would seem advisable to gain this experience on pilot equipment before proceeding to plant tests. The question really is: how does one best simulate a chemical reactor, and also what are the criteria for "best" for a particular simulation study.

These questions have motivated a programme into these aspects.

FIGURE 1-1

MODELLING AS AN OPTIMIZATION PROBLEM



OBJECTIVE: Applicability of the simulation model for its particular use with respect to:
- accuracy of prediction
- variables required to be predicted
- range over which model is to be used (interpolation or possibly extrapolation)
- time to compute model

VARIABLES AVAILABLE TO ACHIEVE OBJECTIVE

(1) Functional form of the model - (fundamental equations, empirical polynomials, etc.)

(2) Method of obtaining parameters
  (a) pertrubing plant reactor in a way determined by statistics or intuition
  (b) obtaining necessary parameters from sources external to plant reactor (pilot plant data, literature values, empirical correlations, etc.)

CONSTRAINTS
- Time
- Money
- Facilities available - (laboratory equipment, computer facilities, etc.)

This thesis is a part of this total program. The basic problem is to investigate the procedures for simulating an industrial chemical reactor, with all the constraints of an industrial environment, in the "best" way.

This simulation problem may, therefore, be looked upon as an optimization problem where: (i) the objective function reflects the requirements imposed upon the particular model depending upon the overall aims of the particular simulation; (ii) the independent variables reflects the alternative procedures which may be followed in developing the simulation model; and (iii) the constraints reflects the necessity of arriving at a solution, whatever it may be. A diagrammatic representation of this idea is shown in Figure 1-1. This approach emphasizes the fact that there are many alternative models for a particular unit and the most "sophisticated" need not necessarily be "best".

The total program is involved with investigating these various alternatives and evaluating the resulting simulation models in an effort to find the "best" way of proceeding in the simulation of an industrial reactor. The models employed may cover the most sophisticated models based on fundamental mechanisms only, to the completely empirical model containing very little basic descriptions. In this study a completely mechanistic approach is employed since it is expected to give the most information about the reaction and, therefore, is expected to be the basis of comparison for other models and modelling procedures.

An advantage of this method is that the data or parameters extracted from a reactor using a mechanistic model reflects to some degree the fundamentals of the process, that is, the parameters obtained to a certain extent have physical meaning. Also, the same model may be used with some confidence in different situations with perhaps some minor parameter adjustments. With the mechanistic approach, the simulation of a complicated reactor system may be broken down into several easier simulations or the component parts of the total complicated system. The effect of various levels of sophistication of these component parts on the total reactor simulation may then be studied.

With the mechanistic approach it is not at all surprising and perhaps inevitable that several concepts may be proposed to try to explain a physical or chemical occurance. Statistical model discrimination theory may then be useful in determining which of the several proposed models best describes the physical system.

The type of reactor chosen to represent the general industrial reactor was the fluidized bed reactor. It was chosen because it was an example of a reactor where complicated fluid mechanics occur together with rather complicated catalytic reactions. There has been a general increase in interest in these reactors as indicated by the current literature and recently published books(D4,L4).

Thus, in the framework of the total program, the following aspects can be considered: (i) determination of the chemical kinetics in a separate bench scale experimental apparatus and using these kinetics along with plant data to estimate the parameters describing the fluid mechanics, (ii) obtaining of fluid mechanical parameters through measurements in the large reactor or in pilot-plant equipment and using these to determine the kinetics from the plant data, (iii) determination of all parameters simultaneously from the plant data, (iv) obtaining all information a priori in pilot experiments and using this to describe the plant-scale reactor. To carry out this study a pilot-plant scale fluidized bed reactor was built by Mr. I.D. Shaw, a fellow graduate student involved in this program. This was built as large as economically feasible (initial capital outlay plus operating costs); it has a height of 8 ft. and an internal diameter of 8 in.(S8).

The reaction chosen for the fluidized bed was the hydrogenolysis of normal butane over a 10% nickel on silica gel catalyst. The hydrogenolysis of n-butane over a 0.5% ruthenium on γ-alumina catalyst was being thoroughly investigated by a Ph.D. graduate student in the heterogeneous catalysis group in the department and the experience gained in this work would be very useful for this project. Also, this reaction may be carried out at fairly low temperatures (500°F.). Moreover, the kinetics involved was thought interesting and complex enough to give some idea of the complications encountered in industrial reactors.

This thesis is mainly concerned with developing a kinetic model to be used in the mechanistic modelling of a fluidized bed reactor.

2. SCOPE OF THIS WORK

RELATIONSHIP TO TOTAL PROGRAM

In the mechanistic modelling of a fluidized bed reactor, the number of parameters is large. These involve the parameters which describe the fluid behaviour in the bed and the parameters which describe the chemical reaction kinetics. One modelling procedure involves estimating the kinetic parameters from experiments performed outside the fluidized bed reactor. In this way, the complicated description of the fluid mechanics in the reactor can be avoided.

Some basic requirements which will be incorporated in a fluidized bed reactor may be specified at the outset. The kinetic rate expressions need to be in differential rate form and must not be so complex that their inclusion in the fluidized bed reactor model leads to disproportionately long computer times.

It was felt also that the kinetic model should predict the total product distribution of the cracking reaction (selectivities). This was particularly important in this case because the rate of reaction and rate of production of the hydrocarbons involved in this reaction is very sensitive to the partial pressure of hydrogen. Because there is this strong interaction of all components, a meaningful rate model must consider the concentrations of all components and this, therefore, means that the entire product distribution must be predicted.

Since one of the objectives of the overall project was to apply statistical model discrimination theory to several proposed fluidized bed models, it was felt that the product distribution may give extra information and perhaps better discrimination among the various kinetic models than just overall butane conversion. Moreover, this additional information could make discrimination easier among the fluid mechanical models in which mixing characteristics, diffusion, by-passing, etc. must be included.

THIS WORK

The main concern of this work is in obtaining a kinetic model which may be incorporated in a fluidized bed reactor model. The kinetics are to be investigated in a packed bed integral reactor where transport phenomena and fluid mechanical effects may be largely eliminated.

The packed bed reactor operated as an integral reactor was chosen for the following reasons: (i) The butane conversion ranges obtained from this reactor would be close to the range experienced in the fluidized bed. (ii) This reactor allows an assessment of the quality of data that may be obtained from inexpensive equipment which could be built quickly and justified on a plant site. (iii) It allows a direct comparison of the quality of the data and ease of analysis with the more expensive Carberry-type reactor being used by Kempling and Anderson(K1) to investigate the hydrogenolysis of butane over ruthenium and finally, (iv) Using a packed bed integral reactor provides experience in modelling and applying parameter estimation techniques to a system which is non-linear in the parameters and whose responses must be described by a set of non-linear ordinary differential equations.

The product distribution of reactants and products (including methane, ethane, propane, butane and hydrogen) for the n-butane hydrogenolysis reaction, occurring on a 10% nickel on silica gel catalyst, was to be studied over the following operation ranges:

(i) Temperature 240° to 283°C.

(ii) Hydrogen to butane molar feed ratios - 4 to 9.

(iii) Superficial velocities of the gases are to be those expected in the emulsion phase of a fluidized bed (corrected for voidage differences)

Similar experiments were performed on propane, over essentially the same operating ranges, and an experiment was performed with ethane, in order to check some assumptions made in the butane cracking model.

The catalyst used in the packed bed studies was a sample taken from the fluidized bed after the catalyst in the fluidized bed was mixed by fluidizing.

The kinetic expressions were incorporated into a few of the simpler fluidized bed models and a sensitivity analysis was performed to obtain an indication of the behaviour to be expected in a fluidized bed.

3. LITERATURE SURVEY

3.1 HYDROGENOLYSIS OF SMALL PARAFFINIC HYDROCARBONS

INTRODUCTION

Studies reported in the literature on the hydrogenolysis of small paraffinic hydrocarbons over a nickel catalyst have been mainly concerned with ethane; relatively little work has been reported for propane; and only one study has been made with butane. Moreover this work of Anderson and Baker(A-1) on butane, was carried out at low pressure.

ACTIVATION ENERGY

A summary of the studies reported to date is given in Table 3.1-1. Recent work has been done by Kikucki and Morita(K3) on the cracking of n-pentane over an 8% nickel on silica gel catalyst; however, only selectivities and no activation energies were reported. From Table 3.1-1. the inverse dependence of rate of cracking of hydrocarbon on hydrogen partial pressure, and the approximate proportionality between rate and hydrocarbon partial pressure should be noted. The data of Anderson and Baker(A1) indicate a decrease in activation energy from ethane to propane; essentially no difference between propane and butane activation energies was observed. The investigations of Tajbl(T3) on the cracking of ethane and propane over a 0.5% ruthenium on γ-alumina catalyst show a decrease in activation energy from 42 kcal./mole for ethane cracking to 35.8 kcal./mole for propane cracking. Kempling and Anderson(K1),

TABLE 3.1-1

HYDROGENOLYSIS OF PARAFINNIC HYDROCARBONS OVEN NICKEL CATALYST

	AUTHORS	TYPE OF CATALYST	TEMPERATURE °C.	$P_{H.C.}^{m}$ m =	$P_{H_2}^{n}$ n =
ETHANE	Anderson, Baker (A1) (1963)	Ni. Films	254.-273.		
	Taylor, Sinfelt, Yates (T1) (1965)	Ni. on 1.% Silica 5.% Gel 10.% (Impreg.)	287. 218. 177.	.8 .6 1.0	-1.1 -1.8 -2.2
	Yates, Taylor, Sinfelt (Y2) (1964)	10.% Ni. on Kieselguhr	187.-227.	1.0	-2.0
	Morikawa, Benedict, Taylor (M1) (1936)	15.% Ni. on Kieselguhr	172.-184.		-2.5
	Kemball, Taylor (K2) (1948)	15.% Ni. on Kieselguhr	182.	0.7	-1.2
	Tajbl (T3)	58.% Ni. on Kieselguhr	182.	0.7	-1.2
PROPANE	Shepard (S1) (1969)	Co-precipt'd. 75. Wt. % Ni. on Alumina	200.-350.	1.0	-2.0
	Anderson, Baker (A1) (1963)	Ni. Film	217.-267.		
	Morikawa, Trenner, Taylor (M2) (1937)	15.% Ni. on Kieselguhr	138.-172.	.92	-2.6
n-BUTANE	Anderson, Baker (A1) (1963)	Ni. Film	184.-209.		

TABLE 3.1-1 CONT'D.

	AUTHORS	ΔE kcal./mole ACTIVATION ENERGY	OPERATING H_2/H.C. RATIO	OP'G. PRESS.	CONVERSION RANGE
ETHANE	Anderson, Baker (1963)	58.	12.	50. Torr.	<10.%
	Taylor, Sinfelt, Yates (1965)	28.7 38.2 40.6	3.-10.	Atm.	<1.%
	Yates, Taylor, Sinfelt (1964)	40.	3.-10.	Atm.	<.5%
	Morikawa, Benedict, Taylor (1936)	43.	.5-1.1	1 Atm.	Up to 100.%
	Kemball, Taylor (1948)	52.	>1.		
		40.	<1.		
	Tajbl	46.4	1.1-15.		1.-27.%
PROPANE	Shepard (1969)	50.	~7.		$\leq$1.%
	Anderson, Baker (1963)	31.	~12.	50. Torr.	<10.%
	Morikawa, Trenner, Taylor (1937)	34.			
n-BUTANE	Anderson, Baker (1963)	34.		50. Torr.	

however, working with the same type of catalyst and flow reactor reported an activation energy of 48.1 kcal./mole for the hydrogenolysis of butane. The activation energy as reported in the literature seems to depend on the state of the catalyst (arising out of the techniques used in its formation and/or pretreatment) and the experimental conditions under which the reaction was studied. Working with propane, Shepard(S1) found that by decreasing the hydrogen partial pressure by one half and making up the difference in total pressure with nitrogen diluent, the activation energy was reduced by 7 to 8 kcal./mole. Kemball and Taylor(K2) found a 12 kcal./mole decrease in activation energy when changing the hydrogen to ethane molar feed ratio from greater than one to less than one.

Activation energy also seems to depend upon the state of dispersion of the nickel on the catalyst support. Taylor, Sinfelt and Yates(T1) found that upon increasing the nickel surface area from 0.7 to 13.6 m.^{2}/(gm. catalyst) by increasing the weight percent nickel from 1% to 10%, the activation energy for the cracking of ethane increased from 28.7 to 40.0 kcal./mole. Shepard(S1), however, did not observe an increase in activation energy, although he was able to increase the nickel surface area from 5. to 56.m.^{2}/(gm. catalyst). The catalyst used was a 75 percent nickel on alumina (coprecipitated) catalyst, obtained by varying the reducing temperature from 340. to 1160°C. For one highly sintered* catalyst, in which the surface area of active nickel had

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* Sintering process - decrease of surface area of active metal by agglomeration of the metal crystallites of the catalyst particles.

decreased tremendously to 2. $m.^2$/gm. catalyst, he observed an activation energy of 34. kcal./mole as compared with the average value of 50. kcal./mole he observed with the rest of the catalyst samples.

CATALYST ACTIVITY

Catalyst activity has been defined as the number of molecules or moles reacting per catalyst site per unit of time(S5). The activity with reference to a standard activity is, therefore, the ratio of rate constants under similar reacting conditions. The specific activity is usually taken with respect to the surface area of active metal catalyst exposed to the reacting products.

Schuit and Van Reijen performed various investigations of nickel on silica catalysts. They report that the percentage reduction of the catalyst is a function of the reducing temperature for various concentrations of nickel and that the activation energy for reduction of nickel oxide is approximately 20. kcal./mole. For the sintering process occurring simultaneously, this activation energy increased to 44. kcal./mole, the activation energy depending upon the size range of the nickel crystals on the surface.

Shepard(S1) found that the activity of most of his catalysts varied directly with metal surface areas as measured by hydrogen chemisorption. He could not detect any trend of activity with maximum observable crystallite size. Sinfelt(S4), on varying the nickel crystallite size from 29 to 88 Angstrom units by varying the pretreatment temperature from 370.° to 700.°C., found that the specific activity of his nickel on silica catalyst decreased from 1070 to 56 for the cracking of ethane. Yates(Y1), in studying the cracking of ethane over a rhodium on silica catalyst, found a maximum catalyst activity with increasing state of dispersion (i.e. smaller crystallite size).

RATE EXPRESSIONS

There are two commonly used approaches to formulate mathematical expressions to describe the rate of reaction in hydrogenolysis of short-chain paraffinic hydrocarbons: (i) that proposed by Hougen and Watson(H4) where all the possible steps are described by appropriate rate expressions and then the whole matrix of equations combined to give an overall rate expression, (the matrix of equations made up of Hougen and Watson-type equations for the cracking of butane is given in Appendix I.2. (ii) that suggested by Cimino, Boudart and Taylor(C1) in which equilibrium is assumed between the gaseous and adsorbed hydrocarbon and the cracking of the adsorped hydrocarbon is the rate determining step (the kinetic equations developed by this approach is given in Appendix I.1).

The latter type of analysis leads to the general relationship:

$$r = k \, P_{H.C.}{}^{m} \, P_{H_2}{}^{n}$$

where r = rate of cracking of the hydrocarbon

$P_{H.C.}$ and P_{H_2} are partial pressures of the hydrocarbon and hydrogen respectively.

k = Arrhenius rate constant

ΔE = activation energy

m and n are constants

3.2 PACKED BED REACTORS

An excellent review article by Hlavaček (H8) describes the various phenomena occurring in fixed bed reactors and under what conditions they are important in determining the reactor performance. Hlavaček gives the mass and energy balance equations for this type of reactor; he discusses heat and mass transfer within and outside porous catalyst particles; he discusses axial and radial mixing; he discusses heat transfer considerations in the packed bed reactor, and finally he reviews numerical methods of solving the mass and energy balance equations and describes methods of estimating kinetic parameters in the packed bed. Another excellent review article is given by Beek (B16).

Petersen (P4) gives a summary of experimental work performed to study diffusion of the flowing component and develops expressions to consider the importance of the axial mixing of a component involved in first order reaction.

The effect of mass transfer and heat transfer rates, in and around the catalyst particles, on the overall rate controlling step in the reaction is discussed by Carberry (C3) and Satterfield and Sherwood. (S7). Satterfield and Sherwood give j_D and j_H curves which enable the calculation of mass and heat transfer coefficients around the catalyst particles in a packed bed.

Since the up-to-date comprehensive reviews mentioned above are readily available, there is little need to repeat the details here.

The phenomena which need to be considered in the present case are discussed in Section 6.1.3.

3.3 MODEL BUILDING AND PARAMETER ESTIMATION

The state of the art in studying rates of catalyzed hetergenous chemical reactions is such that the true mechanistic rate expression is virtually impossible to find. Because of the uncertainty and usually complicated forms of the proposed models, correct statistical analysis of the data become essential.

Model building includes; (i) proposing a mechanism, (ii) evaluating the mechanism in light of experimental data and (iii) rejecting certain models according to some criterion. Insights into possible forms of rate expressions arising from various mechanisms that can be suggested have been given by Hougen and Watson(H4), Cimino Boudart and Taylor(C1), and Kittrell and Mezaki(K9). Methods for attempting to determine whether a proposed mechanism actually represents the physical behaviour have been discussed by various authors(K8, K10, Y3, B10, B11, M7).

A proposed model may be modified during experimentation. Box and Hunter(B6) and Hunter and Mezaki(H2) determine whether a model should be modified by treating the parameter estimates as observations after a certain number of experiments. If the model is correct, these parameter estimates should have little interaction and should remain constant with experimental operating conditions and the number of experiments performed.

In catalyzed kinetics, the trend has been to develop models that have fundamental significance, but contain simplifications so that all detailed paths of a reaction need not be described mathematically.

Usually the models developed are still quite complicated and non-linear* in the parameters. Reviews of methods of estimating these parameters for a single response are given by Bard and Lapidus(B7), Behnken(B5), and Bard(B13) and for multi-response cases by Box and Draper(B8). A good comparison of the several methods available is given by Kittrell, Mezaki and Watson(K11).

Depending upon the non-linearity of the model with respect to the parameters, the confidence intervals of the parameter estimates may be obtained in several ways. These are discussed by Beale(B9), Hartly(H3), and Draper and Smith(D5).

A fuller development of techniques used in this thesis work to estimate parameters and obtain confidence intervals for these parameters, along with pertinent references is given in section 6.2.1.

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* The derivative of the function with respect to the parameters is independent of the parameters.

4. EXPERIMENTAL STUDY

A description of the experimental program will be given in three sections: experimental apparatus, experimental procedure and experimental designs.

4.1 EXPERIMENTAL APPARATUS

To study the hydrocracking of butane and propane, a flow system, shown in Figure 4.1-1, operating essentially at atmospheric pressure was used. Reaction was carried out by a down flow of reactants, at a desired temperature, through a packed bed containing 10.% nickel on silica gel catalyst. All the lines were ¼ in. O.D. copper tubing, except for the reactor and preheater lines which were stainless steel. The analysis of the reactor effluent was carried out by gas chromatography; on-line sampling of reactor effluent was carried out by means of a gas sampling valve.

The experimental system will be discussed under three headings covering the feed, reactor and analytical systems in turn.

4.1.1 FEED SYSTEM

A schematic of the feed system is given in Figure 4.1-2. The butane, propane and hydrogen feed gases were obtained from Matheson Co. By chromatographic analysis, the butane was found to contain approximately 0.4% iso- butane impurity. Ultra-pure grade hydrogen was used and no impurities could be detected by chromatography.

The flowrates of the reactant gases, fed from high pressure

FIGURE 4.1-1 SCHEMATIC OF REACTOR APPARATUS

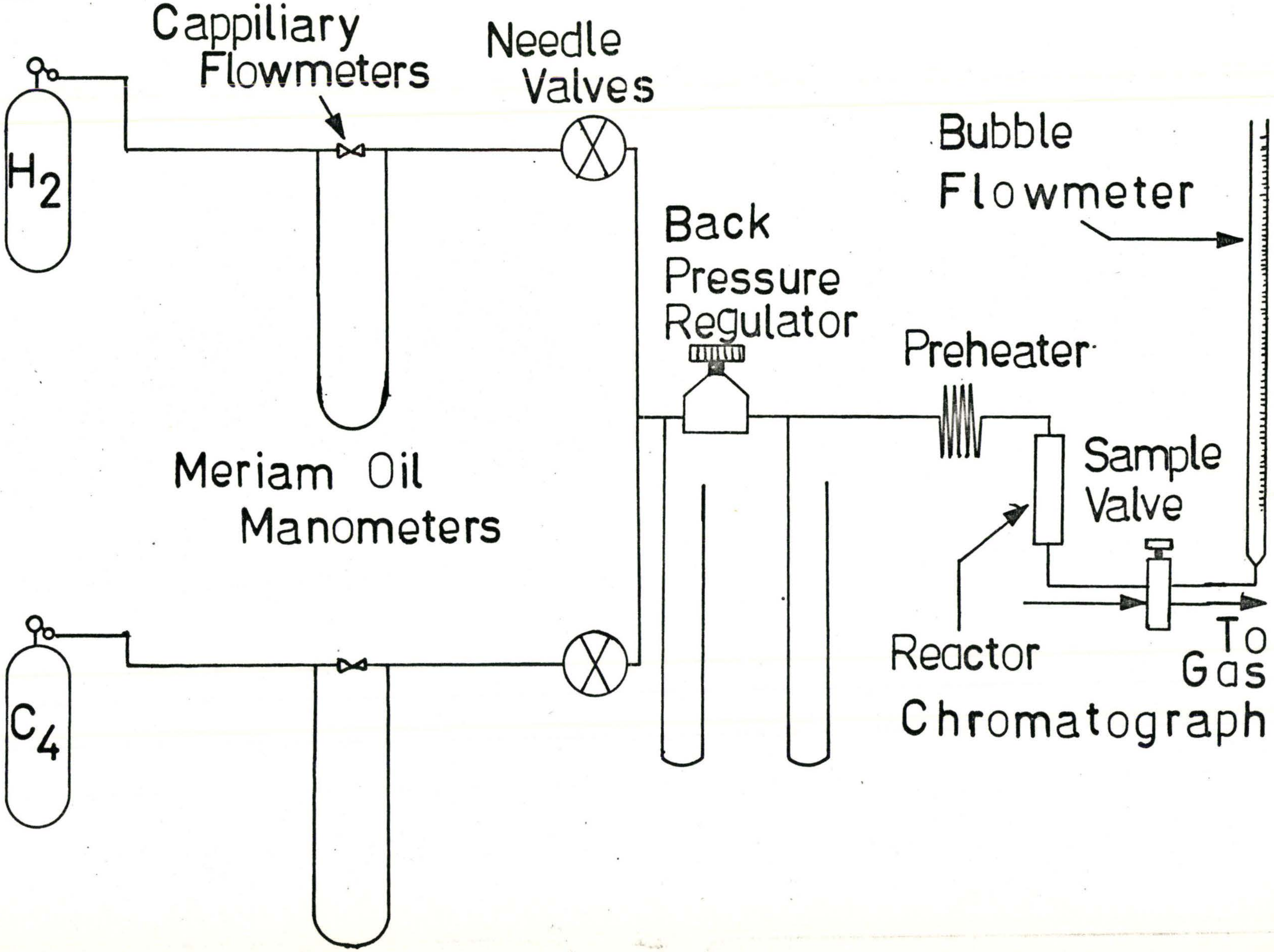
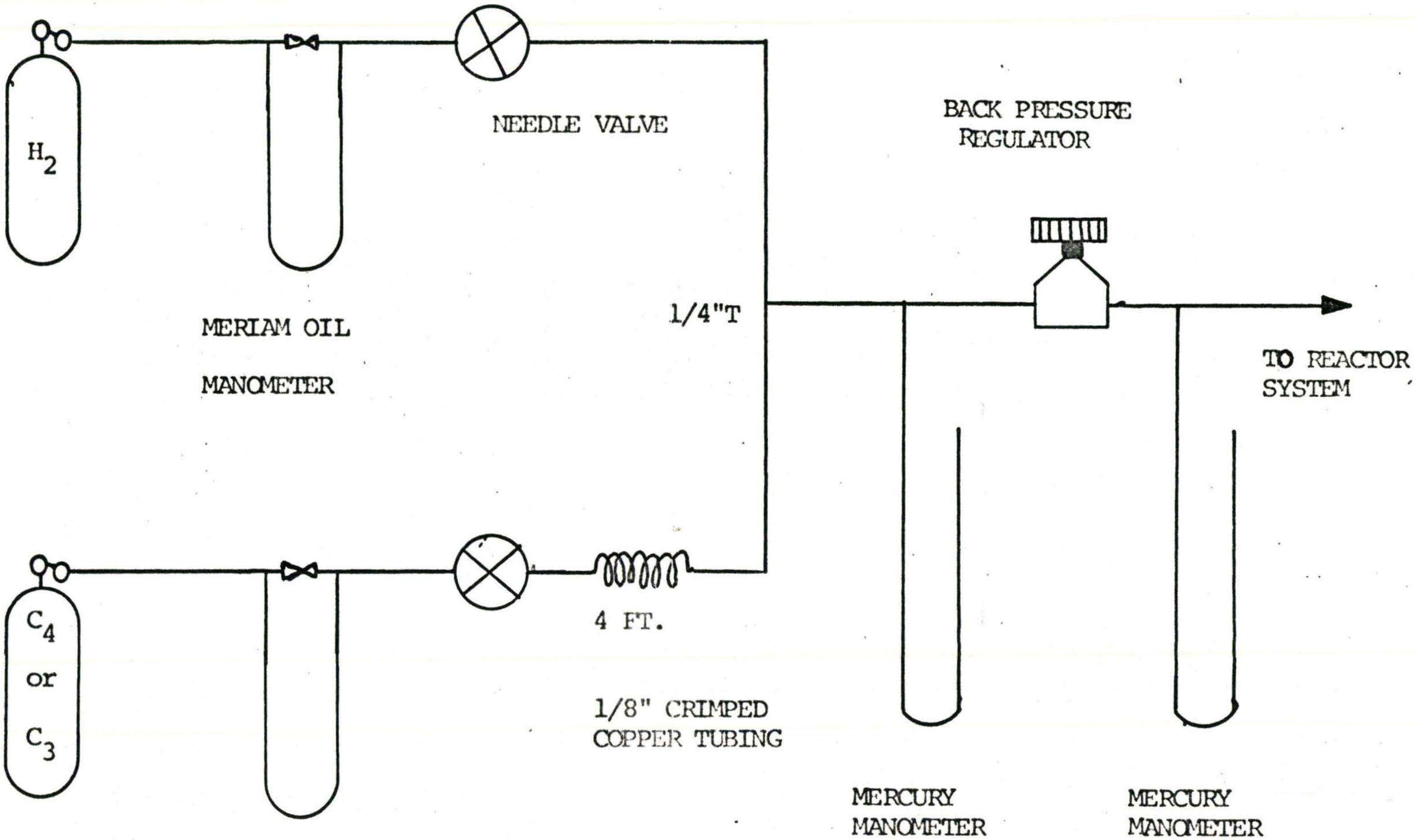


FIGURE 4.1-2

SCHEMATIC OF FEED SYSTEM



cylinders, were controlled by needle valves and measured by "capilliary" flowmeters which consisted of crimped portions of ¼ in. copper tubing. The pressure drops across the constrictions were measured with meriam oil (S.G. = 1.1) manometers. Calibration procedures and graphs are given in Appendix E.2. The flowmeters were isolated from each other by 3. ft. of 1/8 in. copper tubing and from the stirrer motor vibrations by flexible tygon tubing (see Appendix E.2).

The reactant gases were then mixed in a ¼ in. tee before being fed to the reactor.

The total pressure in the feed system was held constant at 1210. mm. Hg., as measured by a mercury manometer, with a Fairchild-Hiller model 10BP back-pressure regulator.

A mercury manometer was located immediately downstream of the back-pressure regulator; it was used to monitor the pressure drop across the reactor.

4.1.2 REACTOR SYSTEM

The reactor system consisted of a constant temperature bath, a preheater coil and the reactor proper; the equipment will be described in this order. A schematic of the reactor system is given in Figure 4.1-3.

CONSTANT TEMPERATURE BATH

The reactor and preheater were placed in a bath of "Hitec" heat transfer salt (E.I. Dupont Corp.).* Heat was supplied by two 1500 watt

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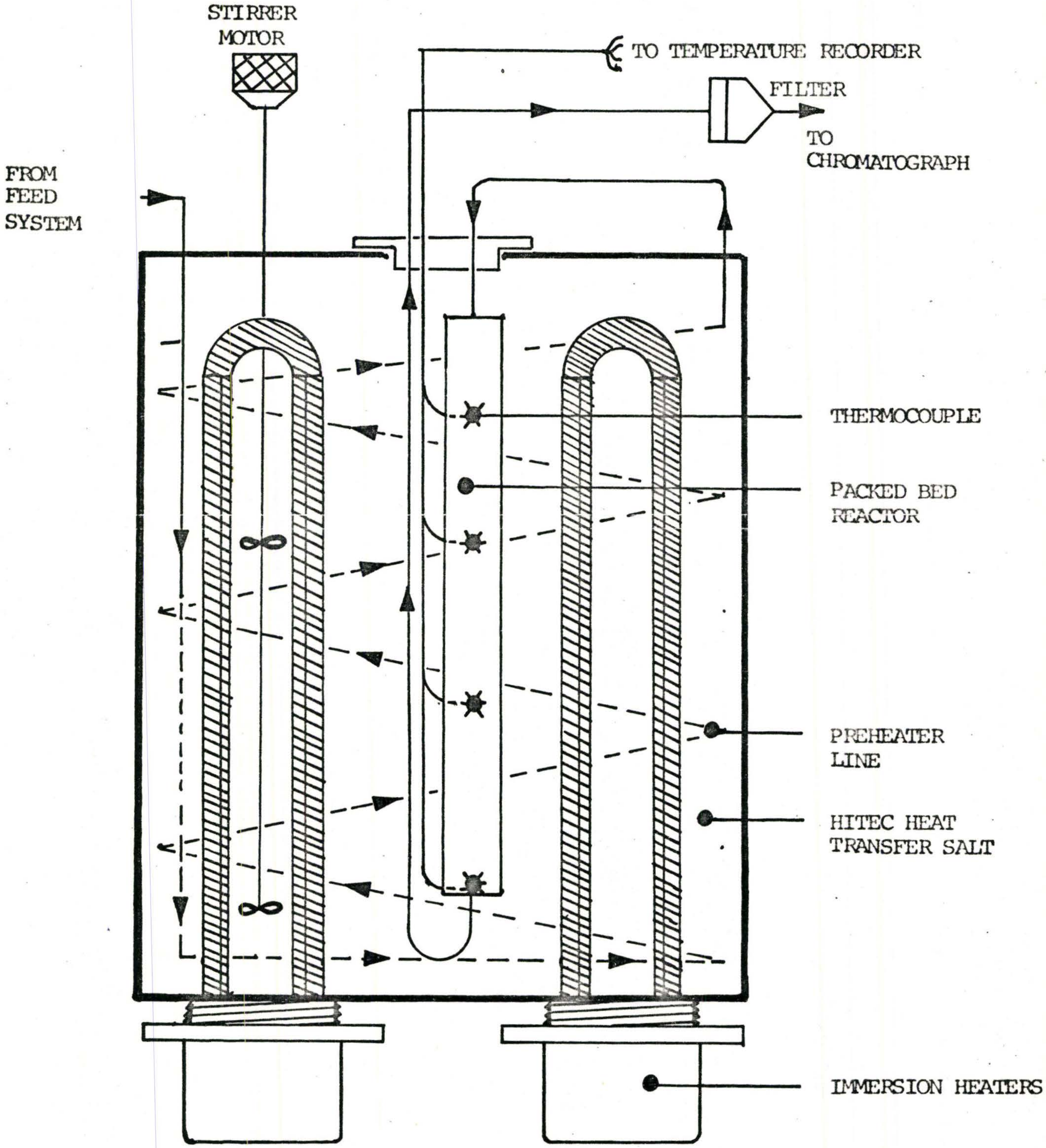
* "Hitec" salt is a eutectic mixture of potassium nitrite, sodium nitrite and sodium nitrate. It has a melting point of 275°F. and may be used safely without decomposition to 1100°F.

FIGURE 4.1-3

SCHEMATIC OF REACTOR SYSTEM



Chromalox immersion-type heaters and this heat input was controlled by a Variac autotransformer. A two-blade stirrer and variable speed motor were used to produce uniform temperature throughout the bath. The position of the stirrer blades and the motor speed was chosen so as to produce uniform thermocouple readings along the length of the reactor, with no reaction in the reactor.

PREHEATER COILS

The preheater coils consisted of approximately 4. ft. of ¼ in. diameter stainless steel tubing immersed in the constant temperature bath.

REACTOR

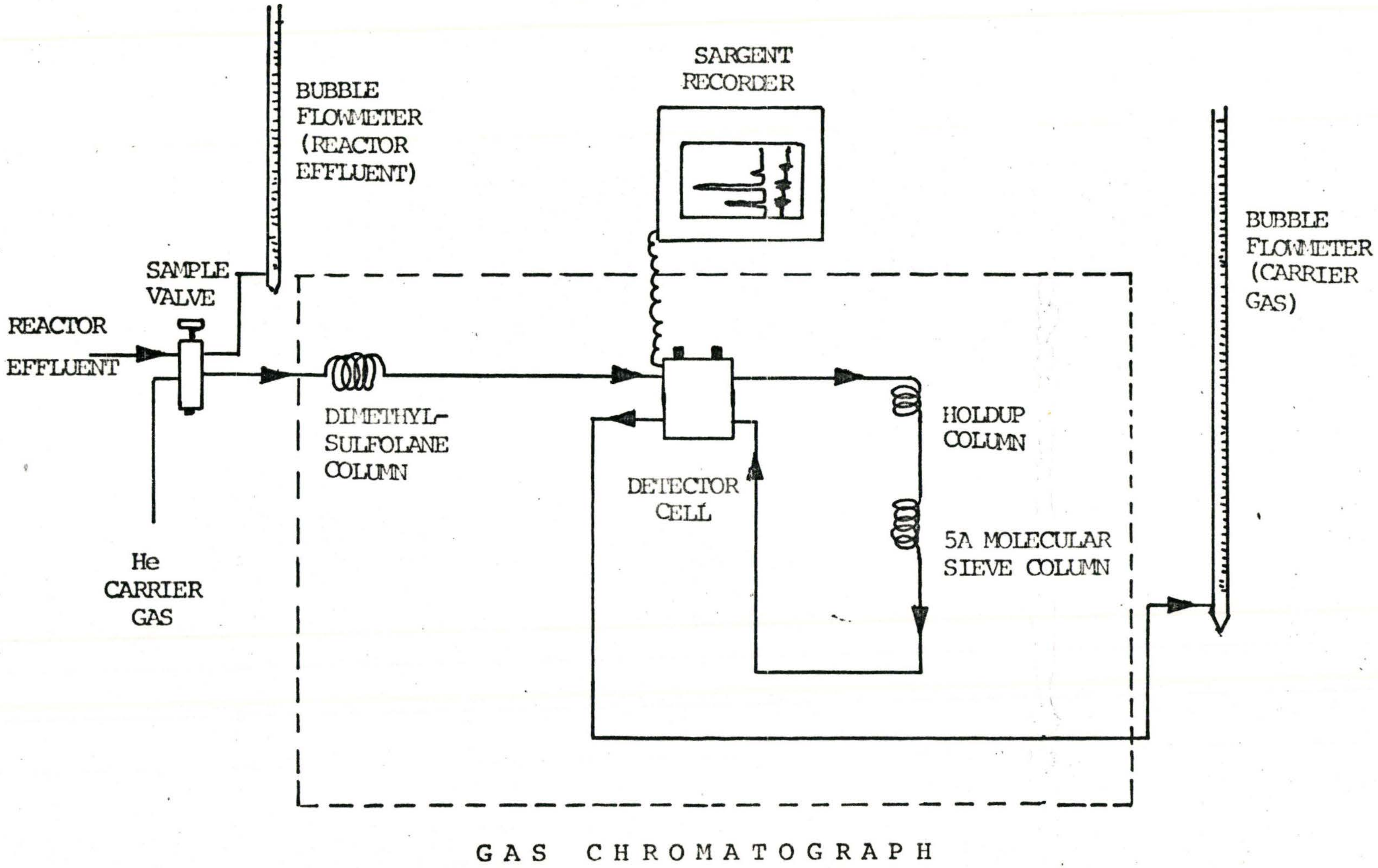
The reactor was 0.276 in. I.D., 3/8 in. O.D. by 12. in. long stainless steel tube, held in a vertical attitude. The reactor contained a charge of 5.650± .001 gm. of 10.% nickel on silica-gel catalyst to a depth of 25.0± 0.4 cm. The catalyst was supported on a 200 mesh stainless steel screen clamped to the bottom of the reactor with a Swagelok fitting.

Four chromel-alumel thermocouples were positioned in the centre of the reactor to measure axial temperature gradients. The top thermocouple was located approximately 1 cm. below the top of the catalyst bed and the bottom thermocouple was just below the 200 mesh support screen. The remaining two thermocouples were spaced evenly between these two.

The thermocouple e.m.f. (cold junction in ice water) was recorded with Honeywell recording potentiometer. Thermocouple calibrations

FIGURE 4.1-4

SCHEMATIC OF ANALYTICAL SYSTEM



were obtained from the Chemical Handbook[(W3)]. They were not calibrated, except that all read the same temperature in the absence of reaction.

4.1.3 ANALYTICAL SYSTEM

A schematic of the analytical system is given in Figure 4.1-4. The products of the cracking reactions were analyzed by a Beckman GC2A gas chromatograph equiped with a Solex constant voltage transformer on the input. A 200. ma. filament current and a 35. ml./min. helium carrier gas flowrate were used; the columns were operated at room temperature. Prior to use, the thermal conductivity cell was washed in a chromic acid solution and rinsed with ethyl alcohol and acetone. All cell inlet parts were blocked with glass wool plugs to prevent entry of packing from any of the columns.

Samples were introduced into the chromatograph columns with an on-line, Varian plunger-type, sample valve. Two columns in series were used to effect the required separation. All of the products, except for methane and hydrogen, were separated in a 24. ft., ¼ in. O.D. copper tube packed with 20.% dimethyl-sulfolane on 80./100. mesh P acid washed chromasorb. The products from this first separation were fed to one side of the detector cell and then held up in a 40. ft. delay column of ¼ in. O. D. copper tubing until all the sample had passed through the first column. The final separation of methane and hydrogen was effected by a 3. ft. column of 60./80. mesh 5A molecular sieves. All other components, except these two have a semi-infinite retention time on the sieves and are permanently held up there. This final separation, consisting only of methane and hydrogen, is then passed through the other side of the detector block.

A Sargent 1. mv. recording potentiometer with a rotating ball mechanical integrator was used to record the chromatograph signals.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 START UP

The catalyst preparation is given in Appendix D. A charge of 5.650 ± .001 gm. of catalyst was placed in the reactor and the tube was vibrated for three minutes with a hand vibrator. Separate experiments in which the catalyst was put into glass tubes with about the same diameter showed that no further packing of catalyst occurred after this time.

The height of the catalyst bed was measured by knowing the location of the support screen and by passing a wire probe with a horizontal loop at the lower end down into the top of the reactor tube, until the top of catalyst bed was detected. By performing separate experiments on glass tubes, it was determined that the observed bed height of 25.0 cms. could be measured to at least ±0.4 cm.

4.2.2 STEADY-STATE OPERATION

This section explains the step-by-step procedure followed in operating the reactor according to the experimental designs and obtaining the desired data.

The required flowrates of the feed gases were adjusted so as to always ensure a hydrogen-to-hydrocarbon feed ratio greater than 4:1; this was done to minimize, if not prevent, carbon deposition on the catalyst Atmospheric pressure was checked periodically and the back pressure regulator was adjusted to maintain a constant pressure of 1210. ± 2. mm.

Hg. in the feed system. After setting the hydrogen and butane flows to the desired values, the pressure drops (as indicated by the manometers) across the flowmeters were recorded. The temperature of the reactor system was controlled to any desired value by adjusting the voltage across the salt-bath heaters. Temperatures were recorded continuously on a Honeywell recording potentiometer. The pressure drop across the reactor was measured on the mercury manometer. The filament current and helium carrier-gas flowrate were checked periodically. The total gas flowrate through the reactor was measured with a bubble flowmeter and recorded. At least five minutes were allowed for the system to reach steady state after the desired flowrates were set and the desired temperature was reached. A sample of the reactor effluent was then taken by means of the gas sample valve and was analyzed with the gas chromatograph. The chromatogram was recorded on a Sargent recorder equipped with a mechanical integrator. Attenuations of the chromatogram were always chosen so as to keep the peak height within a range that may be recorded by the mechanical integrator. The areas under the chromatogram peaks were then converted to partial pressures by means of calibration factors given in Appendix E.2. Mole fraction compositions of all the components were then calculated.

4.3 EXPERIMENTAL DESIGNS

Two experimental studies were carried out: the hydrogenolysis (cracking) of butane and the hydrogenolysis of propane.

Two factors were important when considering the experimental program at the outset. Firstly, little was known for this reaction system about the effects of the independent variables (temperature, flowrate and feed composition) on the conversion of butane and selectivities of the products; hence these effects had to be studied over a wide range of the independent variables. Secondly, since a mechanistic model for the reaction was not conceived at the outset, the independent variables were chosed according to an experimental design(D6) so that interaction effects caused by variables could be reduced. Moreover, these data would be very efficient in providing parameter estimates for any models that would be conceived. This experimental design would also provide a good starting point for any planned program for model discrimination and for parameter estimation, if needed.

Propane cracking experiments were performed to provide a check on any assumptions relating to propane behaviour (e.g. adsorption or desorption of propane) when formulating a butane cracking model.

For the butane cracking experiments a blocked factorial design was chosen with three levels of temperature, two levels of hydrogen-to-butane feed ratio, and two levels of feed flowrate. The temperature levels were chosen to produce a wide range of butane conversion as determined by preliminary experiments. The minimum feed ratio was

TABLE 4.3-1

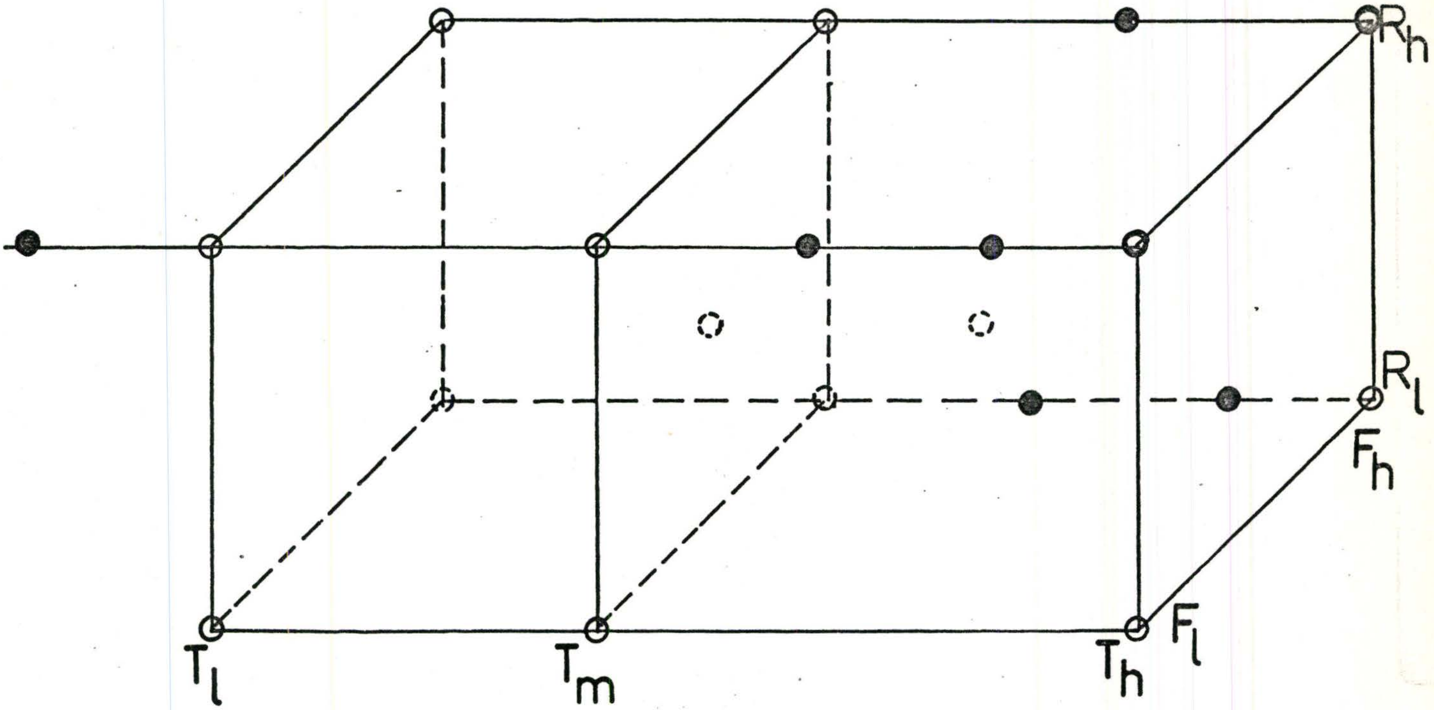
EXPERIMENTAL DESIGN LEVELS FOR BUTANE AND PROPANE CRACKING EXPERIMENTS

INDEPENDENT VARIABLE	LEVEL	LEVEL VALUE	
		BUTANE EXPERIMENTS	PROPANE EXPERIMENTS
TEMPERATURE	LOW	246.*	258.
(°C)	MID.	258.	270.
	HIGH	282.	
MOLAR	LOW	4.	4.
FEED RATIO	MID.	6.5	6.5
(H_2 : HYDROCARBON)	HIGH	9.	9.
FEED FLOWRATE	LOW	1.0	1.0
(CM.^{3}/SEC.)	MID.	1.4	1.4
	HIGH	1.8	1.8

* One low temperature run was performed at 240.°C. This was run No. 5.

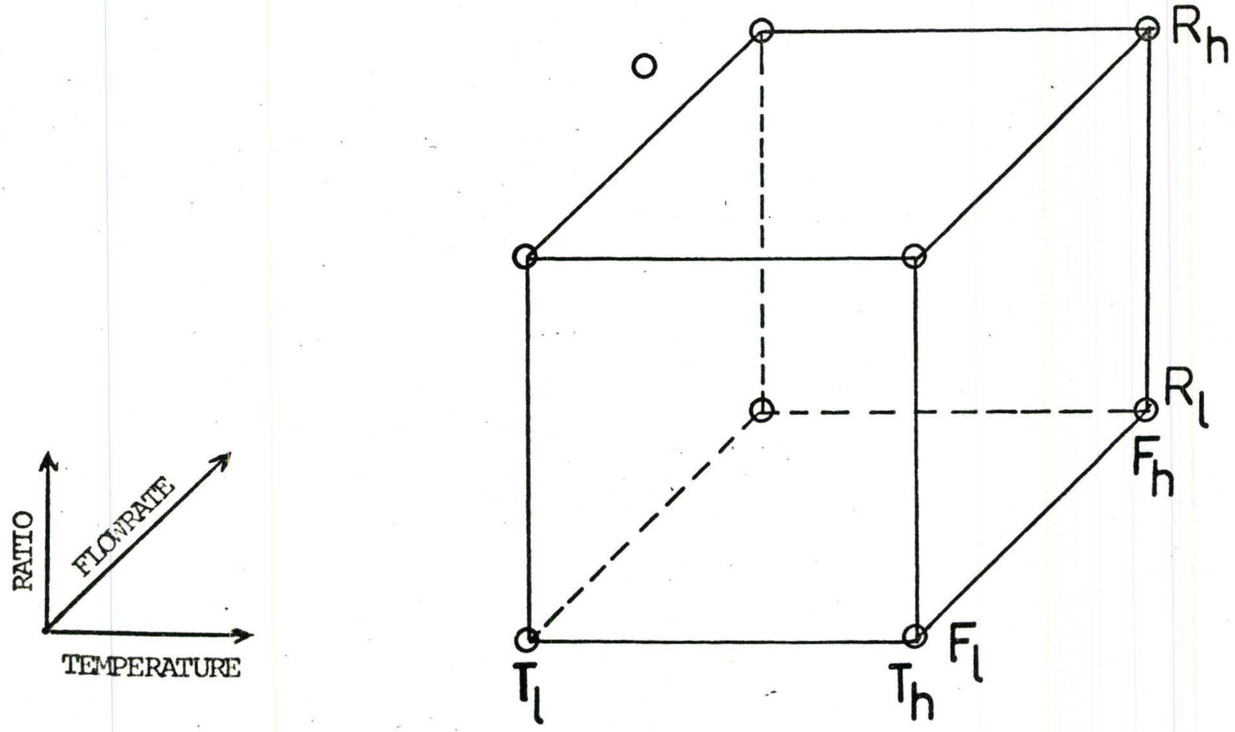
FIGURE 4.3-1

BUTANE CRACKING EXPERIMENTAL DESIGN



PROPANE DESIGN

(SAME SCALE AS BUTANE DESIGN)



○ DESIGN POINTS
● ADDITIONAL RUNS

chosen so as always to have an excess of hydrogen, even if complete conversion of butane to methane occurred. The maximum ratio was set arbitrarily at the maximum to be studied in the fluidized bed reactor. An attempt was made to set the feed superficial velocity range so as to include the superficial velocity of the emulsion phase of the fluidized bed reactor, taking into account the difference in voidage between this phase and the packed bed reactor. At least two replicates were performed at each experimental level.

A centre point was chosen at the middle of the experimental design grid and this "centre-point experiment" was performed before and after each experimental design point. This enabled any changes in catalyst activity to be followed.

For the propane experiments, a 2^3 factorial design (D6) was chosen (three variables, two levels of each variable). Again centre-point replicates were taken throughout experiment. Since it appeared that catalyst activity had stabilized, these centre-point replicates were not taken as frequently as in the butane experiments.

Table 4.3-1 gives the values of the independent variables at their respective levels for the butane and propane experiments. Schematic diagrams of the experimental designs are given in Figure 4.3-1.

DISCUSSION OF DESIGNS

These factorial designs may not be the most efficient (i.e. give minimum variance estimates with least experimentation) for any given non-linear model. The design of experiments for precise estimation of parameters in non-linear models was first discussed by Box and Lucas (B3).

According to the Box and Lucas criterion: if the predicted value from a mathematical model is given by

$$\eta_u = f(\underline{x}, \underline{\theta}) \qquad 4.1$$

where $\underline{x}$ is a vector of operating conditions for the u^{th} experiment, $\underline{\theta}$ is a vector of parameters, then the most efficient operating conditions for parameter estimation should be chosen so as to maximize the determinant

$$|F^{*\prime} F^{*}|$$

$$\text{where } F^{*} = \{f^{*}_{ru}\}$$

$$\text{and } f^{*}_{ru} = \left[\frac{\partial f(\underline{x}, \underline{\theta})}{\partial \theta_r}\right]_{\theta = \theta^{*}}$$

for the r^{th} parameter in the u^{th} run, and θ^{*} is a vector of best estimates of $\underline{\theta}$.

Geometrically speaking, the experiment is chosen so as to minimize the volume in parameter space enclosed by a surface which is determined by a confidence region for the parameters. A modification of the design criterion in order to determine some parameters more precisely than others is given by Hunter, Hill and Henson$^{(H1)}$. These papers refer to situations where there is a single response (e.g. conversion). When multi-response systems (e.g. conversion plus product selectivity) are encountered and/or when prior information about parameter values is available then the design criteria suggested by the work of Draper and Hunter$^{(D1, D2, D3)}$ should be used. Box$^{(B4)}$ has shown theoretically that in certain cases, replications of experiments predicted by the Box and Lucas criterion represent the optional design procedure. Mezaki (M3) suggests that, before experimentation, sensitivity analyses should be performed on the design criteria. This sensitivity analysis reflects the ability of the data to produce precise parameter estimates. It also tells the experimenter to which operating variables the design criterion is most sensitive. This is important since it may be found that experimental procedures and/or equipment may not allow the setting of the independent variables precisely enough to improve parameter estimates significantly enough to warrant this type of complicated design. A good review of the design of experiments in nonlinear situations as well as the application of these methods in the estimation of copolymer reactivity ratios is given by Behnken (B5).

5. EXPERIMENTAL RESULTS

All of the primary data obtained from the butane and propane cracking runs are given in Appendix G. Included here are the measured experimental operating conditions for each run performed, the observed mole fraction of all the components in the reactor effluent, the selectivities of these products and the conversions of the feed hydrocarbon.

For the butane cracking experiments, the selectivity of component i is defined as:

$$S_i = \frac{\text{moles of component i produced}}{\text{moles of butane reacted}}$$

Similarly for component i in the propane cracking experiments:

$$S_i = \frac{\text{moles of component i produced}}{\text{moles of propane reacted}}$$

BUTANE CRACKING EXPERIMENTS

The product distributions at the low and middle temperature levels for the butane cracking experiments are given in Figure 5-1.* These distributions are given as plots of the integral selectivity (selectivity after the reaction has been allowed to proceed for a certain time) of methane, ethane and propane as a function of the conversion of butane. There appear to be a separate set of curves for each temperature; no significance test was performed, however.

All of the runs carried out at the high temperature level produced greater than 99.% conversion of butane. The selectivities and operating conditions of these runs are shown in Table 5-1.

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* The spread in these points is due partly to differing hydrogen to butane feed ratios.

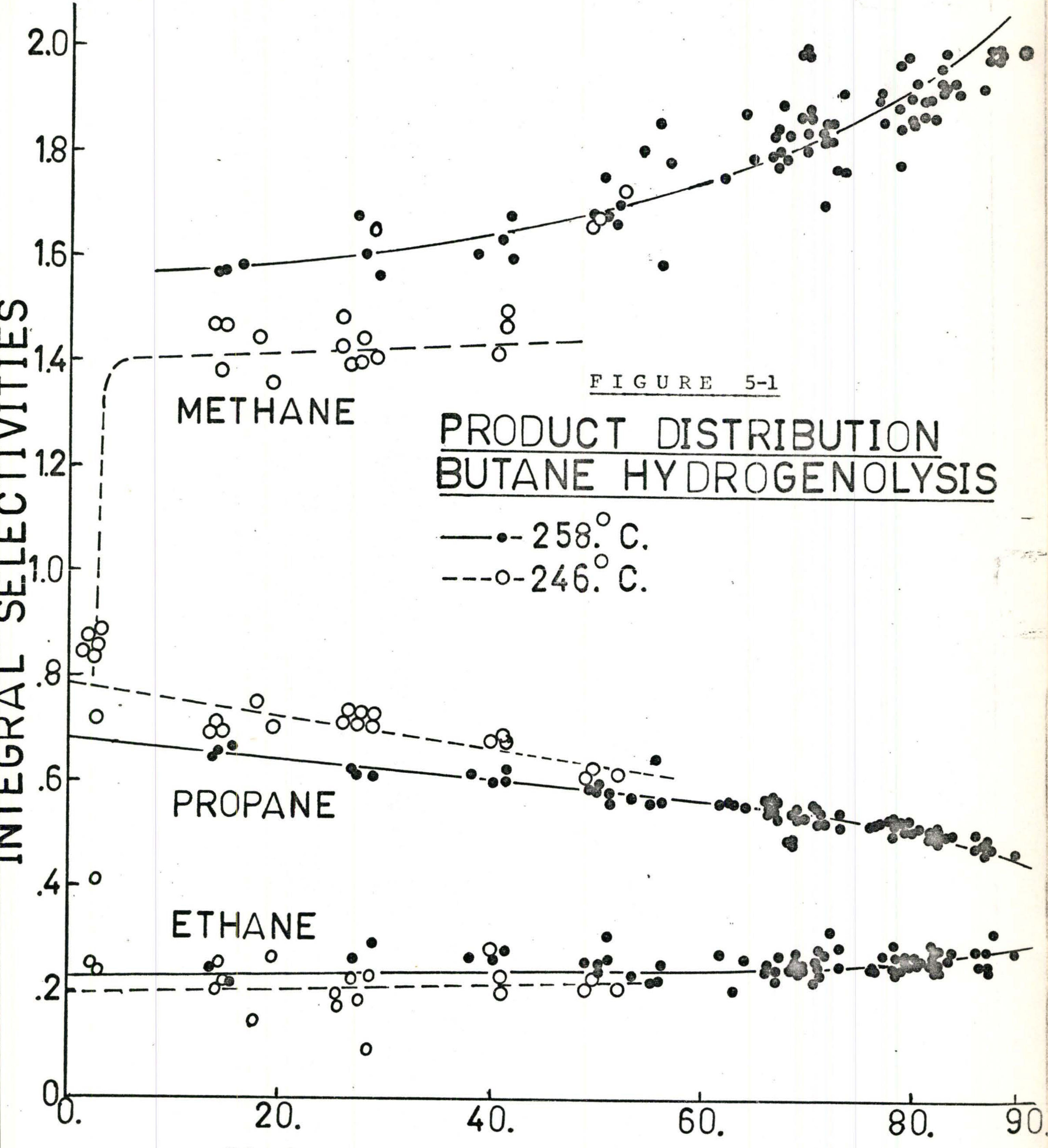


FIGURE 5-1

PRODUCT DISTRIBUTION BUTANE HYDROGENOLYSIS

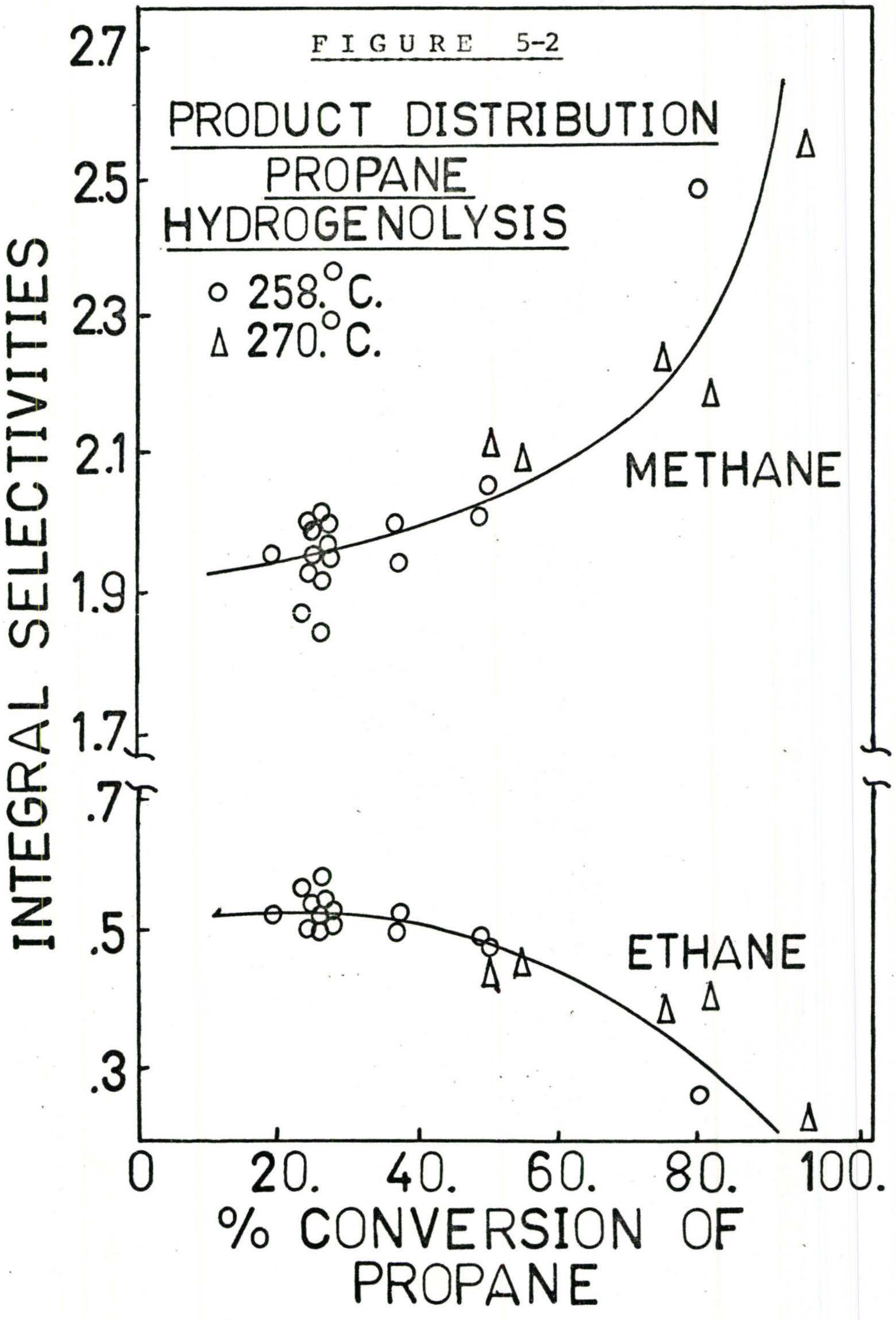


FIGURE 5-2
PRODUCT DISTRIBUTION
PROPANE
HYDROGENOLYSIS
○ 258.°C.
Δ 270.°C.
METHANE
ETHANE
INTEGRAL SELECTIVITIES
2.7
2.5
2.3
2.1
1.9
1.7
.7
.5
.3
0
20.
40.
60.
80.
100.
% CONVERSION OF PROPANE

FIGURE 5-3

EXPERIMENTAL RESULTS FOR PROPANE CRACKING

EXPERIMENTS-CONVERSION OF PROPANE

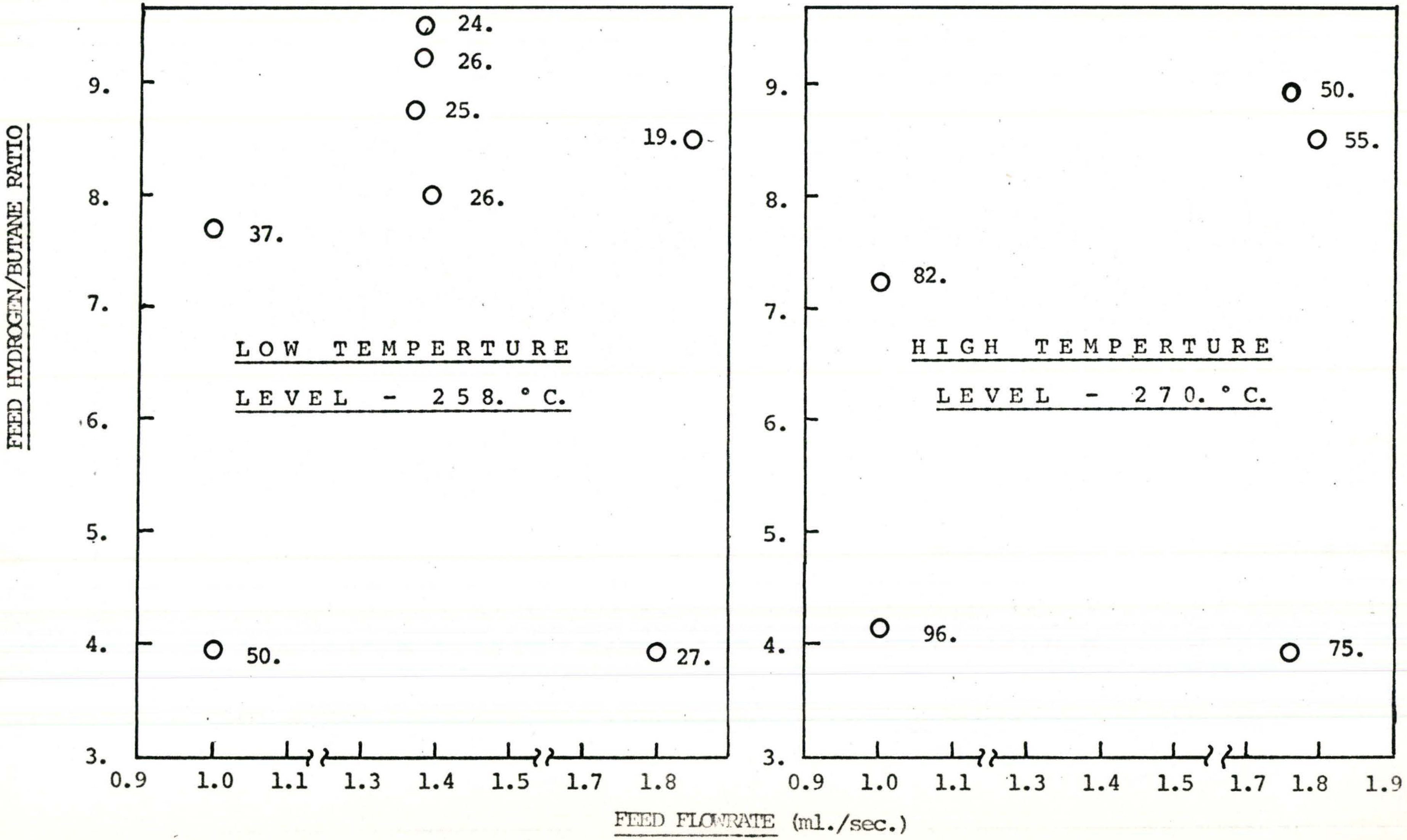


FIGURE 5-4

PLOT OF ALL MID-POINT RUNS IN THE BUTANE EXPERIMENTS

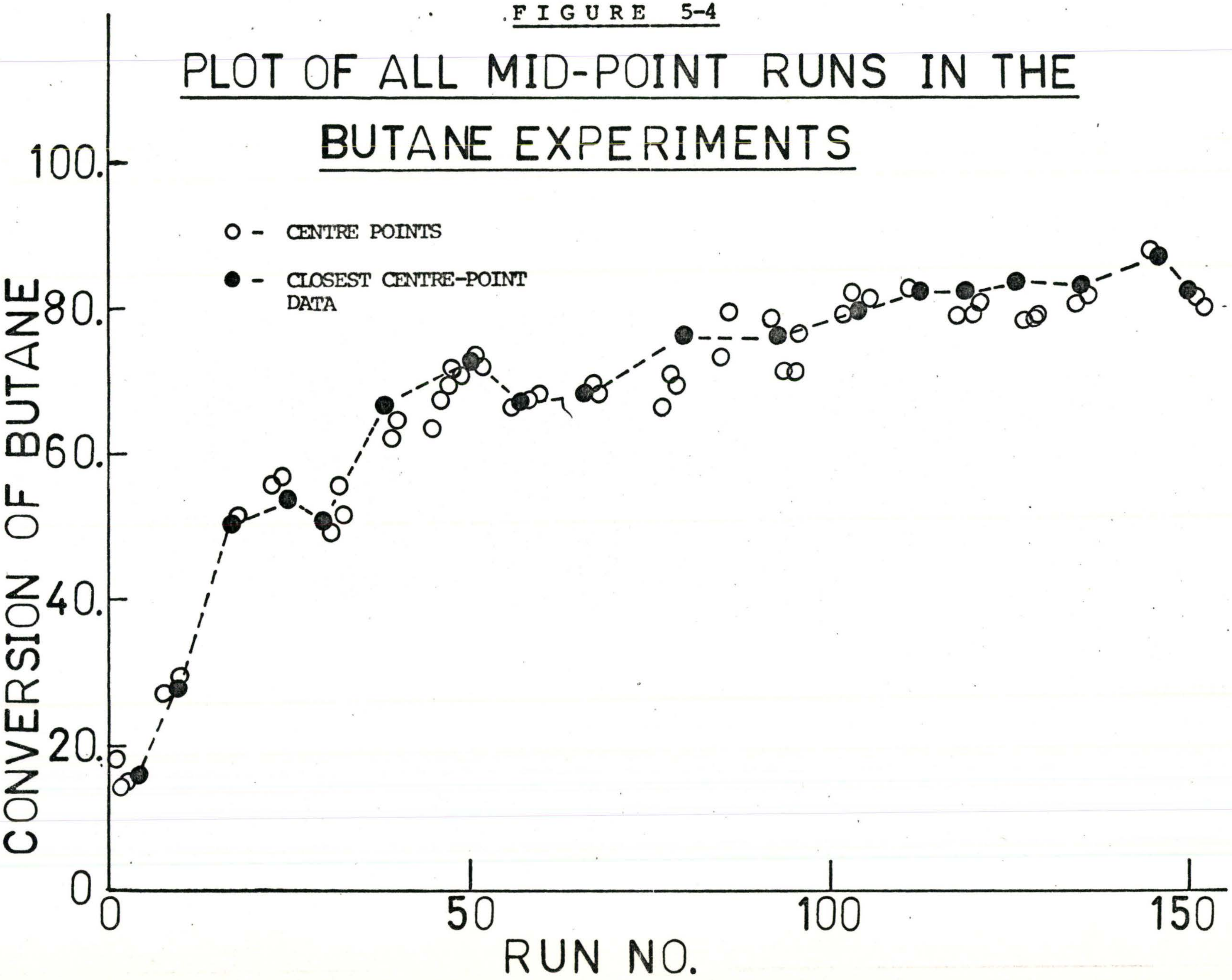


FIGURE 5-5

PLOT OF MID-POINT RUNS IN THE PROPANE EXPERIMENTS

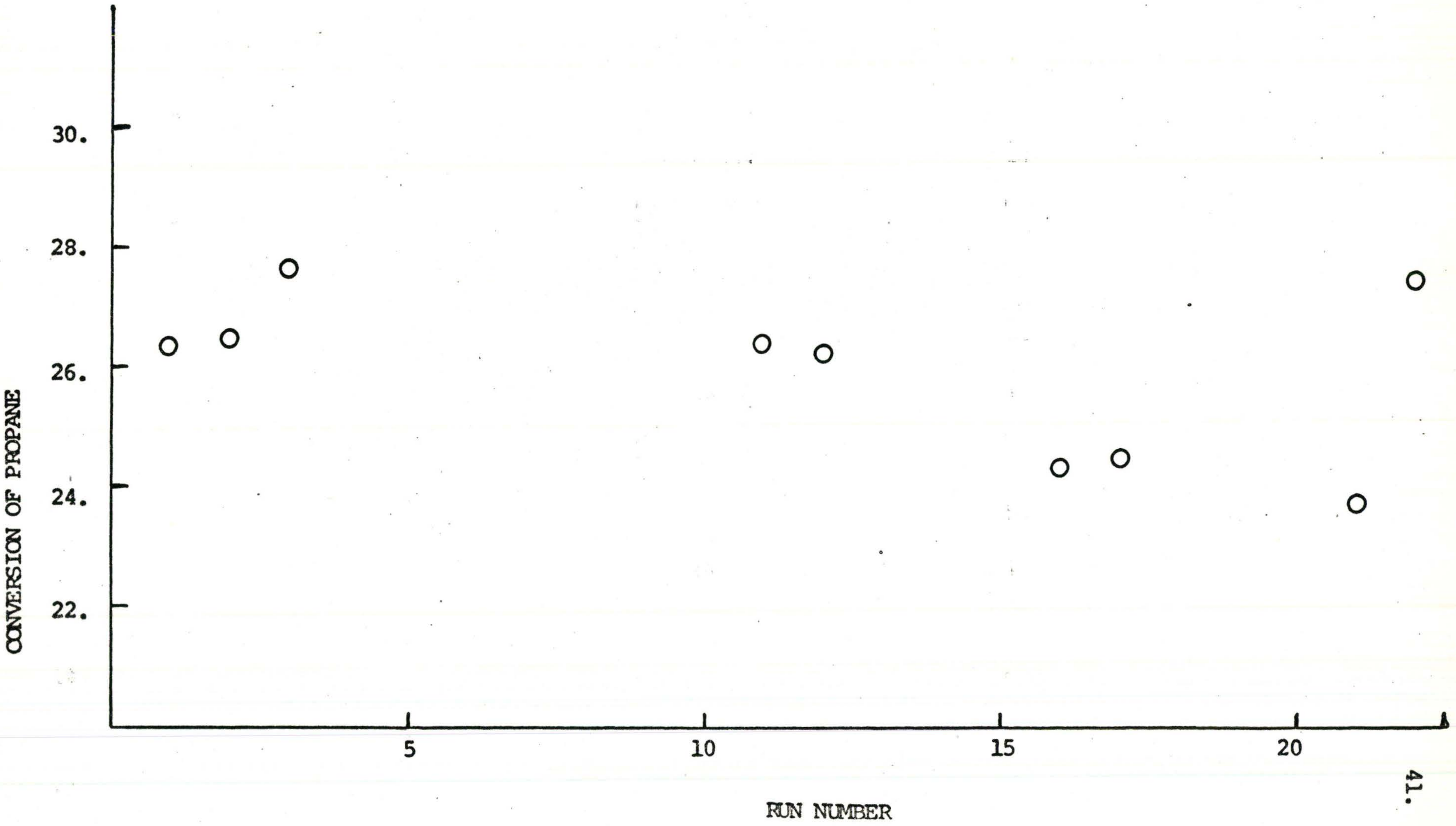


TABLE 5-1

PRODUCT DISTRIBUTIONS OF BUTANE CRACKING EXPERIMENTS HIGH CONVERSION RUNS(APPROXIMATELY 100. PERCENT)

AVERAGE REACTOR TEMPERATURE DEG.C.	FEED RATIO H2/C4	FEED FLOWRATE ML./SEC.	SELECTIVITIES MOLES PRODUCED PER C4 REACTED			CONVERSION OF BUTANE PERCENT	RUN NO.
			METHANE	ETHANE	PROPANE		
266.	8.08	1.03	2.69	.347	.204	99.81	75
266.	9.75	1.01	2.55	.345	.253	99.85	76
267.	3.80	1.73	3.78	.109	.000	100.0	99
270.	6.06	1.43	3.20	.343	.038	99.83	137
270.	5.99	1.41	3.27	.309	.038	99.87	139
270.	5.98	1.42	3.25	.318	.039	99.86	140
270.	6.36	1.41	3.15	.335	.059	99.77	141
270.	6.09	1.42	3.23	.312	.047	99.85	142
270.	8.34	1.79	2.65	.352	.213	100.0	116
270.	9.17	1.79	2.69	.300	.238	99.75	117
275.	3.80	1.75	3.82	.089	.000	100.0	98
275.	8.34	1.03	3.39	.267	.026	99.90	73
274.	3.75	1.00	3.77	.117	.000	100.0	35
281.	3.80	1.77	3.93	.035	.000	100.0	97
283.	7.48	1.04	3.72	.138	.001	99.91	69
283.	8.60	1.04	3.58	.207	.001	99.92	70
283.	8.61	1.82	3.67	.151	.009	99.88	113
284.	8.79	1.04	3.60	.200	.001	100.0	71
281.	8.80	1.93	3.08	.302	.104	99.76	13
283.	8.90	1.87	3.05	.333	.096	99.83	14
282.	8.98	1.82	3.43	.269	.011	99.87	115

TABLE 5-2

TEMPERATURE HISTORY OF REACTOR

Time Interval Number* and Operating Temperature of Reactor (°C.)

258.2	13	238.6	25	258.2	37	258.2	49	283.3	61	258.2	73	258.2	85	247.2	97	258.2	109	272.9	121	255.7
251.5		237.4		259.4		258.2		282.7		258.2		258.2		243.5		258.2		268.0		255.1
240.4		239.8		260.6		258.2		283.3		258.2		258.2		244.7		258.2		267.4		258.2
238.6		242.3		258.2		258.2		282.7		258.2		258.2		246.0		258.2		268.0		255.7
238.7		253.3		258.2		258.2		282.7		258.2		258.2		246.0		258.2		261.9		258.2
240.0		263.1		258.2		266.2		271.7		258.2		258.2		246.0		260.6		258.2		258.2
239.7		265.5		258.2		275.3		259.5		258.2		257.6		246.0		269.2		258.2		258.2
238.6		257.0		258.2		279.9		258.2		258.2		257.6		246.0		276.6		258.2		258.2
238.7		258.2		258.8		290.0		258.2		258.2		258.2		246.0		282.7		258.2		258.2
243.4		259.4		258.4		282.1		258.2		258.2		258.8		246.0		283.3		255.7		258.2
243.9		256.7		258.2		283.3		258.2		258.2		258.8		257.6		276.6		258.0		258.2
244.7		257.0		258.2		283.3		258.2		258.2		258.2		258.2		274.7		257.8		259.4

* Each time interval represents 12. minutes.

TABLE 5-2 CONT'D

	145	157	169	181	193	205	217	229	241	253
259.7	259.4	242.3	258.2	258.2	283.9	266.8	246.0	258.2	258.2	258.2
258.2	258.6	246.0	258.2	258.2	283.9	258.2	246.0	258.2	258.2	258.2
258.2	258.2	246.0	258.2	258.2	283.9	257.0	246.0	258.2	258.2	258.2
258.2	258.2	246.0	258.2	258.2	274.1	257.0	246.6	258.2	258.2	258.2
258.2	258.2	246.0	258.2	258.2	275.3	257.0	258.2	258.2	258.2	258.2
258.8	258.2	253.3	258.2	258.2	275.3	257.0	258.2	258.2	258.2	233.7
258.9	258.2	258.2	258.2	258.2	275.3	258.2	258.2	258.2	258.2	233.7
259.4	258.2	258.8	258.2	258.2	275.3	258.2	258.2	258.8	258.2	233.7
259.2	258.2	258.2	258.2	268.0	268.6	248.4	258.2	258.2	258.2	233.7
259.4	258.8	258.2	258.2	276.6	267.4	244.7	258.2	258.2	258.2	233.7
259.2	258.2	258.2	258.2	282.7	267.4	246.0	258.2	259.4	258.2	233.7
259.4	247.2	258.2	258.2	284.5	267.4	246.6	258.2	258.2	258.2	255.7

TABLE 5-2 CONT'D

255.7	277 282.7	289 264.3	301 259.4	313 246.0	325 283.3	337 258.2	349 258.2	361 258.2	373 271.7	385 246.0
255.7	282.7	257.0	259.4	246.0	282.7	258.2	249.0	258.2	271.7	246.0
255.7	281.5	255.7	257.0	258.2	275.3	258.2	247.2	258.2	271.7	246.0
255.7	281.5	253.3	257.0	258.2	270.4	258.2	246.0	258.2	271.7	246.0
255.7	275.3	258.2	258.2	258.2	270.4	258.2	246.0	258.2	269.2	246.0
255.7	276.0	258.2	258.2	258.2	269.8	258.2	246.0	264.3	258.2	253.3
255.7	268.0	258.2	258.2	258.2	258.2	258.2	246.0	271.7	258.2	258.2
258.2	268.0	258.2	258.2	260.6	258.2	259.4	246.0	271.7	258.2	258.2
258.2	266.8	258.8	258.2	270.4	258.8	258.8	253.3	271.7	258.2	258.2
259.4	258.2	258.8	246.0	279.0	258.2	258.2	260.6	271.7	258.2	258.2
265.5	258.8	259.4	246.0	282.7	258.2	257.6	252.1	271.7	258.2	258.2
274.7	259.4	259.4	246.0	282.7	258.2	258.8	258.2	271.7	258.2	258.2

PROPANE CRACKING EXPERIMENTS

The integral selectivities of methane and ethane as a function of the conversion of propane is shown in Figure 5-2.

Since only two temperature levels were investigated, it is convenient to observe the conversions of propane on an experimental design grid. This is shown in Figure 5-3.

CATALYST ACTIVITY CHANGES

In the butane cracking experiments each of the experimental design points was straddled by two experiments performed at standard operating conditions. These experiments should give an indication of the change in catalyst activity during the course of the experiments. A plot of the conversion of butane for all of the mid-point runs versus the run number is shown in Figure 5-4. An apparent steady increase in catalyst activity to an asymptotic maximum may be observed. Unfortunately the operating conditions of these mid-point runs were not all exactly the same and, in fact, some differed considerably. One replicate at each mid-point run was chosen which had measured operating conditions closest to a standard operating condition. These runs are given in Table 6.2-2, and are also identified in Figure 5-4.

The temperature history of the reactor and the reducing temperature of the catalyst are given in Figure 6.3-9 and Table 5-2.

Mid-point runs were also performed in the propane cracking experiments, though not as frequently as in the butane experiments. A plot of the conversion of propane for these mid-point runs as a function of the run number is given in Figure 5-5. No general trends in catalyst activity may be observed.

6. ANALYSIS OF RESULTS

This section of the thesis describes the development of mathematical models of the chemical reactions involved in this experimental program and the use of these models with the experimental data to extract kinetic parameters.

In the first part the development of the models is described; the strategy for the estimation of the parameters is presented in the second part; and in the third part the validity of the models is discussed.

6.1 MATHEMATICAL MODELLING

This section describes the modelling work done in order to simulate the observed physical phenomena and where possible, to estimate meaningful kinetic parameters. It is convenient to present the development of the mathematical models in four parts: The first part gives the development of the equations describing the butane hydrogenolysis and includes the modification for changing catalyst activity. The second part presents the rate expressions for propane hydrogenolysis. In the third part, the packed bed reactor model, in which the differential rate expressions are used, is described. Part four discusses the problem of changing (increasing) catalyst activity and models to account for these changes are suggested.

6.1.1 THE KINETIC MODEL FOR BUTANE HYDROGENOLYSIS

6.1.1.1 INTRODUCTION

In the hydrogenolysis of butane, the following reactions are possible:

$$C_4H_{10} + H_2 \longrightarrow C_3H_8 + CH_4 \qquad 6.1$$

$$C_4H_{10} + H_2 \longrightarrow 2C_2H_6 \qquad 6.2$$

$$C_3H_8 + H_2 \longrightarrow C_2H_6 + CH_4 \qquad 6.3$$

$$C_2H_6 + H_2 \longrightarrow 2CH_4 \qquad 6.4$$

$$C_4H_{10} + 3H_2 \longrightarrow 4CH_4 \qquad 6.5$$

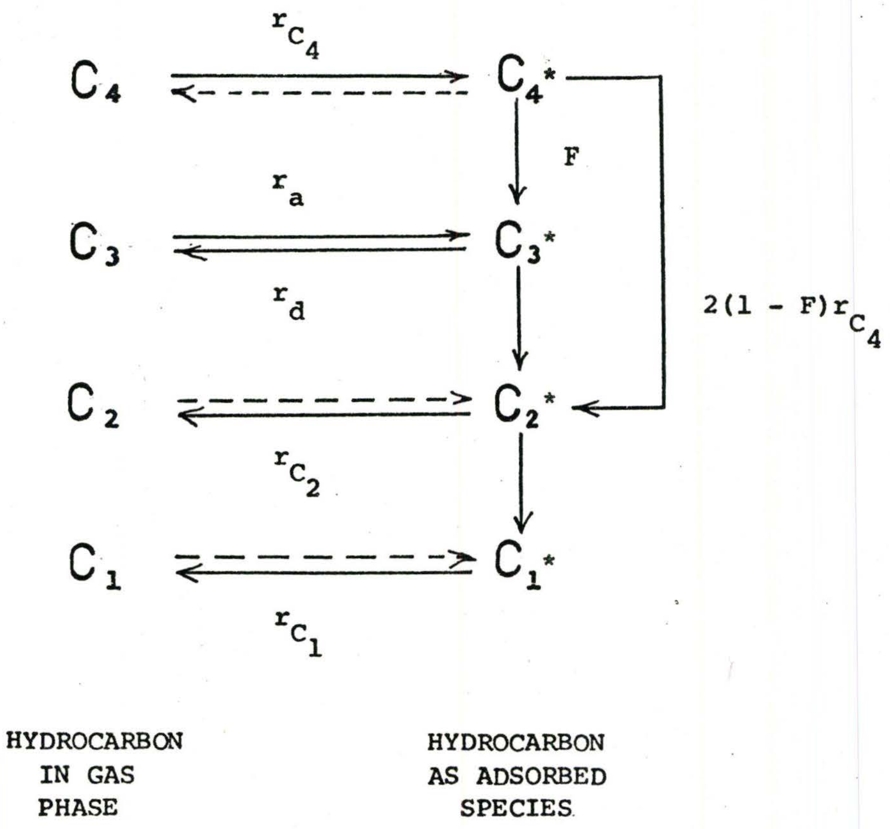
$$C_3H_8 + 2H_2 \longrightarrow 3CH_4 \qquad 6.6$$

In order to describe the reaction rate of butane, in an integral reactor, it is necessary to know the hydrogen concentration at every point. Since the hydrogenolysis of the products, propane and ethane, (equations 6.3, 6.4, and 6.6) occurs simultaneously, it may be necessary to include these reactions in the description as well, in order to predict the hydrogen concentration. Moreover, there may be other interactions, such as surface coverage by adsorbed molecules, that would affect the butane kinetic model. Therefore, a full or partial description of the other reactions is necessary in order that the parameters estimated from the experimental, integral bed data be meaningful.

Using the Hougen and Watson approach (H4) which assumes first-

FIGURE 6.1-1

OVERALL REACTION SCHEME FOR
HYDROGENOLYSIS OF BUTANE



r_{C_4} = rate of cracking of butane

r_a = rate of adsorption of propane

r_d = rate of desorption of propane

r_{C_2} = rate of production of ethane

r_{C_1} = rate of production of methane

F = fraction of C_4^* that crack to C_3^* and C_1^*

⟶ REACTION PATHS CONSIDERED

- - → ASSUMED = 0

order reaction on the surface and the adsorption-desorption phenomena, 30 parameters would be required for a full description (Appendix I.2). Since this would lead to excessive experimentation and computer time, it was decided to combine their approach with that of Cimino, Boudart and Taylor(C1), (Appendix I.1). Moreover, some assumptions could be made concerning some of the above reactions on the basis of experimental observations.

Reactions (6.1) and (6.2) are assumed to occur because of the product distribution in the reactor effluent. Propane hydrogenolysis experiments indicated that reaction (6.3) proceeded at an appreciable rate under the experimental conditions which prevailed in the butane experiments. On the other hand, tests with ethane feed in the fluidized bed reactor under these conditions indicated very little conversion (6.% at 258.°C.) and, therefore, reaction (6.4) in which the ethane in the gas adsorbs and reacts on the catalyst surface, was assumed not to occur. Reactions (6.5) and (6.6), as such, were assumed not to occur because of the low probability of breaking two or three carbon-carbon bonds simultaneously.

A schematic diagram which shows the reaction paths more effectively is given in Figure 6.1-1*. For simplicity this diagram shows only the major compounds involved in the reaction paths. The compounds labelled C_1, C_2, C_3 and C_4 are the hydrocarbon species in the gas phase. The compounds labelled C_1*, C_2*, C_3*, and C_4* represent

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* This scheme was suggested by Professor R. B. Anderson and Ph.D.-candidate J.C. Kempling of McMaster University, who were studying these reactions on a ruthenium catalyst.

the hydrocarbon species adsorbed on the surface of the catalyst and in a highly active state. All hydrocarbon cracking is assumed to occur through the breaking of the carbon-carbon bonds of these highly active adsorbed complexes. Consistent with the above mentioned assumed reaction paths, the possible reaction paths are shown in Figure 6.1-1 with solid lines. Reaction paths assumed not to occur are shown with dotted lines. Only adsorption of butane and desorption of methane paths are considered, since in the rate equations yet to be developed, only net rates for these compounds will be considered.

6.1.1.2 ASSUMPTIONS

The following assumptions were necessary since no method was available for observing the particular phenomena:

(i) Steady-state prevails on the catalyst surface

The steady-state assumption says that the rate of change with time of active species on the catalyst surface is zero. That is to say, an equal number of active species of a particular type disappear through reaction and desorption as are formed through reaction and adsorption.

(ii) Parallel reaction of butane to propane and ethane

The fraction F represents the amount of $C_4{}^*$ species that cracks down to $C_3{}^*$ and $C_1{}^*$ species. It may be noted from Figure 6.1-1 that if the fractional split, F, is not specified, there exist an infinite number of solutions, as far as simulation is concerned, for the reaction scheme. That is to say, for any given value of F, a set of model parameters may be chosen which will describe the product distribution for any experiment. F could not be predicted from the experimental analysis of the effluent gas. This factor was, therefore, estimated by looking at the propane, ethane and methane selectivities when these quantities were extrapolated to zero butane conversion. These selectivity curves are given in Figure 5-1. It is to be noted, that at zero conversion the selectivity of C_1 is greater than the selectivity of C_3. This poses the question as to whether the C_1 came from further cracking of C_3* or from the cracking of C_2* which came from C_4*. Since experiments with ethane and propane suggested that propane cracks more readily than ethane and since at zero butane conversion the selectivity of ethane was approximately 0.2 and the selectivity of propane was less than 0.9, it was assumed that the C_1 came from further cracking of C_3*.

With this assumption, the experimental data suggest F as being very close to 0.9, although F could be as low as 0.7. These observations do suggest, however, that the end carbon-carbon bond is more easily broken than the centre one, since if these bonds were broken with equal ease, F would be 0.66. It is emphasized that any value of F between 0.7 and 0.9 would probably produce a unique and equally valid, from a simulation point of view, set of kinetic parameters estimates. F was chosen as 0.9 since no measurement technique was available to provide better estimates. Moreover, it must be emphasized that the primary purpose of the kinetic model was to simulate rather than to uncover fundamental mechanisms.

The factor F was assumed constant with temperature and catalyst activity. This says that the difference in energy requirements to break the end or middle carbon-carbon bond in C_4* stay constant with changes in temperature and catalyst activity.

(iii) Catalyst activity

Catalyst activity is defined as the ratio of the rate of reaction at any time to the rate of reaction as similar experimental operating conditions, and at a time at which the activity is defined as the known or reference activity. Catalyst activity is assumed directly related to the number of active sites on the catalyst surface. All sites are assumed to have the same catalytic properties. A more detailed description of the proposed model for catalyst activity changes is given in section 6.1.3. The catalyst activity is assumed to have a linear effect on all rate processes involved in the reaction, and therefore, a factor for activity is included in all rate expressions. This factor is the ratio of the rates or frequency factors at the operating conditions under study to those at a standard operating condition.

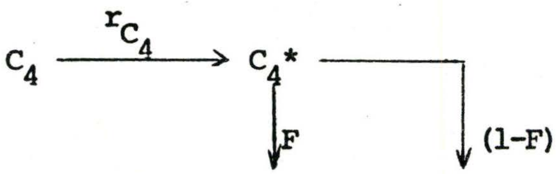
(iv) Kinetic order

First order adsorption, desorption and reaction kinetics are assumed as no data are available to suggest anything different.

6.1.1.3 MODEL DEVELOPMENT

Figure 6.1-1 will be broken down into sections according to components. Equations describing the adsorption/desorption and reaction phenomena will be given in turn.

BUTANE



The net rate of disappearance of butane from an analysis first proposed by Cimino, Boudart and Taylor(C1) and developed for butane in Appendix I.1 is described by:

$$r_{C_4} = \frac{k}{k_o} \cdot k_B \cdot \exp\{-\Delta E_B/RT\} P_{C_4}^{\,m} P_{H_2}^{\,n} \tag{6.7}$$

where r_{C_4} = rate of reaction (moles/sec. gm. catalyst)

$-\Delta E_B$ = activation energy for butane reaction (cal./gm. mole)

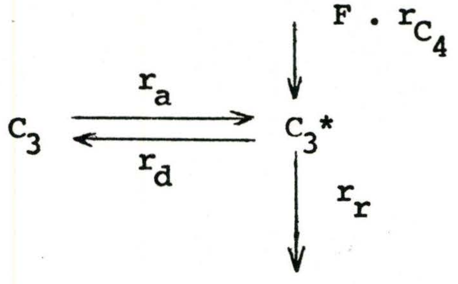
k_B = frequency factor for butane (moles/sec. gm. catalyst atm.$^{-(m+n)}$)

P_{C_4}, P_{H_2} = partial pressures of butane and hydrogen, respectively (atm.)

m,n = constants

The term k/k_o has been included to represent the catalyst activity as defined above. Calculation of these values will be described in Section 6.2.2.3.

PROPANE



For the propane part of the butane model consider separate rate expressions for the adsorption and desorption of propane. Assume that the inhibitory effect of hydrogen on rate of reaction (S1, M2) affects the adsorption of propane and that the rate of reaction of $C_3{}^*$ on the surface is proportional to the fraction surface covered by $C_3{}^*$ species.

Assume then that the rate of adsorption of propane can be described by:

$$r_a = \frac{k}{k_o} \cdot k_a \cdot \exp\{-\Delta E_a'/RT\} \, P_{C_3}{}^{m'} \, P_{H_2}{}^{n'} \qquad 6.8$$

where r_a = rate of adsorption of propane (moles/sec. gm. catalyst)

k_a = frequency factor (moles/sec. gm. cat. atm.$^{-(m'+n')}$)

$-\Delta E_a'$ = activation energy for adsorption process (cal./gm. mole)

P_{C_3} = partial pressure of propane (atm.)

m', n' = constants

Let K_{P2} represent the ratio of rates of reaction to desorption

$$K_{P2} = \frac{r_r}{r_d} = \frac{k_r \exp\{-\Delta E_r'/RT\} \cdot \theta_3{}^*}{k_d \exp\{-\Delta E_d/RT\} \cdot \theta_3{}^*} \qquad 6.9$$

where r_r, r_d = rates of reaction and desorption (moles/sec. gm. catalyst)

k_r, k_d = frequency factors (moles/sec. gm. catalyst)

$-\Delta E'_r, -\Delta E'_d$ = activation energies for reaction and desoroption, respectively (cal./gm. mole)

$\theta_3{}^*$ = fraction of active surface sites covered by $C_3{}^*$ species

Again, assuming in Arrhenius expression:

$$K_{P2} = k_{P2} \exp \{-\Delta E_{P2}/RT\} \tag{6.10}$$

where $k_{P2} = k_r/k_d$

$-\Delta E_{P2} = -\Delta E'_r + \Delta E'_d$

By a mass balance on $C_3{}^*$, assuming a pseudosteady state on the surface:

$$F \cdot r_{C_4} + r_a = r_d + r_r \tag{6.11}$$

$$= r_d + K_{P2} \cdot r_d \tag{6.12}$$

$$\therefore r_d = \frac{F \cdot r_{C_4} + r_a}{(1. + K_{P2})} \tag{6.13}$$

The net rate of desorption of propane is:

$$r_{C_3} = r_d - r_a \tag{6.14}$$

which from equation 6.13 yields

$$r_{C_3} = \frac{F \cdot r_{C_4} - K_{P2}\, r_a}{(1. + K_{P2})} \tag{6.15}$$

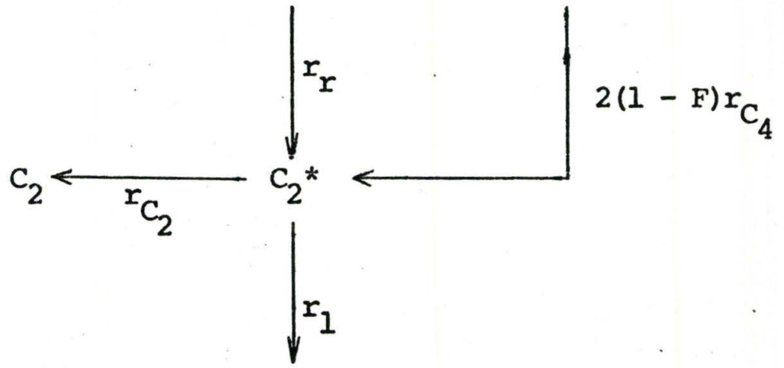
Therefore, the rate of production of propane may be represented by:

$$r_{C_3} = \frac{F \cdot r_{C_4} - \frac{k}{k_o} \cdot K_{P1} \cdot \exp\{-\Delta E_{P1}/RT\}\, P_{C_3}^{\,m'} P_{H_2}^{\,n'}}{1. + K_{P2} \cdot \exp\{-\Delta E_{P2}/RT\}} \tag{6.16}$$

where $K_{P1} = K_{P2} \cdot k_a$

$-\Delta E_{P1} = -\Delta E_r' + \Delta E_d' - \Delta E_a'$

<u>ETHANE</u>



In this case, we assume that there is not an appreciable readsorption of ethane onto the surface.

Let K_E represent the ratio of the rates of reaction on the surface to the rate of desorption:

$$K_E = \frac{r_1}{r_{C_2}} = \frac{k_1 \exp\{-\Delta E_r/RT\} \cdot \theta_2^*}{k_d \exp\{-\Delta E_d''/RT\} \cdot \theta_2^*} \tag{6.17}$$

where r_1, r_{C_2} = rates of reaction and desorption, respectively (moles/sec. gm. cat.)

k_1, k_d = frequency factors for r_1 and r_{C_2}, respectively

$-\Delta E''_r, -\Delta E''_d$ = activation energies for reaction and desorption, respectively (cal./gm. mole)

$\theta_2{}^*$ = fraction of active surface sites covered by $C_2{}^*$ species

By a mass balance on $C_2{}^*$, again assuming pseudosteady state on the surface:

$$r_r + 2 \cdot (1 - F) \cdot r_{C_4} = r_{C_2} + r_1 \qquad 6.18$$

where

$$r_r = F \cdot r_{C_4} - r_{C_3} \qquad 6.19$$

Therefore, by substituting 6.19 and 6.17 into 6.18 and simplifying, the rate of production of ethane is:

$$r_{C_2} = \frac{(2. - F)\, r_{C_4} - r_{C_3}}{1. + k_E \exp\{-\Delta E_E/RT\}} \qquad 6.20$$

where $k_E = k_1/k_d$

$-\Delta E_E = -\Delta E''_r + \Delta E''_d$

METHANE AND HYDROGEN

By overall mass balance on equations (6.1) to (6.6) and assuming pseudosteady state, the rate equations for the production of methane and disappearance of hydrogen are:

$$r_{C_1} = 4 \cdot r_{C_4} - 3 \cdot r_{C_3} - 2 \cdot r_{C_2} \qquad 6.21$$

$$r_{H_2} = 3 \cdot r_{C_4} - 2 \cdot r_{C_3} - r_{C_2} \qquad 6.22$$

6.1.1.4 SUMMARY

The rate equations given by equations (6.7, 6.16, 6.20, 6.21), and (6.22) are needed to describe the butane hydrogenolysis. The kinetic parameters which must be estimated from experiments are:

$$k_B,\ \Delta E_B,\ m,\ n,\ K_{P1},\ K_{P2},\ m',\ n',\ k_E,\ \Delta E_E,\ \Delta E_{P1},\ \Delta E_{P2}$$

The values of m and m′ were assumed equal to one. This appeared to be a reasonable assumption in light of the reported literature (see Table 3.1-1) in which the rates of reaction appeared essentially first order with respect to the hydrocarbon partial pressures. This also would remove two parameters from an already unwieldy long list of parameters.

These kinetic equations must be combined with the fluid mechanical and material and energy balance equations to predict the performance of any chemical reactor.

6.1.2 KINETIC MODEL FOR PROPANE HYDROGENOLYSIS

The model developed to describe the kinetics of the hydrogenolysis of propane is analagous to that developed for butane cracking.

The schematic diagram including the various species involved in the kinetics is given below:

$$\begin{tikzcd}
C_3 \arrow[r, "r_{C_3}"] & C_3^* \arrow[d] \\
C_2 & C_2^* \arrow[l, "r_{C_2}"'] \arrow[d, "r_1"] \\
C_1 & C_1^* \arrow[l, "r_{C_1}"']
\end{tikzcd}$$

All of the assumptions in the butane model are also applied here. The nomenclature used is the same. Since the development of the equations describing the reactions are identical with those presented for the butane system, little detail will be presented. Since no significant change in catalyst activity was observed, catalyst activity factors will not be shown.

PROPANE

The rate of disappearance of propane in the gaseous phase is given by an analagous Cimino-Boudart-Taylor type analysis:

$$r_{C_3} = k_P \exp \{-\Delta E_P/RT\} P_{C_3}{}^m P_{H_2}{}^n \qquad 6.23$$

where k_p = frequency factor (moles/sec. gm. cat. atm.$^{-(m + n)}$)

ΔE_p = activation energy (cal./gm. mole)

ETHANE

Analagous to equation 6.17 let:

$$K_E = \frac{r_1}{r_{C_2}} = \frac{k_1 \exp\{-\Delta E''_r/RT\} \cdot \theta_2^*}{k_d \exp\{-\Delta E''_d/RT\} \cdot \theta_2^*} \qquad 6.24$$

By mass balance on C_2* and assuming pseudosteady state:

$$r_{C_3} = r_{C_2} + r_1 \qquad 6.25$$

By substituting 6.24 into 6.25

$$r_{C_2} = \frac{r_{C_3}}{1. + K_E} \qquad 6.26$$

Thus, the rate of production of ethane is:

$$r_{C_2} = \frac{k_p \exp\{-\Delta E_p/RT\}\, P_{C_3}^{\ m}\, P_{H_2}^{\ n}}{1. + k_E \exp\{-\Delta E_E/RT\}} \qquad 6.27$$

where $k_E = k_1/k_d$

$-\Delta E_E = -\Delta E''_r + \Delta E''_d$

METHANE AND HYDROGEN

By overall mass balance, the rates of production of methane and disappearance of hydrogen are given by

$$r_{C_1} = 3 \cdot r_{C_3} - 2 \cdot r_{C_2} \qquad 6.28$$

$$r_{H_2} = 2 \cdot r_{C_3} - r_{C_2} \qquad 6.29$$

The rate equations given by equations 6.23, 6.27, 6.28 and 6.29 are required to describe the propane hydrogenolysis. The kinetic parameters which must be estimted from experiments are:

k_P, ΔE_P, k_E, ΔE_E, m and n.

6.1.3 MODEL FOR PACKED BED REACTOR

The technique used to estimate the parameters in the models for butane and propane hydrogenolysis involves comparing an observed integral value (i.e. the reactor effluent) with a calculated value which must also be an integral quantity. This calculated value must be obtained by solving the appropriate differential equations describing the packed bed reactor. This section gives the model used to describe the packed bed reactor.

ASSUMPTIONS

Since the reactor used in this study was of a small diameter (0.70 cm.) and the particles were very small (diameter $\simeq$ 120. μ), a number of assumptions could be made which allowed an extremely simple formulation to describe its performance. These are listed below.

(i) The packed bed is assumed statistically homogeneous with all changes in the bed occurring continuously and smoothly. This follows since the bed diameter is approximately 50. particle diameters and its length is approximately 1900. particle diameters. Hlaváček$^{(H8)}$ reports that a heterogeneous packed bed may be treated as a continuum if the tube diameter is greater than 10. particle diameters and the depth of the reactor is greater than 6. particle diameters.

(ii) The velocity is assumed uniform over any cross-section, that is, the gas flows in plug flow. Measurements reported by Beek$^{(B16)}$ have suggested that, if the particles are small, the velocity profile is flat over the central portion at least. The problem is still unresolved, although with the tube diameter many times the particle diameter, the gas flow should tend to be uniform over most of the cross-sectional area.

(iii) Concentration gradients in the radial direction are assumed negligible. The packed bed encourages radical mixing and the diffusion path is small because of the small tube radius (0.35 cm.).

(iv) Axial diffusion is assumed small. The detailed calculations supporting this assumption are given in Appendix F.

(v) The reactor is assumed isothermal. The maximum temperature variation under the worst conditions was measured to be less than 2.°C. Maximum temperatures could have occurred in the reactor at locations other than those indicated by the four thermocouples but at no time were high temperatures recorded. The stirred salt bath was expected to provide good heat transfer on the outside of the reactor.

(vi) The reactor was assumed to operate at constant pressure since less than 0.06 atmospheres pressure drop was observed across the packed bed.

(vii) It was assumed that no interparticle or intraparticle mass transfer limitations existed and the heat transfer rate was sufficient to keep the particles at the same temperature as the gas. Calculations supporting these assumptions are given in Appendix F.

(viii) The gases in the reactor are assumed to obey the ideal gas law.

MODEL

By mass balance on a differential height of packed bed reactor:

$$\frac{dc}{dx} = \frac{r_v}{u}$$

where c = concentration (moles/volume)

$-r_v$ = rate of disappearance of any component with units (moles/sec. - volume of packed bed reactor)

$-u$ = feed superficial gas velocity in reactor (cm./sec.)

x = length along the reactor (cm.)

since $u = \frac{V}{A}$ and $c = \frac{P}{RT}$

$$\frac{dP}{dx} = \frac{R \cdot T \cdot A}{V} \cdot (-r_v) \qquad 6.30$$

where P = partial pressure of any component (atm.)

T = temperature in (°K.)

R = universal gas law constant (atm. cm.^{3}/gm. - mole°K.)

A = reactor cross section area (cm.^{2})

V = volumetric flowrate through reactor (cm.^{3}/sec.)

METHOD OF SOLUTION

In the case of the butane hydrogenolysis reaction, the corresponding rates of disappearance of methane, ethane, propane, butane and hydrogen were substitued into equation (6.30) giving five coupled non-linear ordinary differential equations. These equations were integrated numerically using a fourth order Runge Kutta integration routine. Ample discussion of this generally accepted technique is given by Lapidus(L2). The step-size was allowed to vary by monitoring the integration error and the maximum and minimum allowable errors were $10.^{-6}$ and $10.^{-8}$ atmospheres. One pass through the reactor calculations required less than a second of computer time on a C.D.C. 6400 computer.

6.1.4 MODELS FOR CATALYST ACTIVITY CHANGE

During the course of the butane cracking experiments, a greater than two hundred percent increase in catalyst activity was observed. This increase may be seen in Figure 5-4 and the method used to account for these activity changes is described in section 6.2.2.3 of this thesis. The purpose of this section is to develop models that would describe mathematically the rate of change of catalyst activity.

INTRODUCTION

The catalyst was reduced prior to experimentation for eight hours at approximately 265°C. This temperature was approximately the maximum temperature that could be achieved in the fluidized bed reactor at the time these experiments were performed. The maximum temperature achieved, however, during the butane cracking experiments was over 280°C.

When working with these reduced metal catalysts, reduction temperature should be such as to ensure total reduction of the oxide. Taylor, Yates and Sinfelt(T4) found that 370°C. was a reasonable temperature for their 10.% by weight nickel on silica catalyst. The temperature history of the reactor during the butane hydrogenolysis experiments is given in Figure 6.2-4. Since the reduction temperature was 265°C. and the maximum temperature attained during the butane experiments was 283°C., it was proposed that the catalyst activity increase was due to further reduction of nickel oxide on the catalyst surface to produce a more active nickel catalyst. The activity models were developed as an extension of this hypothesis.

The assumptions to be made in the "varying maximum catalyst

catalyst activity model" arise from work done by Van Eijk van Voorthuysen and Franzen(V3) and reported by Schuitt and Van Reijen(S5). Their nickel catalyst was manufactured by co-precipitation of nickel nitrate and alkali solution at 100.°C. It was noted that hydrosilicate-like structures were always formed. For the reduction of these nickel oxide-silica-water complexes, a sigmasoidal variation of percent reduction (as determined by chemical analysis) with temperature was observed. That is to say, that for a certain reduction temperature there exists a maximum percent reduction of the catalyst. Experiments were performed to ascertain that the reduction process was limited by the decomposition of nickel oxide and not by the decomposition of the hydrosilicate structure into nickel oxide, silica, and water. It was found that the reduction of the nickel oxide was greatly retarded by the presence of silica.

ASSUMPTIONS REGARDING THE CATALYST REDUCTION

The following assumptions were made in postulating the models: In the reduction of the catalyst, inactive nickel oxide is reduced to active nickel metal. All of the nickel metal sites formed are active and have the same catalytic properties. The rate of reaction at a certain time under standard conditions is proportional to the number of active metal sites on the surface. Thus, the catalytic activity may be represented by the rate of reaction at standard conditions at any time, or equivalently, in the case of the case of the butane kinetics, by the frequency factor, k_B in equation (6.7) for the rate of cracking of butane.

The two proposed models assume that the catalyst activity, the number of active nickel metal sites, and the relative frequency factor, are linearly related and the rate of change of these variables with time is proportional to the difference between the maximum number of active metal sites possible and the actual number of active metal sites. No sintering (agglomeration of nickel oxide or nickel crystals so as to reduce the surface area) is assumed so that the rate does not depend on the surface structure, except as it determines active sites. That is to say that the surface concentrations of active and inactive species change only because of chemical reaction, not because of changes in surface structure. The rate constant for this process is assumed to obey the Arrhenius rate law.

The two models differ in the maximum number of possible active nickel sites that may be uncovered. The following two sections describe the two models.

MODEL ASSUMING CONSTANT MAXIMUM ACTIVITY

The first model proposed assumes that the maximum catalyst activity is constant.

The rate equation proposed is:

$$\frac{dc}{dt} = k_n \exp\{-\Delta E_n/RT\} \cdot (c_m - c) \qquad 6.31$$

where c = the relative frequency factor at any time and at standard conditions.

c_m = the maximum relative frequency factor.

t = time (min.).

$-\Delta E_n$ = the activation energy for the reducing reaction in calories per unit relative frequency factor (since this is assumed linearly related to the concentration of active sites on the surface of the catalyst).

By integrating equation (6.30) we obtain:

$$C = C_m - \exp\{\ln(C_m - C_o) - \int_o^t k_n \exp(-\Delta E_n/RT)\,dt\} \qquad 6.32$$

where $C_o = C$ at $t = 0$

Temperature data T_i are available in Figure 6.3-12; these were read from the recorded records at 12-minute time increments and cover the entire period of experimentation. Twelve-minute time intervals were chosen because this time interval was felt small enough to justify using the Trapezoidal rule to perform the integration in equation (6.32).

MODEL ASSUMING VARIABLE MAXIMUM ACTIVITY

In this model, the maximum catalyst activity is assumed to depend upon the reducing temperature. That is, for any reducing temperature there is a unique maximum catalyst activity that may be realized. This assumption stems from work reported by Schuitt and Van Reijen.

Although Schuitt and Van Reijen show a sigmasoidal variation of activity with temperature, it is assumed that the experimental conditions here cover the linear portion of their curve. Therefore, as an approximation the maximum catalyst activity is assumed to depend linearly upon the reducing temperature in the manner:

$$C_m = k'(T - T_o)$$

where k' is a constant

T_o is the temperature in °K. below which reduction of the catalyst does not occur.

T is the operating temperature in °K.

The proposed rate equation is:

$$\frac{dc}{dt} = k_v \exp\{-\Delta E_v/RT\} \cdot [k'(T - T_o) - C] \qquad 6.33$$

Where ΔE_v is the activation energy for the reduction process described by the above assumptions.

It may be noticed that, upon rearrangement, equation (6.33) may be represented by:

$$\frac{dc}{dt} + P(t)c = Q(t)$$

where $P(t) = k_v \exp\{-\Delta E_v/RT\}$

$Q(T) = k_v k' \exp\{-\Delta E_v/RT\} \cdot (T - T_o)$

This equation is a first order linear ordinary differential equation with the general solution:

$$C(t) = \frac{\int_o^t Q \exp\{\int_o^t P dt\}\, dt + c_o}{\exp\{\int_o^t P dt\}} \qquad 6.34$$

where $c(t) = c_o$ at $t = 0$.

Since no oxygen is present in the feed to the reaction, the reduction progress may be considered irreversible

That is $\frac{dc}{dt} \geqslant 0$

Thus, in solving equation (6.32) numerically, the constraint must be imposed:

$$\frac{dc}{dt} = 0 \qquad\qquad \text{if } k' \,(T - T_o) < c$$

Again, the Trapezoidal rule may be used to solve equation (6.34). It must be noted that in integrating the function

$$\int Q \exp \{\int P dt\}\, dt$$

between two time limits, the integral

$$\int P dt$$

must be evaluated at the end of each time interval.

The validity of these two models for catalyst activity change will be discussed in section 6.3.3.

6.2 PARAMETER ESTIMATION

This section deals with the estimation of the parameters for the various models proposed in section 6.1.

Part 1 of this section gives a brief review of the theory of non-linear parameter estimation and the theory from which confidence intervals for these parameters may be obtained. Part 2 describes the strategy, using this theory, to obtain parameter estimates for the butane cracking model. Parts 3 and 4 describe the strategies used to estimate parameters for the propane cracking model and the models proposed to describe the catalyst activity changes. Finally, Part 5 gives the confidence intervals for the parameter estimates for the butane model.

6.2.1 INTRODUCTORY THEORY

This section will be divided into three parts. The theory of non-linear parameter estimation is discussed in the first part. The method used to investigate the errors in the parameters will be discussed in the second part. In the third part, a description of the grid search, the Rosenbrock direct search and the local linearization techniques for obtaining best estimate parameters will be given.

(i) NON-LINEAR LEAST SQUARES THEORY

A mathematical model or set of equations describing a physical process may be represented as

$$\eta_{ui} = \eta_{ui}\,(\underline{\theta}, \underline{x}_u) \qquad 6.35$$

where $\underline{\theta}$ is a column vector of unknown parameters whose values may, at best, be estimated. This column vector of p parameters may be represented by:

$$\underline{\theta} = \{\theta_1, \theta_2, \ldots\ldots\ldots, \theta_p\} \tag{6.36}$$

The best estimate parameter values are usually denoted by:

$$\underline{\theta}^* = \{\theta_1^*, \theta_2^*, \ldots\ldots\ldots, \theta_p\} \tag{6.37}$$

$\underline{x}_u$ is a vector of constants*for the uth experiment. These "independent variables" are usually experimental operating variable settings and are assumed known precisely for each experimental run. The vector of k independent variables for the uth experiment may be denoted by:

$$\underline{x}_u = \{x_{u1}, x_{u2}, \ldots\ldots\ldots, x_{uk}\} \tag{6.38}$$

and η_{ui} is the dependent variable or value predicted for the ith response of the uth experiment given the vector of parameters $\underline{\theta}$ and the vector of independent variables $\underline{x}_u$.

When an experiment is performed at $\underline{x}_u$ and a value y_{ui} is observed for the ith response variable. Assuming that the model describes the physical situation exactly, the measured response, because of experimental error, is given by :

$$y_{ui} = \eta_{ui}\ (\underline{\theta}, \underline{x}_u) + \varepsilon_{ui} \tag{6.39}$$

where ε_{ui} is the error in the ith response of the uth experiment.

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* Perfectly known coefficients which are functionally dependent on the operating conditions.

If the errors are assumed normally distributed:

$$E^* \{y_{ui}\} = \eta_{ui}$$

The main problem to be discussed in this section is: when given a vector of observations,

$$\underline{y} = \{y_{11}, y_{12}, \ldots\ldots\ldots, y_{nr}\} \qquad 6.40$$

for n experiments with r responses at each experiment, observed at the independent variable settings,

$$\underline{x} = \{x_{11}, x_{12}, \ldots\ldots\ldots, x_{nk}\} \qquad 6.41$$

how does one obtain the best estimates of the parameter values:

$$\underline{\theta}^* = \{\theta_1^*, \theta_2^*, \ldots\ldots\ldots, \theta_p^*\} \qquad 6.42$$

In the case where the model is linear in parameters:

i.e. $\frac{\partial \eta}{\partial \underline{\theta}}$ is independent of the respective parameters** 6.43

the parameters may be estimated quite easily using linear least squares theory$^{(D5)}$.

The problem becomes more difficult in the case where the model is non-linear in the parameters:

i.e. $\frac{\partial \eta}{\partial \underline{\theta}}$ depends upon the parameter values 6.44

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* E is the expectation operator.

** This definition of linearity is assumed to suffice for our purposes. Here η is the explicit form of the model.

In this case non-linear least squares methods must be used.

Assume that the errors ε_{ui} are normally distributed with the variance matrix $\underline{\underline{V}}$, where the diagonal elements are given by:

$$\mathrm{var}\ (y_{ui}) = E\ \{ [y_{ui} - E\ (y_{ui} - E\ (y_{ui})] \} \qquad 6.45$$

and the off-diagonal elements are given by:

$$\mathrm{cov}\ (y_{AB}, y_{CD}) = E\ \{ [y_{AB} - E\ (y_{AB})]\ [y_{CD} - E\ (y_{CD})] \} \qquad 6.46$$

The probability density function for the observations $\underline{y}$, given that the model and the parameters are perfectly known, may then be represented by the multivariate normal distribution:

$$f\ (\underline{y}/\eta,\underline{\theta}) = \frac{1.}{\sqrt{2\pi}\ |V|^{\frac{1}{2}}} \exp \{-\tfrac{1}{2}\ (y_{ui} - \eta_{ui})'\ \underline{V}^{-1}\ (y_{ui} - \eta_{ui})\} \qquad 6.47$$

Before experiments, if the probability of a set of observations $\underline{y}_i$ given $\underline{\theta}_i$ is proportional to a function $f\ (\underline{\theta}, \underline{y}_i)$, then after the experiments yielding observations $\underline{y}^*$

$$L(\underline{\theta}) \propto f(\underline{\theta}, \underline{y}^*)$$

where $L(\underline{\theta})$, here, is the likelihood function.

$f(\underline{y}/\eta,\underline{\theta})$ now becomes $L(\underline{\theta}/\underline{y},\eta)$, the likelihood of the parameters, $\underline{\theta}$, given that the model and observations are perfectly known.

The object is to maximize the likelihood function.

From equation (6.47) this may be accomplished by minimizing:

$$S(\underline{\theta}) = (y_{ui} - \eta_{ui})'\ \underline{V}^{-1}\ (y_{ui} - \eta_{ui}) \qquad 6.48$$

Equation (6.48) is the most general form of the weighted least squares criterion for estimating parameters.

If now the errors ε_{ui} are assumed to be independent then the off-diagonal terms of $\underline{V}$ become zero and the criterion expressed by equation (6.48) reduces to:

$$S\ (\underline{\theta}) = \sum_{i=1}^{r} \sum_{u=1}^{n} W_{ui}\ [y_{ui} - \eta_{ui}\ (\underline{\theta}, \underline{x}_u)]^2 \qquad 6.49$$

where $$W_{ui} = \frac{1.}{\mathrm{var}\ (y_{ui})} \qquad 6.50$$

Equation (6.49) is the usual form used for weighted least squares analysis; this is the form used in the analysis of the date in this thesis.

The problem now becomes one of finding the parameter values $\underline{\theta}^*$ which when placed in the model:

$$\eta_{ui}\ (\underline{\theta}^*, \underline{x}_u)$$

produces the value $S\ (\underline{\theta}^*)$
where $S(\underline{\theta}^*)$ is the minimum of $S(\underline{\theta})$ with respect to the values of $\underline{\theta}^*$. Several methods are available for finding the minimum sum of squares and these are described in Part (iii) of this section.

(ii) CONFIDENCE LIMITS FOR PARAMETER VALUES

Confidence contours refer to surfaces of equal likelihood value in parameter space. For models which are linear in the parameters these contours are ellipsoids whose axes are parallel to the parameter axes(D5) so that indicating two confidence limits of a parameter has some meaning. In models which are non-linear in the parameters these contours need not be elipsoids and are usually elongated ridges with the length of these ridges usually not parallel to any parameter axis. This indicates correlation among the parameters values and in this case, to give confidence limits to parameter values, without giving an indication of the non-linearity of the model, or the extent to which the parameters are correlated, provides little information$^{(B9)}$.

A good indication of the variance of the estimates of the parameters is obtained by plotting contours of equal likelihood ratio (R4, B18, J1).

That is, find the co-ordinates, $\underline{\theta}$, in parameter space that satisfy the equation:

$$\frac{L\ (\underline{\theta}^{*}/\underline{y},n)}{L\ (\underline{\theta}^{*}/\underline{y},n)} = \frac{10.^{*}}{1.} \qquad 6.51$$

where the likelihood function is given by equation (6.47) and a reasonable likelihood ratio of 10. is chosen.

If the covariances in the matrix $\underline{V}$ are not known, or may be assumed equal to zero, $\underline{V}^{-1}$ may be approximated or replaced by a diagonal matrix whose elements are represented in equation (6.50).

The two ways in which the covariance matrix for the experimental observations was calculated in this work are given in Appendix H.

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* Perhaps a value of 100 would be a better choice, in view of the large number of parameters, however, in this case it would make little difference in the results.

(iii) MATHEMATICAL METHODS FOR FINDING THE MINIMUM SUM OF SQUARES OBJECTIVE FUNCTION

To obtain the minimum value of $S(\underline{\theta})$, the weighted sum of squares objective function, this continuous function may be treated as a response surface in parameter space. The problem becomes one of finding the minimum point on the response surface. Direct search methods utilize only the values of $S(\underline{\theta})$ at a point, $\underline{\theta}$ to find the minimum, but gradient methods also utilize the derivatives of $S(\underline{\theta})$ with respect to $\underline{\theta}$.

DIRECT SEARCH METHODS

The simplest to use, but least efficient direct search method, is the grid search. Here, values of $S(\underline{\theta})$ are plotted at various discrete grid points in parameter space and the minimum $S(\underline{\theta})$ is found by observing these values and decreasing the grid spacing in regions of minimum $S(\underline{\theta})$ until the minimum (as determined by an appropriate criterion) is found.

A much more efficient search method, especially where ridges are present, was developed by Rosenbrock(R1, R5). This is a trial and error method. The parameters are varied one at a time and the effect of these changes on the objective function determine how the parameter will be changed on the next trial with respect to step to size and direction of change. If, after changing the p parameter in turn and encountering p successive successes (i.e. noting p successive decreases in the objective function) the axes which determine the direction of movement along the response surfaces are rotated. This rotation aligns the axes so that the parameters are changed in a direction which depends upon the magnitude of change of each of the parameters since the axes were last rotated.

LINEARIZATION METHOD

In this method, the model is linearized about initial parameter estimates $\underline{\alpha}$ in parameter space and the results of linear least squares analysis as well as the initial parameter estimates are used to iterate the the best estimate parameter values.

Expanding the model about the initial estimates of $\underline{\theta}$ by Taylor expansion and neglecting second and higher order devrivatives:

$$\eta_{ui} (\underline{\theta}, \underline{x}_u) = \eta_{ui} (\underline{\alpha}, \underline{x}_u) + \sum_{m=1}^{p} \left[\frac{\partial \eta_{ui} (\underline{\theta}, \underline{x}_u)}{\partial \theta_m}\right]_{\underline{\theta} = \underline{\alpha}} (\theta_m - \alpha_m) \qquad 6.52$$

The predicted and experimental responses for n runs with r responses at each run may be considered as two vectors of length n X r$^{(B8)}$.

Thus equation (6.52) may be written:

$$\eta_j (\underline{\theta}, \underline{x}_j) = \eta_j (\underline{\alpha}, \underline{x}_j) + \sum_{m=1}^{p} \left[\frac{\partial \eta_j (\underline{\theta}, \underline{x}_j)}{\partial \theta_m}\right]_{\underline{\theta} = \underline{\alpha}} (\theta_m - \alpha_m) \qquad 6.53$$

where $j = 1, 2, \ldots\ldots\ldots, (n \times r)$

$\underline{x}_j = \{x_{ji}, x_{j2}, \ldots\ldots\ldots, x_{jk}\}$

Using the modification proposed by Box and Hunter$^{(B6)}$ in evaluating numerically the partial derivatives:

let $z_m = \eta_j\ (\alpha_m + \delta_m, \alpha_m, \underline{x}_j) - \eta_j\ (\alpha, \underline{x}_j)$ 6.54

where δ_m is the increment for α_m in evaluating the derivative numerically.

Since the "true" value predicted by the model is best approximated by the experimental value:

$$y_j = \eta_j\ (\underline{\theta}, \underline{x}_j) \tag{6.55}$$

let $Y_j = y_j - \eta_j\ (\underline{\alpha}, \underline{x}_j)$ 6.56

and $\beta_m = \dfrac{\theta_m - \alpha_m}{\delta_m}$ 6.57

Therefore, equation (6.53) may be written:

$$\underline{Y} = \underline{Z}\ \underline{\beta} + \underline{\varepsilon} \tag{6.58}$$

when $\underline{Y}$ is a vector of observations of size n X r

$\underline{Z}$ is a matrix of constants with n X r rows and p columns

$\underline{\beta}$ is a vector of parameters of size p.

Assume the errors are independent and normally distributed with constant variance:

$$\underline{V}\ (\underline{\varepsilon}) = \underline{I}\ \sigma^2 \tag{6.59}$$

From linear least squares, the best estimates of $\underline{\beta}$ are

$$\underline{\beta}^* = (\underline{Z}' \underline{Z})^{-1} \underline{Z}' \underline{Y} \qquad 6.60$$

and the new values of $\underline{\theta}$ from (6.60) and (6.57) are given by

$$\theta_m = \alpha_m + t\delta_m \beta_m^* \qquad 6.61$$

$\underline{\theta}_m$ becomes the $\underline{\alpha}_m$ for the next iteration.

t is a relaxation factor by which the step change in $\underline{\alpha}$ values from one iteration to the other may be controlled to induce most efficient convergence.

6.2.2 PARAMETER ESTIMATION FOR BUTANE HYDROGENOLYSIS MODEL

This section describes the strategy used to estimate the parameters in the butane cracking model given integral reactor data in which a 200% change in catalyst activity was observed. An algorithm for this strategy is given in Figure 6.2-1. The strategy for estimating the parameters may be resolved into four component parts: preliminary investigations, estimating kinetic parameters, estimating catalytic activities, and testing the model by extrapolation.

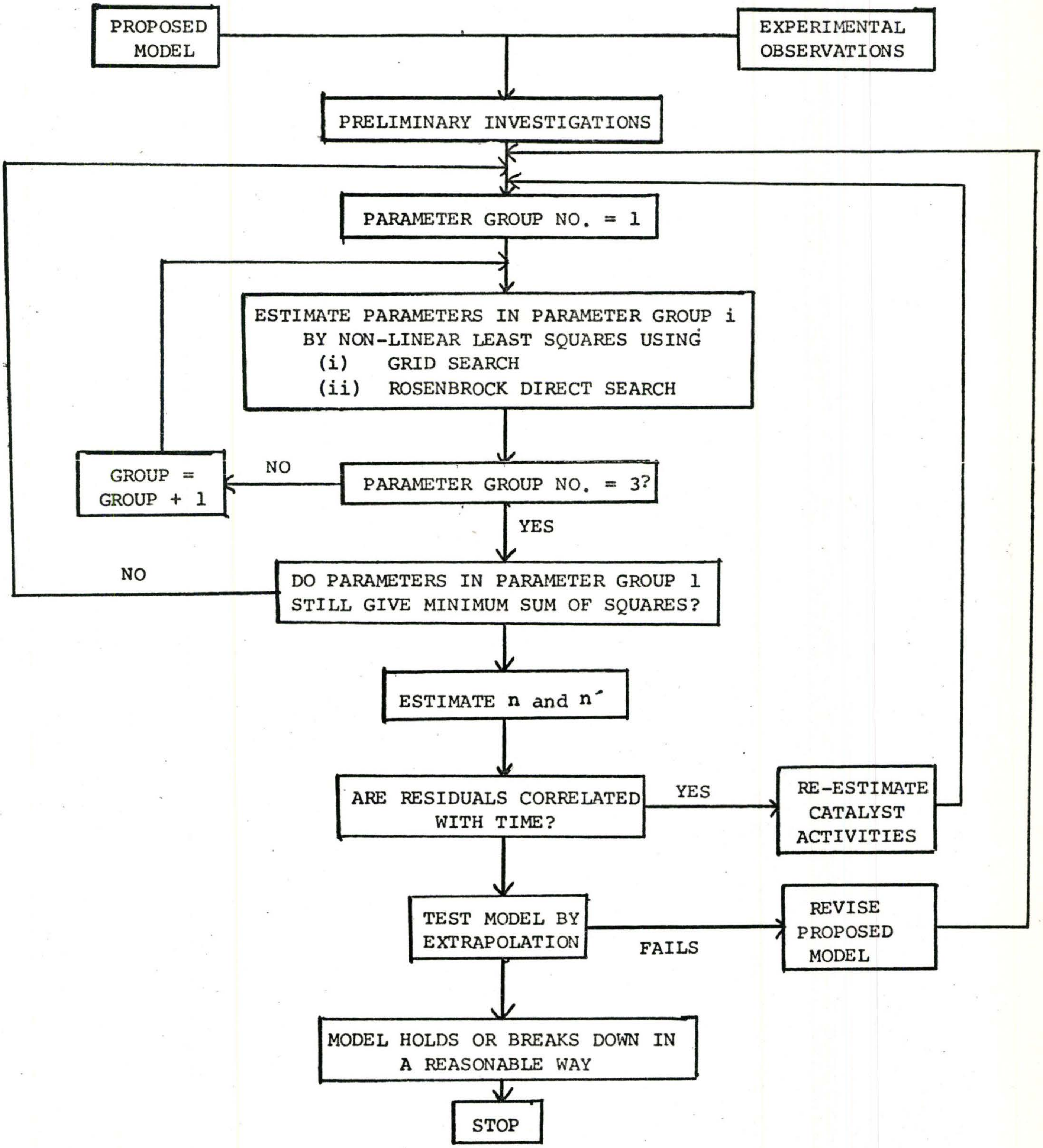
6.2.2.1 PRELIMINARY INVESTIGATIONS

(i) CHOICE OF EXPERIMENTAL RUNS IN ESTIMATING PARAMETERS

In non-linear parameter estimation, the evaluation of the sum of squares objective function involves solving the kinetic model once for each experimental run included. Solving the model with integral reactor data, in this case involves solving numerically a set of five non-linear ordinary differential equations. Since for the number of parameters to be estimated, the sum of squares objective function would have to be evaluated a large number of times, a minimum number of experimental runs were chosen to minimize the computation time. The experimental runs used in the parameter estimation are shown by asterisks in Table G-1. These include all experimental runs at different operating conditions, in which the butane conversion was less than ninety-nine percent. The range of butane conversion for those runs included in the parameter estimation was 5.- 90.%; these runs represent ten different experimental operating conditions, viz. three feed ratios (4,7 and 9) three feed flowrates (1.0, 1.4 and 1.8 ml./min.) and three temperature

FIGURE 6.2-1

STRATEGY FOR ESTIMATING BUTANE KINETIC PARAMETERS



levels (240., 246. and 258.°C). Five centre point replicates were chosen equally distributed throughout the course of experimentation to give an indication of correlation of residuals (difference between experimental and calculated mole fractions of components) with time.* In the case of each experimental design point and centre point only one of the several replicate runs was chosen for the sum of squares of objective function. This was felt justified because of the extremely large amount of computation time that would be required if replicate runs were included. Moreover, by looking at the experimental mole fractions, it is noted that small differences in feed flow, temperature and ratio among replicate runs seems to cause greater variation in the observed component mole fractions than the variation observed at exactly the same reacting conditions. This was interpreted to mean that the differences in the mole fraction due to analytical errors could be considered small in comparison to the differences caused by small variations in the operating conditions. This also justifies including one of several replicates in the evaluation of the objective function.

The very high conversion runs were not included in the parameter estimation since little information about concentration profiles and rate distributions in the reactor may be extracted for such high conversions. This may be considered as an extreme case in the general problems of estimating parameters or testing a model when integral data rather than point value or differential data are available. For example, an infinite number of butane rate constants may be chosen to give 100. percent conversion.

The 18 runs used in the parameter estimation are given in

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* Compromise was made here with respect to statistical considerations; the choice of one replicate was made mainly because of computer time limitations.

TABLE 6.2-1

RUNS USED IN THE SUM OF SQUARES OBJECTIVE FUNCTION FOR PARAMETER ESTIMATION IN BUTANE MODEL

RUN #	TEMP.	FLOW	FEED	EFFLUENT MOLE FRACTIONS				
	°C.	ml./min.	RATIO	C_1	C_2	C_3	C_4	H_2
5	239.7	.89	9.97	.003	.000	.005	.087	.905
26	246.0	1.86	3.78	.045	.007	.021	.179	.748
53	245.8	1.81	8.23	.028	.003	.015	.089	.866
84	246.7	1.04	3.58	.197	.024	.070	.104	.605
109	246.0	1.03	7.81	.069	.011	.032	.067	.822
133	245.9	1.63	8.66	.040	.006	.020	.075	.858
149	245.2	1.78	8.24	.043	.006	.022	.078	.851
21	258.8	1.85	8.81	.068	.011	.025	.061	.835
64	258.7	1.85	3.89	.281	.036	.069	.064	.550
90	258.5	1.02	9.06	.175	.022	.042	.013	.747
101	257.7	1.72	3.96	.340	.045	.078	.036	.501
125	258.1	1.85	8.84	.122	.016	.039	.034	.789
8	258.6	1.50	6.20	.063	.008	.023	.102	.804
23	258.8	1.44	6.72	.134	.016	.040	.058	.782
60	258.5	1.45	6.68	.171	.020	.048	.041	.719
86	259.2	1.40	7.67	.175	.025	.047	.024	.729
105	258.1	1.44	7.09	.192	.025	.051	.025	.707
121	258.3	1.40	8.99	.151	.022	.042	.020	.765

Table 6.2-1.

As will be shown later, the high conversion runs provide an excellent test of the validity of the kinetic model.

(ii) PRELIMINARY ESTIMATES OF PARAMETERS

In order to search on parameter values to minimize the sum of squares objective function, initial estimates on starting point values are required. To obtain order of magnitude estimates of these parameters the integral data was treated as differential reactor data.

The differential equation for each component in the packed bed:

$$\frac{dP_i}{dx} = \frac{RTA}{V} \cdot r_{vi} \qquad 6.62$$

where P_i = partial pressure of component i

R = gas constant (atm) (cm.^{3})/(gm. moles) (°K.)

T = temperature °K.

V = feed volumetric flowrate (ml./sec.)

r_{vi} = rate of disappearance of component i moles/(sec.) (volume of reactor)

x = distance along packed bed reactor (cm.)

was approximated by

$$\frac{P_i^{out} - P_i^{in}}{L} = \frac{RTA}{V} \cdot r_{vi} \qquad 6.63$$

where L = length of the reactor (cm.)

and r_{vi} is evaluated at

$$\frac{P_i^{out} + P_i^{in}}{2.}$$

To obtain the constants for the butane part of the model, runs 39 and 53 where chosen. These two runs have approximately the same catalyst activity and the conversions of butane are widely different; (18.% and 62.%). The two rate equations given by (6.63) for these runs were solved simultaneously yielding a butane activation energy of -47. kcal./mole and a frequency factor of approximately 10^{13} moles/sec. - volume of packed bed reactor.

Since four parameters are involved in the propane part of the butane model, ten experimental runs were chosen to obtain preliminary estimates. Making the differential reactor approximation, a grid search was used to obtain initial parameter estimates. A range of 10^5 to 10^{25} was searched over for the pre-exponential factors and a range of -10. to -50. kcal./mole was searched over for the activation energies. A large amount of intuition about the response of the model to changes in parameters was obtained at this stage and this proved useful during the later stages.

Similarly by working through the mechanistic model shown in Figure 6.1-1 of section 6.1.1, the activation energy for the ethane part of the butane model was calculated to be approximately -30 kcal./mole and the pre-exponential factor was estimated at 10^{12} (dimensionless).

These initial estimates of the parameters were good order-of-magnitude estimates for two reasons: the reactions are approximately first order with respect to the hydrocarbons and the effect of hydrogen on the rates, which causes non-linearity in the rate expressions, is not extremely severe since the hydrogen partial pressure may change at most by 40. percent.

(iii) GROUPING THE PARAMETERS*

After the initial estimates of the parameters are obtained, a systematic, economic search for the parameters must be performed. Optimum seeking techniques may be employed, but a ten-variable search still requires a large amount of computer time. Fortunately a simplification is possible. It was observed that some responses (mole fractions of the components in the reactor effluent) were more sensitive to some parameters than to others. For example, the butane response is most sensitive to the butane parameters, the propane response is most sensitive to the propane parameters and the ethane response is most sensitive to the ethane parameters. Hence, by choosing groups of parameters properly, it was felt that the overall efficiency of the search could be improved. The strategy was adopted, therefore, that involved a search on a group of parameters, holding the other groups constant. Each group of parameters could be estimated in turn producing an iterative type solution. The link between the responses and the respective least sensitive parameter groups was the hydrogen partial pressure. This hydrogen partial pressure affects the butane, propane and, therefore, the ethane and methane rate and a change in the hydrogen partial pressure caused by a change in one parameter group will affect

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* It has been drawn to the attention of the author that there may be better methods available for obtaining the parameters in this case.

the responses of all of the hydrocarbon components. This effect of hydrogen is not extremely severe, however, since as mentioned previously the hydrogen partial pressure changes are relatively small for the runs used in the parameter estimation; thus, it would appear that the iteration on parameter groups in turn should be stable.

These considerations led to the following parameter groups:

Group 1: butane activation energy : $-\Delta E_B$
butane frequency factor : k_B

Group 2: propane activation energies : $-\Delta E_{P1}$, $-\Delta E_{P2}$
propane frequency factors : K_{P1}, K_{P2}

Group 3: ethane activation energy : $-\Delta E_E$
ethane frequency factor : k_E

Thus, an iterative procedure may now be used where each parameter group is estimated in turn, holding the other groups constant. Since the interaction among the groups, caused by the hydrogen partial pressure, is relatively small, only a few interactions should be necessary.

(iv) CHOOSING THE LEAST-SENSITIVE PARAMETERS

The least-sensitive parameters are here defined as those for which a relatively small change in the calculated values of the responses occur for relatively large percent changes in the parameters. In this study these parameters were found to be the exponents on the partial pressure of hydrogen terms in the rate expressions. Problems arise in attempting to find unconstrained values of these exponents when the most sensitive parameters (the activation energies and pre-exponential factors) are not yet near their best values. If these exponents were unconstrained at this point, the search routines would force large changes in their values in an attempt to remove large sum of squares deviations when, in fact, these would be more appropriately removed by changes in the most sensitive parameters. For example, for poor estimates of activation energies and pre-exponential factors, unconstrained exponents on the hydrogen partial pressure were forced to values as small as -200. This is incompatible with expected mechanisms and with data reported in the literature. For this reason, the least sensitive parameters were held at reasonable values (previous work suggests exponents of about -2) until minimum sum of squares estimates for the most sensitive parameters were obtained. At this point correlations of residuals with feed ratio i.e. partial pressure of hydrogen, were removed by unconstrained searching on the exponents of the hydrogen partial pressure terms. Reasonable parameter estimates were obtained in this way.

(v) TRANSFORMATION OF PARAMETERS

In the direct search routines used, the parameters are increased or decreased in a linear way. This tends to make ridges in the response surface since non-linear transformations of certain parameters are made in the model. Thus, for linear changes in the parameters imposed by the search routine, and for non-linear transformation of some of the parameters by the model, it may be seen that the sensitivity of the objective function (which determines the shape of the sum of squares response surface) may be totally different for different parameters.

Thus, the parameters were transformed in a search routine in an attempt to make the objective function equally sensitive to all the parameters.

The transformations used were: -

ΔE searched upon = ΔE actual/1000.0

k searched upon = $\log_{10.}$ k actual

(vi) WEIGHTING MATRIX

Weights are required for each difference between an experimental and predicted value so that the particular difference may be properly translated into its contribution to the value of the total sum of squares of differences. For the parameter estimation it was decided to weigh equally all five mole fractions in the reactor effluent for each run. This was done for two reasons. At the time, no comprehensive error analysis and thus, varience matrix was available. The second and most important reason relates to the experiments which were included in the parameter estimation and the type of parameters that were to be estimated. The most sensitive parameters to be estimated were the rate constant parameters, i.e. the frequency factors and the activation energies. All but one of the 18 runs included in the parameter estimation occurred at two temperature levels. When for each response two parameters are being estimated from essentially two experiment levels, it should not matter whether the inverse of the real covariance matrix is used as the weighting matrix for the data or whether the data are weighted equally, as long as the parameters are those corresponding to the minimum of the sum of squares of the deviations and the residuals are randomly distributed about a zero mean. In each case the parameter estimates should be the same. When more than two levels are used and the error variance cannot be assumed constant, then the inverse of the covariance matrix for the response variables should be used.

The weighting matrix for the mole fractions consists of five columns, one for each component, and eighteen rows, one for each run. The elements of the matrix are determined as follows:

let x_{ij} represent the experimental mole fraction of component j in run i

w_{ij} represent weighting factor for the difference between the calculated and experimental mole fraction for component j in the i^{th} run.

if $x_{ij} < 0.01$ $w_{ij} = 10000.$

if $x_{ij} < 0.1$ $w_{ij} = 1000.$

if $x_{ij} > 0.1$ $w_{ij} = 100.$

The sum-of squares objective function is thus calculated as:

$$S\ (\underline{\theta}) = \sum_{i=1}^{n} \sum_{j=1}^{r} (SSQ_{ij} * SSQ_{ij}) \qquad 6.64$$

where n = number of runs (18)

r = number of components (5)

and

$$SSQ_{ij} = w_{ij}\ (x_{ij} - \eta_{ij}) \qquad 6.65$$

where η_{ij} is the mole fraction of the j^{th} component in the i^{th} run predicted from the reaction model.

(vii) INITIAL ESTIMATES FOR CATALYST ACTIVITIES

Since catalyst activity varied during the course of the experimental program (as evidenced by changing conversion under identical experimental conditions), some estimate of catalyst activity had to be made so that all runs could be included in the parameter extimation. The exact procedure for obtaining this activity will be discussed in Section 6.2.1.3. At the outset, catalyst activity for each run was calculated from conversion data for the "centre-point conditions".

That is, initial estimates of catalyst activity were given by:

$$\text{Activity} = \frac{c}{c_0} \qquad 6.66$$

where c_0 is some arbitrary conversion taken as the standard, in this case $c_0 = 0.65$,

and c is the conversion that would be obtained for any experimental run if the run were performed at "centre point" operating conditions. For a centre-point run, c was taken as the observed conversion and for each experimental design run, c was taken as the average conversion of the two straddling centre-point runs. Thus, for each run in the sum of squares objective function, a separate catalyst activity could be included

6.2.2.2 ESTIMATING KINETIC PARAMETERS

This section describes the procedures for estimating the ten parameters given the kinetic model, the experimental data and a set of catalyst activity values.

Since the ten-variable search has been broken up into three searches involving the butane, propane and ethane parameter groups, an iterative procedure must be followed. The butane, propane and ethane groups of parameters are estimated in turn. In estimating the butane parameters, the total sum of squares is decreased for the most part by a decrease in the sum of squares of differences between the calculated and observed butane mole fractions, i.e. the most sensitive response for the butane parameter group is the butane mole fractions. Similarly, the total sum of squares is reduced mostly by a decrease in sum of squares of propane and ethane mole fractions in estimating the propane and ethane parameter groups respectively.

Both a grid search and the Rosenbrock direct search was used to minimize the objective function given by equation (6.64). The grid search was used to get in the region of the minimum $S(\underline{\theta})$ and the direct search was used to obtain the final estimates. The optimum objective function was reached when three main conditions were satisfied: (i) the sum of the squares was a minimum, (ii) no correlation of the residuals* (difference between observed and calculated mole fractions) with operating temperature and flowrate could be observed, and finally, (iii) any correlation of residuals with time was to be split, as well as possible, into an equal number of positive and negative residuals. This was to be useful in estimating catalyst activities.

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* This is inherently observed in Figure 6.2-2.

In attempting to attain the minimum objective function by means of the Rosenbrock search, numerous local minima were encountered. These were generally characterized by a local minimum sum of squares of deviations, but the residuals of the mole fractions of one or more of the responses was correlated with temperature. In this case, a grid search was extremely helpful in scanning the response surface and enabling new starting parameter values to be found. These new starting parameter values were chosen in a region with less correlation among residuals. These regions, also, always produced a lower value of total sum of squares of differences.

The iterative procedure of considering the butane, propane, and ethane groups, in turn, was continued until essentially no change in the parameters, and no further decrease in the sum of squares was observed. At this point correlation of residuals with feed ratio was removed by an unconstrained search on the exponents of the partial pressure of hydrogen in the butane and propane rate expressions. After these exponents were changed, an eight variable search, using the Rosenbrock routine and the parameters in the three groups, showed negligible changes in the parameters because of the updating of exponent parameters. Any remaining correlation of residuals with time was to be removed by re-estimating catalyst activities.

6.2.2.3 ESTIMATING CATALYST ACTIVITIES

Catalyst activity is defined as the ratio of the rate of reaction under standard operating conditions to the rate of reaction under the same operating conditions, but at an arbitrary constant catalyst condition. This may also be expressed as the ratio of rate constants.

Thus, the catalyst activity may be defined as:

$$\text{ACTIVITY} = \frac{k}{k_0} \qquad 6.67$$

where k is the reaction rate constant observed at any time and at standard operating conditions and k_0 is the reaction rate constant at the same operating conditions and at a standard catalyst condition.

The catalyst activity is assumed to affect the reaction rate in a linear way. Since the reaction rate is proportional to the partial pressures of the reactants, the effect of catalyst activity on the conversion of the reactants is non-linear. Thus, the ratio of conversions, used as initial estimates of catalyst activity, can only be considered first approximations to the ratio of rate constants.

It is to be noted that the calculated catalyst activity depends on the form of the kinetic model and parameter values. The calculated catalyst activity represents the true catalyst activity if the model and the parameters are correct. It is, therefore, necessary to iterate on the catalyst activities of the centre-point runs. This iterative procedure involves estimating a set of catalyst activities for the centre-point runs; interpolating from these centre-point runs the catalyst activities of the experimental design-point runs; using these catalyst activities and the model to obtain estimates of the kinetic parameters; and finally using these estimates of the kinetic parameters and the model (which would produce correlations of the residuals of the butane mole fractions with time) to re-estimate the catalyst activities

TABLE 6.2-2

CENTRE-POINT RUNS USED FOR ITERATION ON CATALYST ACTIVITY

RUN NO.	TEMPERATURE (°C)	FEED FLOWRATE (CM.^{3}/SEC.)	H_2/C_4 FEED MOLAR RATIO	CONVERSION OF BUTANE (PERCENT)
4	258.7	1.39	7.14	15.7
9	258.7	1.61	6.36	27.4
17	258.6	1.45	7.04	50.1
25	258.7	1.44	7.08	53.5
30	258.7	1.48	7.37	50.4
38	258.6	1.45	7.84	66.2
50	258.6	1.49	7.08	72.3
57	258.5	1.44	7.13	67.2
66	258.6	1.46	7.00	69.0
80	258.6	1.44	7.15	76.3
86	259.2	1.40	7.67	79.4
93	258.1	1.45	6.63	76.3
105	258.1	1.44	7.10	79.9
112	258.5	1.45	6.71	82.1
119	258.5	1.37	8.88	82.0
126	258.9	1.41	8.05	83.9
135	258.2	1.42	7.50	83.4
146	258.4	1.44	6.75	87.0
150	257.9	1.43	6.97	82.4

of the centre-point runs. This iteration must be continued until no correlation of residuals is detected with time and no further change in the catalyst activities of the centre-point runs is observed upon continued iteration. This iteration procedure will now be discussed in more detail.

It was difficult to set operating conditions precisely for each centre-point run. For this reason, a single replicate was chosen from each centre-point experiment such that the measured independent variable settings were close to those chosen to represent the standard operating conditions. Table 6.2-2 shows the centre-point runs used and the operating conditions.

In estimating the catalyst activities, k values rather than k/k_0 values were searched upon. The value of k_0 was chosen arbitrarily as 65. in the first iteration involving conversions as the estimates of activities. For the second and subsequent iterations a k_0 value of 59. was chosen. This value was chosen as a convenience so that in graphs (to be described) which follow the iterations, curves will not cross a 45.° line.

After the initial estimates of the catalyst activities were chosen (as described in a previous part of this section), and after kinetic parameters were estimated using the activities and the experimental design-point runs, the centre-point catalyst activities were re-estimated. For each of these centre-point runs, given the model and a set of parameters, different k/k_0 values were chosen over an appropriate range. The kinetic model was calculated at these k/k_0 values and the residuals of the butane mole fractions were then plotted

FIGURE 6.2-2

ITERATION ON CATALYST ACTIVITY

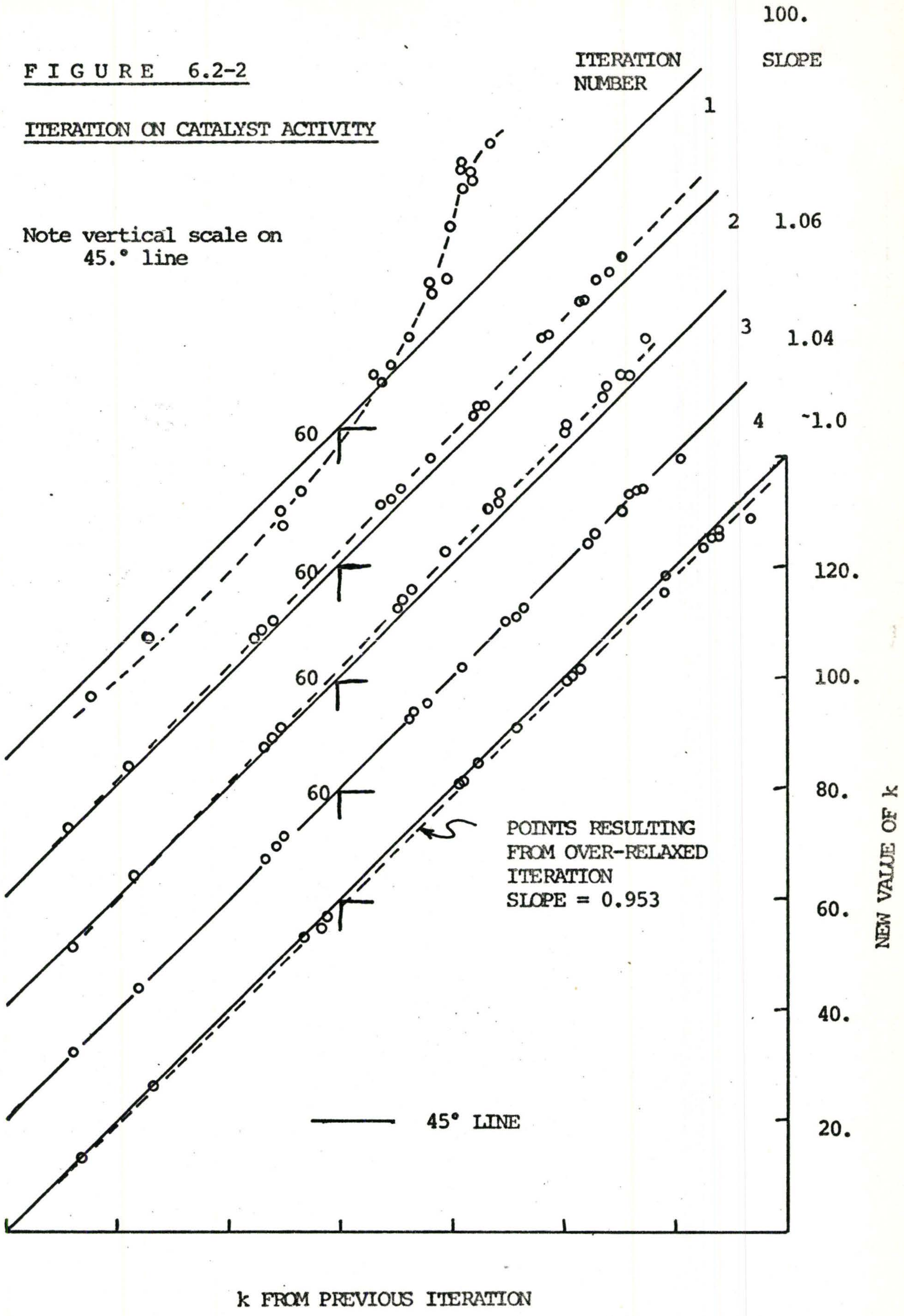


TABLE 6.2-3

k VALUES OF CENTRE POINTS FOR CATALYST ACTIVITY ITERATIONS

RUN NO.	CONVERSION OF BUTANE (initial catalyst activity)	FIRST ITERATION	SECOND ITERATION	THIRD ITERATION	FOURTH ITERATION	OVER-RELAXED ACTIVITIES	RESULTING ACTIVITIES
4	15.5	11.7	12.4	12.1	12.4	14.0	13.6
9	25.5	22.8	23.7	24.0	24.1	27.0	26.5
17	50.0	45.0	47.0	47.5	47.7	54.0	53.3
25	53.5	48.2	50.0	50.6	51.1	58.0	57.0
30	50.5	56.8	58.3	49.0	50.6	57.5	55.0
38	66.0	69.7	72.0	73.1	73.5	82.5	81.4
50	72.6	76.8	79.1	82.4	82.1	92.0	92.0
57	67.2	68.5	71.2	73.1	73.0	82.0	81.8
66	69.0	71.1	73.8	76.0	75.9	85.0	84.6
80	76.3	84.4	87.6	90.6	90.8	101.0	100.2
86	79.0	86.9	89.0	91.5	90.7	102.0	101.0
93	76.2	85.5	89.5	93.0	92.3	103.8	101.6
105	80.0	96.5	101.2	105.0	105.0	118.6	115.5
112	82.0	96.9	101.3	105.5	105.5	119.0	119.0
119	82.0	108.9	112.8	114.5	114.6	128.5	125.0
126	83.9	104.9	108.3	111.0	110.7	125.0	123.5
135	83.4	106.2	111.1	115.0	114.1	123.5	127.0
146	87.0	111.0	115.8	121.5	119.3	134.0	128.1
150	82.4	103.0	108.1	112.9	113.1	127.7	125.5

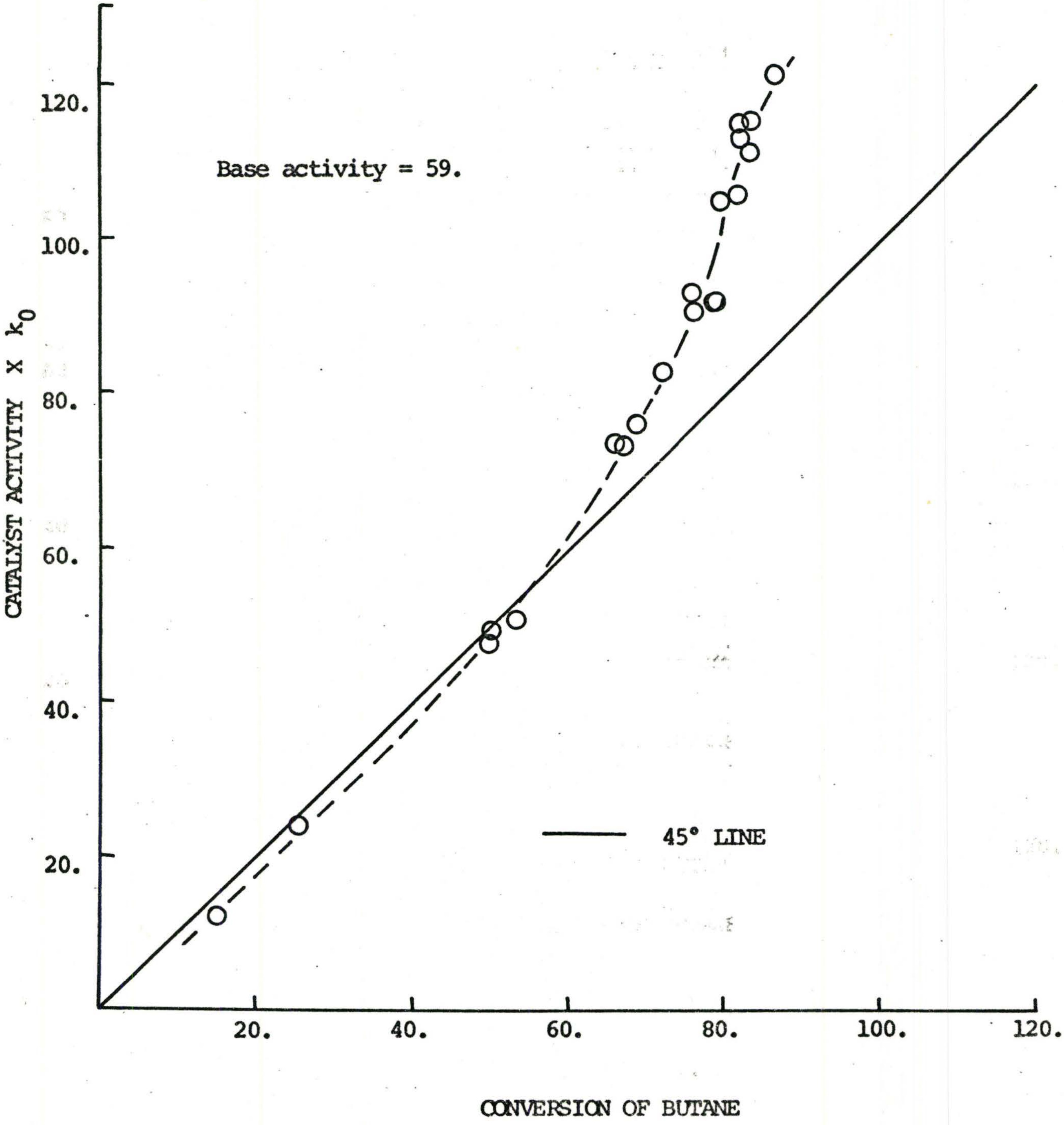
against k. One such plot was made for each centre-point run. The value at which the resulting curve crosses the abscissa (residual = 0) represents the true k/k_0 or activity value assuming that the model and the parameter values are true. This statement may be made since all the centre-point experiments were performed at a standard operating condition, and therefore, if residuals occur and are correlated, they may be said to be correlated with time, and hence, catalyst activity. Thus, removing error by re-estimating k/k_0 for each centre-point run is actually removing error by obtaining a better estimate of catalyst activity.

For each centre-point run, the new value of k_0 obtained by the above method was plotted against the one used in the previous iteration (the very first being c). New activities for use with the experimental design points for re-estimating parameters were found from this curve, knowing the original activity values.

After the kinetic parameters were re-estimated using these experimental design points, these new parameters were used with the centre-point runs to re-estimate the catalyst activities, k/k_0. This iteration was continued until, for the centre-point runs, the plot of the new k values versus the k values from the previous iteration approached a 45.° line. These curves are shown in Figure 6.2-2. The k values of the centre points for these iterations are also given in Table 6.2-3. A large change in the k values may be observed for the first iteration with relatively much smaller changes occurring in subsequent iterations. It appears that covergence had been reached after the third iteration. To check this, instead of re-estimating

FIGURE 6.2-3

CATALYST ACTIVITY VERSUS CONVERSION OF BUTANE FOR CENTRE - POINT RUNS



parameters using the k values from the fourth iteration, over-relaxed k values were used. The resulting centre-point activities are shown in Table 6.2-3. These activities tend to decrease. This is also evidenced by a slope of less than one (Figure 6.2-2) in plotting the resulting activities versus the over-relaxed activities. This was taken as sufficient evidence that the correct catalyst activities had been converged upon. A plot of the final catalyst activities for the centre-point experiments, versus the conversion of butane, is given in Figure 6.2-3.

The parameters changed during the catalyst activity iterations. Since the propane part of the butane model was revised during these iterations only changes in the butane activation energy will be discussed. The best estimates of the butane activation energy changed in the following way.

	ΔE_B (k.cal./gm. mole)
Initial Estimates of k (conversion of butane)	48.11
First Iteration	58.00
Second Iteration	54.454
Third Iteration	56.900
Over-relaxed k values	56.747

An extremely large jump in activation energy is noted in the first iteration and in subsequent iterations the activation energy stabilizes.

6.2.2.4 TESTING THE MODEL BY EXTRAPOLATION

During the experimental program, essentially 100.% conversion runs were obtained at the high temperature levels; these were not used for parameter estimation. They could be used, however, to test the model by extrapolating to conditions outside of the range of those used to estimate the parameters. This test proved fruitful in that an initially proposed propane part of the butane cracking model broke down completely on extrapolating. Such was not the case for the subsequently modified model, as will be shown in section 6.3.1 of this thesis.

PARAMETER ESTIMATES

The kinetic parameter estimates obtained for the butane model using the parameter estimation technique described in this section are:

ΔE_B = 56.900 (k.cal./gm. mole)

ΔE_{P1} = 54.3339 (k.cal./gm. mole)

ΔE_{P2} = 37.5794 (k.cal./gm. mole)

ΔE_E = 16.8528 (k.cal./gm. mole)

$\log_{10}. k_B$ = 17.703 (moles/sec. vol. reactor atm.$^{(.78)}$)

$\log_{10}. K_{P1}$ = 16.1328 (moles/sec. vol. reactor atm.$^{(.78)}$)

$\log_{10}. K_{P2}$ = 14.9729 (dimensionless)

$\log_{10}. k_E$ = 6.9776 (dimensionless)

n = 1.59

n' = 2.47

6.2.3 PARAMETER ESTIMATION FOR THE PROPANE HYDROGENOLYSIS MODEL

The parameter estimation strategy for the propane model was much simpler than for the butane model because no significant catalyst activity changes were observed during the propane experiments and because only six parameters were to be estimated. Much of the propane parameter estimation was carried out in the same way as that for butane. The initial parameter estimates and the weighting matrix were determined in the same way. The Rosenbrock direct search routine with a similar objective function was also used.

There was, however, one major difference in strategy. In the butane parameter estimation work, strong correlations among residuals were removed by starting the direct search routine at different parameter estimates. In the propane parameter estimation work, these correlations could be removed by using the linearization technique described in section 6.2.1 of this chapter.

To begin the parameter estimation, initial estimates were obtained by assuming the reactor operated differentially. Better parameter estimates were then obtained by non-linear regression using the Rosenbrock search routine. The algorithm for the non-linear regression technique is shown in Figure 6.2-4.

Most precise estimates were then obtained by two methods; the linearization technique and minimizing the weighted sum of squares of differences between observed and calculated mole fractions. The weighting matrix was obtained in the same way as in the butane parameter estimation, except that in this case all the weights for the propane mole fractions were doubled. This was done to determine the

FIGURE 6.2-4

ALGORITHM FOR NON-LINEAR PARAMETER ESTIMATION

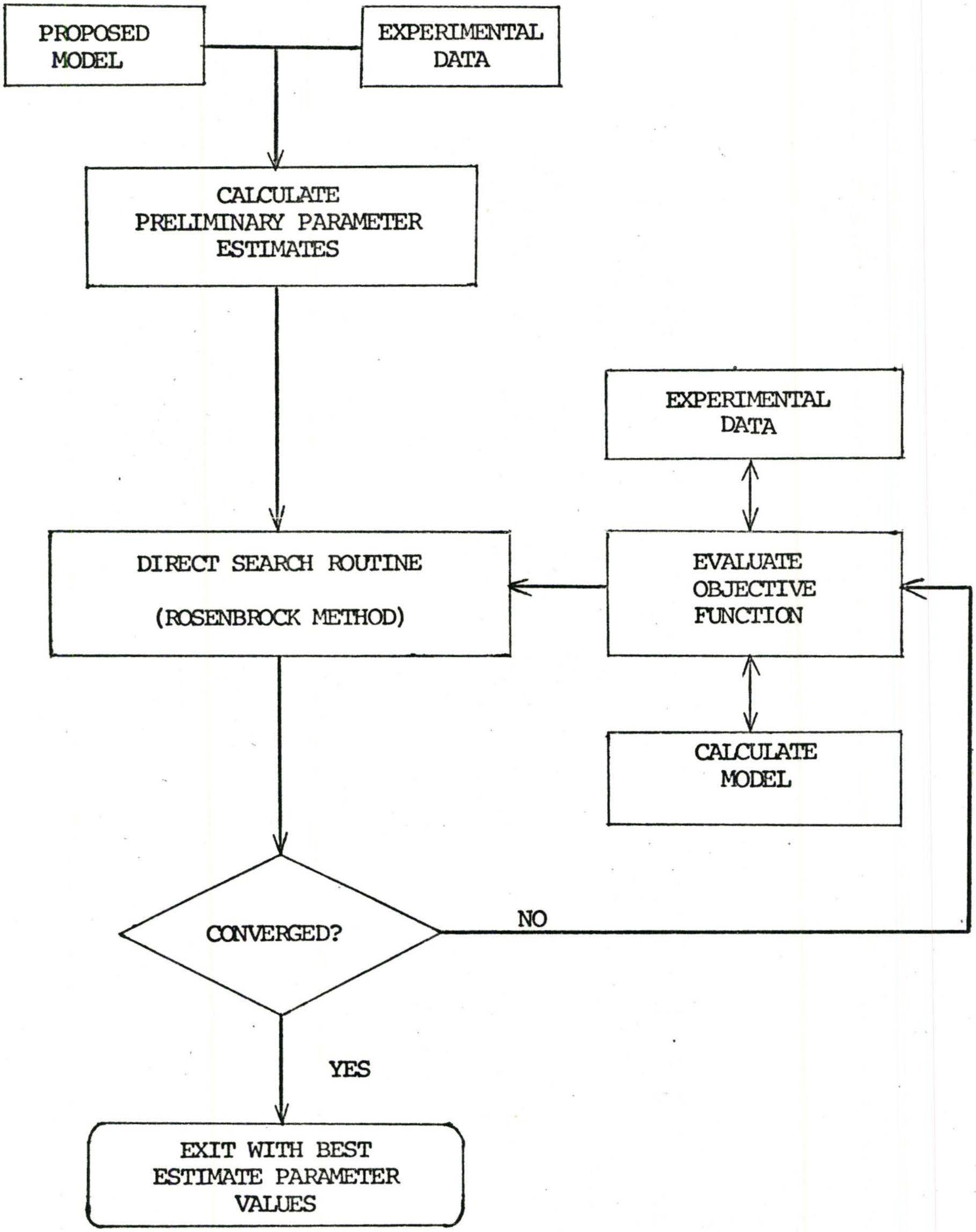


FIGURE 6.2-5

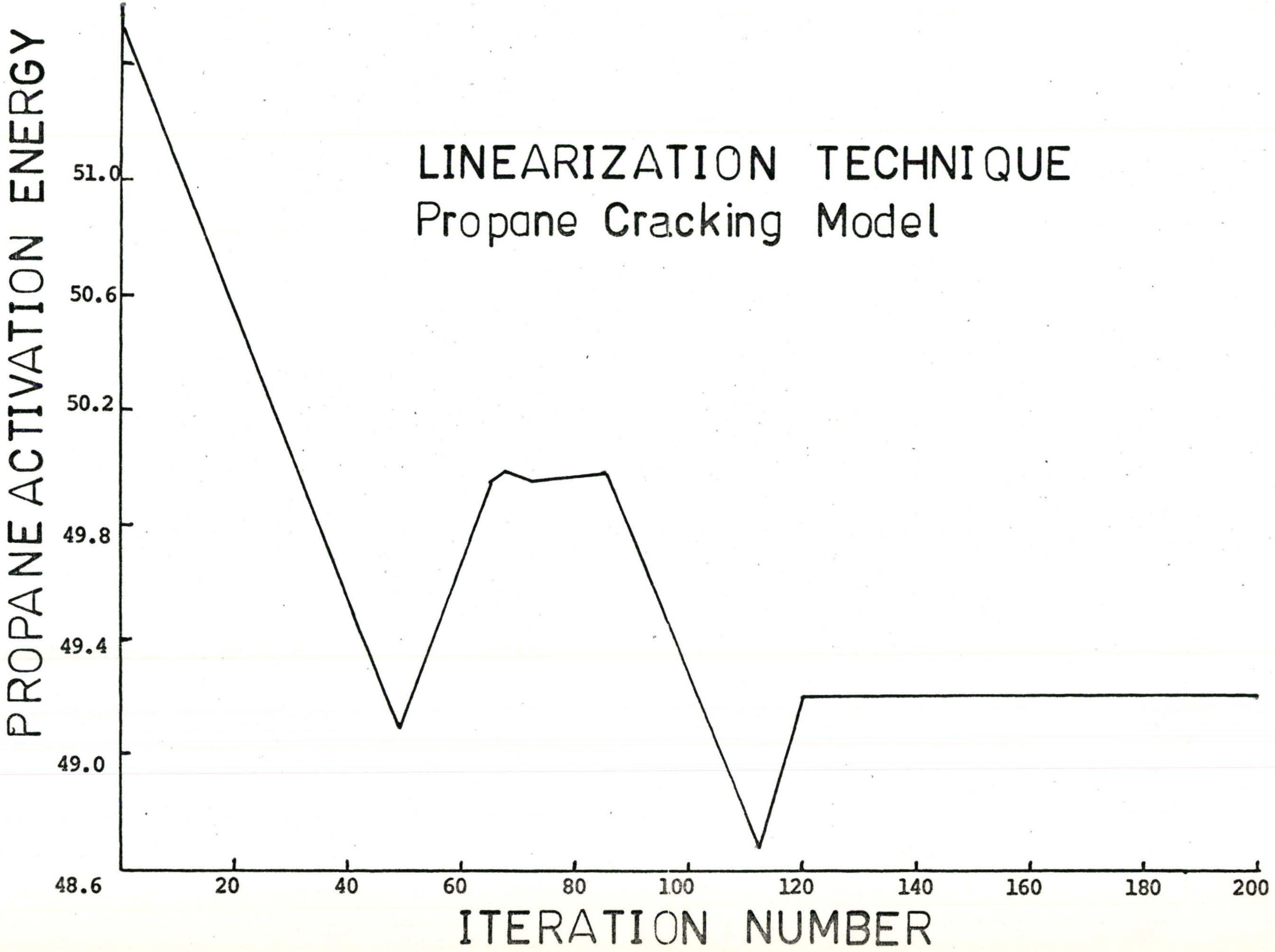

LINEARIZATION TECHNIQUE
Propane Cracking Model
PROPANE ACTIVATION ENERGY
51.0
50.6
50.2
49.8
49.4
49.0
48.6
20
40
60
80
100
120
140
160
180
200
ITERATION NUMBER

FIGURE 6.2-5 CONT'D.

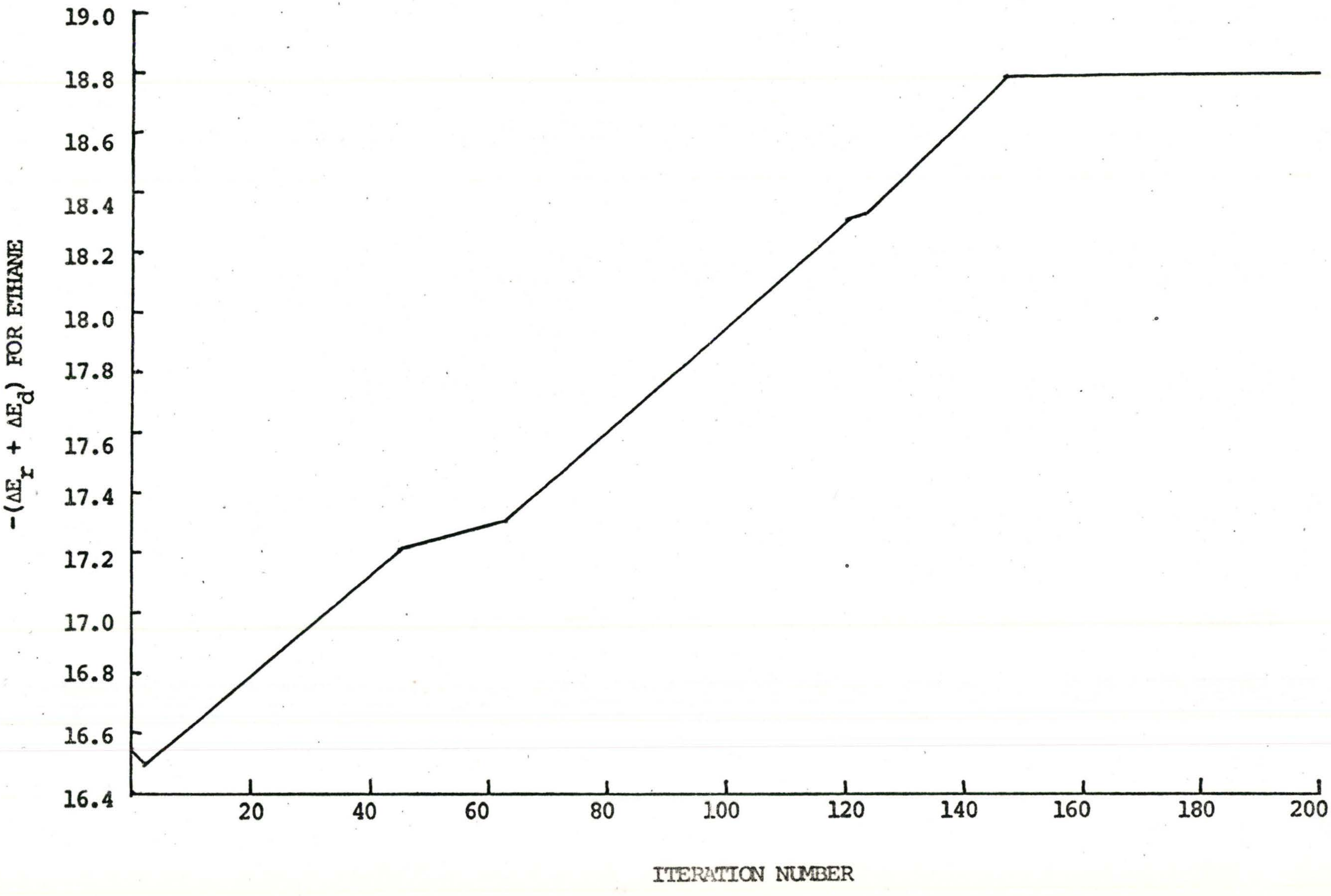


FIGURE 6.2-5 CONT'D.

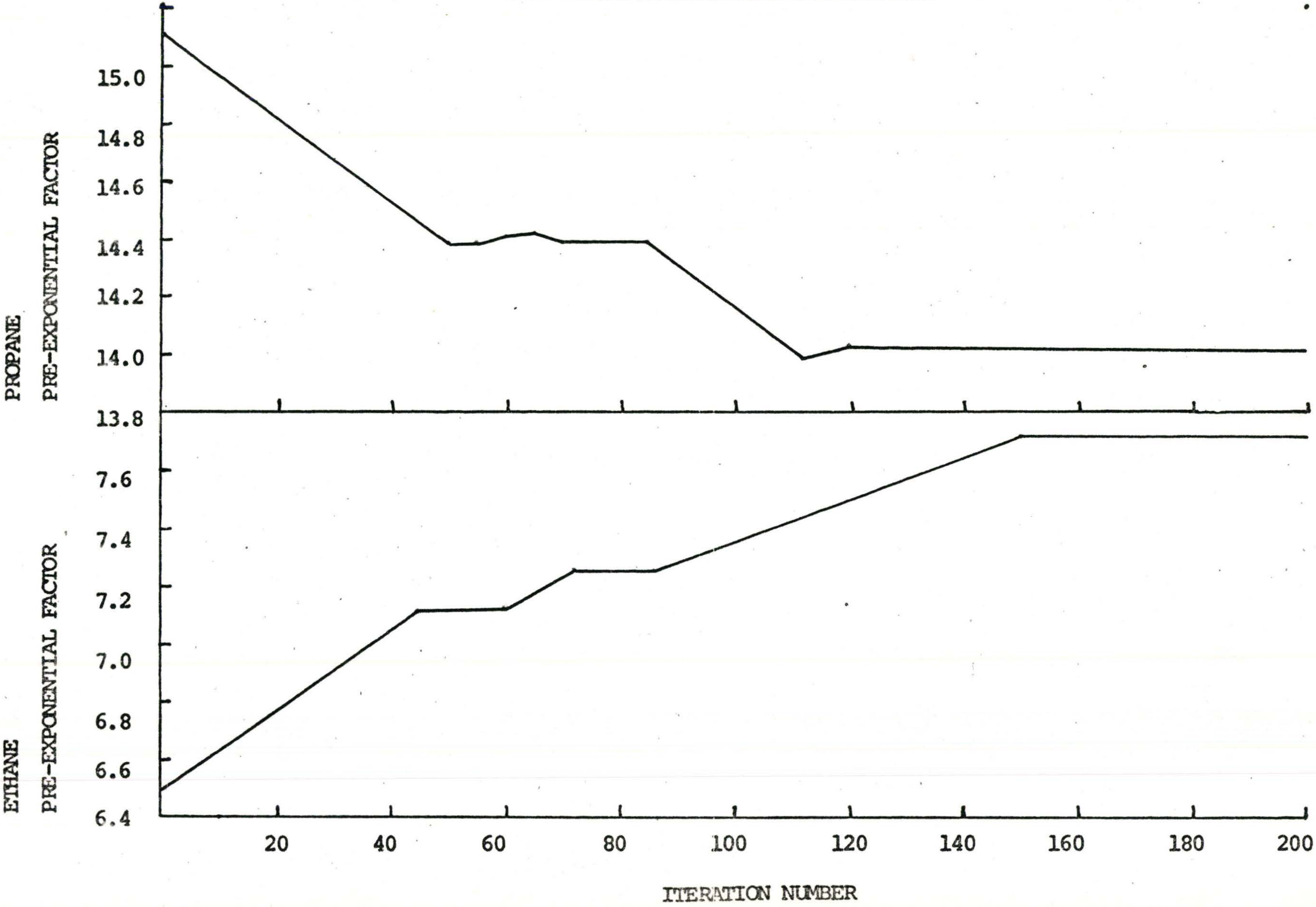


FIGURE 6.2-5 CONT'D.

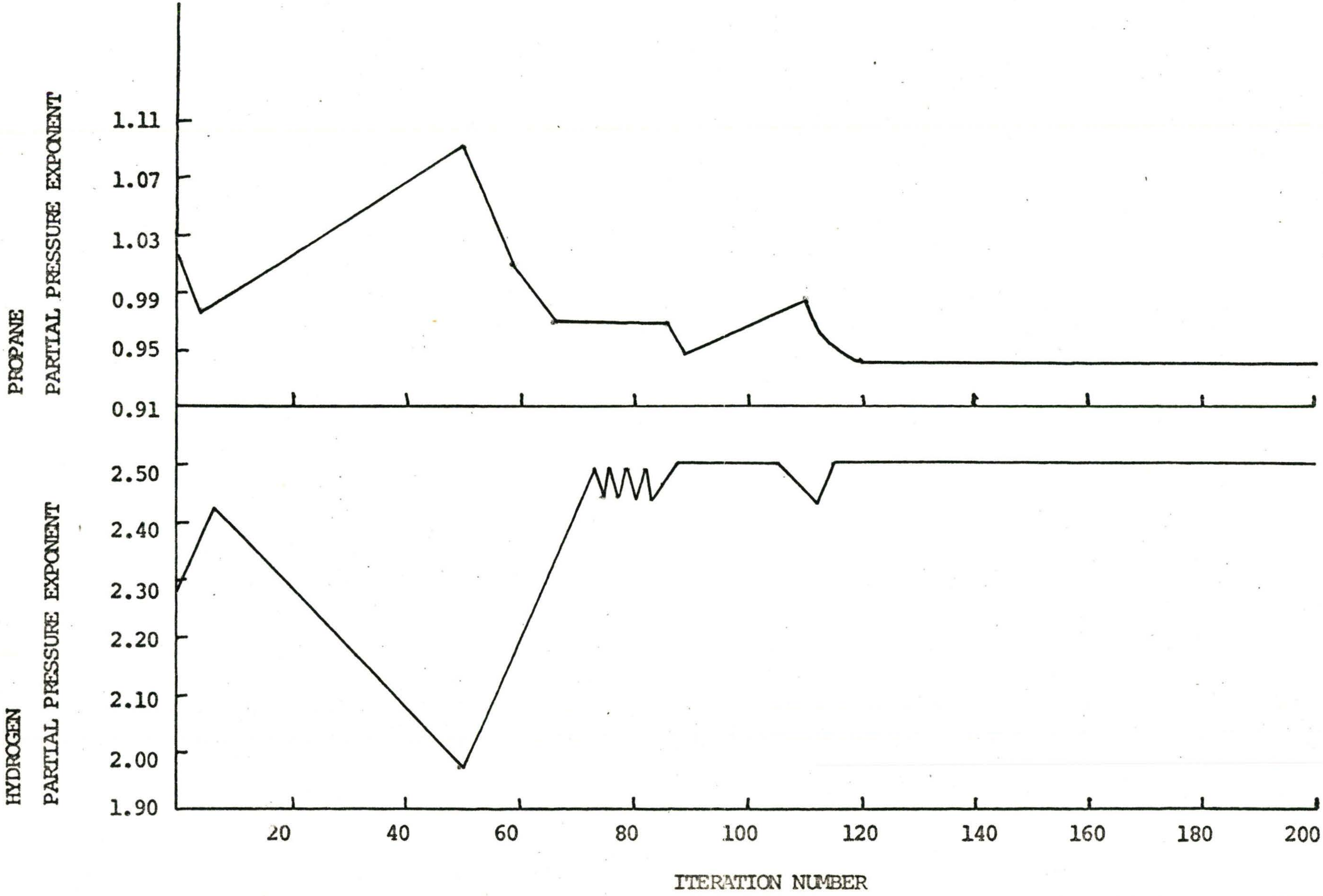


TABLE 6.2-4

COMPARISON OF LOCAL LINEARIZATION AND DIRECT SEARCH* METHOD

		LOCAL LINEARIZATION	DIRECT SEARCH
	ΔE_P	49.183	49.183
	ΔE_E**	18.791	18.449
PARAMETER	$\log k_P$	14.023	14.036
VALUES	$\log k_E$	7.719	7.557
	m	0.94	0.94
	n	-2.5	-2.5
WEIGHTED SUM	C_1	0.32	0.42
OF	C_2	0.59	0.60
SQUARES OF	C_3	0.36	0.09***
DIFFERENCES OF	H_2	0.01	0.01
COMPONENTS	Total	1.29	1.12

* Rosenbrock search technique was used with propane residuals weighted twice as much as the ethane residuals.

** $\Delta E_E = \Delta E_{reaction} - \Delta E_{desorption}$

*** This arises because of greater weight on C_3

effect of weighting the propane response more than the responses of the other components. These two methods were used since the linearization technique effectively weighs all data equally and in minimizing the weighted sum of squares by direct search, more weight was placed on the propane component. Figure 6.2-5 shows the parameter values versus iteration number for the linearization technique in estimating the six parameters in the propane cracking model. The paths show sharp changes in direction since a very small maximum percent change per iteration (0.1%) was allowed for each parameter. It was felt that this would stabilize the solution and prevent divergence. Instabilities were in fact observed if this maximum percent change per iteration was increased 0.5%. This observation reflects the sensitivity of the predicted responses to the parameters, especially the activation energies.

The differences in the parameter estimates and the sum of squares of weighted differences in mole fractions is shown in Table 6.2-4. Although unequal weights were used in the direct search method, equal weights are used in Table 6.2-4 in calculating the weighted sum of squares for the direct search method, so as to obtain a basis of comparison.

6.2.4 PARAMETER ESTIMATION FOR MODELS DESCRIBING CATALYST ACTIVITY CHANGE

The models for which the parameters are to be estimated are developed in section 6.1.4. The parameters were estimated by means of a direct search on the parameters to minimize the usual sum of squares objective function. The algorithm used is shown in Figure 6.2-4 in the previous section. Temperature, one of the independent variables in the catalyst activity models was recorded at 12-minute intervals throughout the continuous 80-hour period covering all of the experimental runs. These values are given in Table 5-2 and Figure 6.3-9.

Catalyst activity, the dependent variable, was calculated as a function of time by solving numerically equations 6.32 and 6.34 which are analytical solutions of the proposed differential equation models. The experimental catalyst activities were the final k/k_0 values obtained in the catalyst activity iteration described in section 6.2.2.3 of this thesis.

Because of the small time increments and because temperature always varied linearly within these time increments, the trapezoidal rule was assumed satisfactory in performing the integrations in equations 6.32 and 6.34.

In searching for the parameter estimates in both models,several initial parameter values were used to ensure that the minimum in the objective function was acutally the global rather than just a local one.

The models along with the parameter values obtained by this procedure are:

(i) model assuming constant maximum catalyst activity:

$$\frac{dc}{dt} = 8.05 \text{ X } 10.^{15} \exp \{-47700./RT\} \; . \; [145. - c] \qquad 6.68$$

(ii) model assuming that the maximum catalyst activity is a function of temperature:

$$\frac{dc}{dt} = 7.26 \text{ X } 10.^{3} \exp \{-17400./RT\} \; . \; [7.5 \; (T - 518.) - c] \qquad 6.69$$

6.2.5 "CONFIDENCE LIMITS" ON ESTIMATED PARAMETERS

The procedures for estimating the parameters for the kinetic models for butane and propane hydrogenolysis in a fixed-bed reactor and for the models describing the changing catalyst activity with time have been described. It remains to demonstrate the "confidence intervals" on these parameters; this is done by considering these confidence intervals for the ten parameters in the butane hydrogenolysis model. "Confidence intervals" for the parameter estimates of the propane model may be found in an analagous way. Because of the functional form of this model, the type of data used to estimate the parameters and the order of magnitude of the parameter values, the limits of propane parameter values should be of the same order of magnitude as the parameters in the butane cracking model.

In estimating the parameters in the models proposed to describe the catalyst activity change, k values, obtained by iterating on catalyst activity, were used as observations. Because of the way these k values were determined, it is not immediately obvious how one would go about estimating the covariance matrix for these observations. In order to obtain estimates of the errors in the parameters using the Likelihood ratio method, at least three courses of action seem open: (i) an attempt at estimating the covariance matrix for the k value "observations" could be carried out, (ii) likelihoods could be maximized with respect to the error variance, (iii) or likelihoods which have the effects of the error variance integrated out may be used. Time did not permit the estimation of the errors in the parameters for these models.

In estimating the "confidence intervals" for the parameters in the butane cracking model, the likelihood ratio method* was used. This method is discussed in Section 6.2.5. A much more rigorous discussion of this method is given by Barnard, Jenkins and Winsten$^{(B18)}$ and Jenkins and Watts$^{(J1)}$. The term "confidence interval" is used loosely in this thesis to describe a region in parameter space bounded by contours of equal likelihood ratio. The value of the likelihood ratio chosen to describe these limits was arbitrarily chosen as 10., although as will be shown later, with such large ratios possible, values as high as 60. may be considered small.

In order to evaluate the likelihood ratios, a covariance matrix or weighting matrix must be obtained to take into account the errors in the observations. In this study, three matrices, each evaluated independently were available to describe these errors. An analytical or a priori estimate of the covariance matrix is given in Appendix H. This appendix also contains a statistical or a posteriori formulation of this matrix. A third formulation of this weighting matrix is described in Section 6.2.2.1. The elements of this matrix were used in the parameter estimation and this matrix will be described as the "equal-weighting matrix", that is, a matrix which puts equal weight on all the data. The most correct form of the weighting matrix that should be used in parameter estimation and in obtaining confidence intervals of parameters is the inverse of the analytically formulated covariance matrix. The equal-weighting matrix was used throughout for two reasons. Firstly, since essentially two levels of the most important variable, temperature, were used in the parameter estimation, it was felt that the parameter estimates would be insensitive to the

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* Interval estimates based on likelihood ratio were used because of the method's capability of direct generalization to any set of joint interval estimates.

TABLE 6.2-5

"CONFIDENCE INTERVALS"* FOR BEST ESTIMATE PARAMETER VALUES IN BUTANE HYDROGENOLYSIS MODEL

PARAMETER	WEIGHTED LEAST SQUARES ESTIMATES	LOWER LIMIT	UPPER LIMIT
ΔE_B	56.900	56.891 (-.009)	56.907 (+.007)
ΔE_{P1}	54.334	54.283 (-.051)	54.370 (+.036)
ΔE_{P2}	37.579	37.534 (-.045)	37.609 (+.030)
ΔE_E	16.853	16.817 (-.036)	16.879 (+.026)
$\log_{10} k_B$	17.703	17.700 (-.003)	17.706 (+.003)
$\log_{10} K_{P1}$	16.133	16.117 (-.016)	16.154 (+.021)
$\log_{10} K_{P2}$	14.973	14.961 (-.012)	14.991 (+.019)
$\log_{10} k_E$	6.978	6.966 (-.012)	6.990 (+.012)
n	1.59	1.57 (-.02)	1.66 (+.07)
n'	2.47	2.36 (-.11)	2.58 (+.11)

* The confidence intervals are determined by a likelihood ratio of 10 and are evaluated at the best estimate values of the remaining parameters.

weighting matrix. That is, for two levels of an independent variable, the parameter estimates are independent of the weighting factors. A straight line will always go through two points regardless of the error limits on these two points. If it is realized that essentially two levels are available and thus, all data should be believed equally, an equal weighting matrix seems reasonable. If data are weighted unequally, approximately the same parameter values will be estimated; however, now the minimum objective function must be found to more digits since contributions of lower weighted residuals, that must be taken into account, will affect the weighted residual sum of squares to a much lower degree than with the equal weighting matrix. This second consideration is important here because of the time required to evaluate the objective function.

Four different investigations are presented below to give some idea of the "confidence intervals" of, and the correlation among, the estimates of parameters for the butane hydrogenolysis model.

(i) "CONFIDENCE LIMITS" OF THE PARAMETERS IN THE BUTANE CRACKING MODEL

The "confidence limits" were obtained in the following way. The weighting matrix was that one which put equal weight on all the observations. The maximum likelihood was that likelihood calculated using the parameter estimates which minimized the weighted sum of squares of differences between observed and calculated mole fractions given by equation (6.49). The calculated likelihood ratio was then the ratio of this maximum likelihood to a smaller likelihood caused by the perturbing a parameter away from its best estimate value. The "confidence limits" of a parameter was, then those values of the parameter for which the likelihood ratio, calculated at the best estimate values of the remaining parameters, was equal to about 10. Thus, the "confidence limits" for each parameter were evaluated by perturbing each parameter about its best estimate value and calculating the likelihood ratio. The "confidence limits" obtained in this way are given in Table 6.2-5.

TABLE 6.2-6

"CONFIDENCE INTERVALS"* FOR BUTANE ACTIVATION ENERGY USING THREE DIFFERENT WEIGHTING MATRICES

		WEIGHTING MATRICES USED		
		Equal - Weighting Matrix	Analytically Formulated Covariance Matrix	Statistically Formulated Weighting Matrix
ΔE_B evaluated at parameters given below		56.900	54.348	56.4431
Lower limit of ΔE_B		56.891 (-.009)	54.338 (-.010)	56.4326 (-.012)
Upper limit of ΔE_B		56.907 (+.007)	54.356 (+.008)	56.4530 (+.011)
Remaining Parameter Values	ΔE_{P1}	54.3339	54.3339	54.3339
	ΔE_{P2}	37.5794	37.5794	37.5794
	ΔE_E	16.8528	16.8528	16.8528
	$\log_{10}k_B$	17.703	17.5155	17.5155
	$\log_{10}K_{P1}$	16.1328	16.1328	16.1328
	$\log_{10}K_{P2}$	14.9729	14.9729	14.9729
	$\log_{10}k_E$	6.9776	6.9776	6.9776
	n	1.59	1.59	1.59
	n'	2.47	2.47	2.47

* A likelihood ratio of 10 was used to describe the limits of the parameter values.

Table 6.2-5.

(ii) COMPARISON OF "CONFIDENCE LIMITS" FOR THE ACTIVATION ENERGY OF BUTANE

For this investigation the three weighting matrices described previously were used to evaluate the "confidence intervals" in order to get some idea of the differences that might arise for example, in the activation energy of butane. To do this, best estimates of the activation energy of butane were obtained in turn using each of these different covariance matrices. The remaining parameters were held at their best estimate values found by using the equal-weighting matrix. The "confidence limits" of the best estimate activation energies were then calculated as described in the previous section, using the respective covariance matrices.

The three best estimates of the activation energy of butane and their respective "confidence limits" are given in Table 6.2-6. It may be noted that the three estimates, and the deviations of the upper and lower limits of the parameters about their respective best estimate values, are quite similar. This would, in a rather rough sort of way, justify the use of the less-correct equal-weighting matrix in estimating the parameters and in estimating the errors in these parameters.

It must be noted that there is no direct basis of comparison of the "confidence limits" shown in Table 6.2-6. This is because, for each weighting matrix, the likelihood ratio was not evaluated at the best estimate parameter values for the particular weighting matrix. This means that the "confidence limits" for the activation energy of butane were not evaluated at the same relative position in parameter space for the three cases. Comparison is, however, justified for the following two reasons. Firstly, only order of magnitude comparisons are being sought. Secondly, as shown in the following section, the "confidence intervals" for the activation energy of butane are approximately constant for any value of the pre-exponential factor. This constancy appears to hold until very close to the combination of parameters that yield the maximum allowable likelihood ratio. For this reason it is suspected that the "confidence interval" at some point in parameter space is an approximation to the confidence interval at the point in parameter space described by the best-estimate parameter values for the particular weighting matrix.

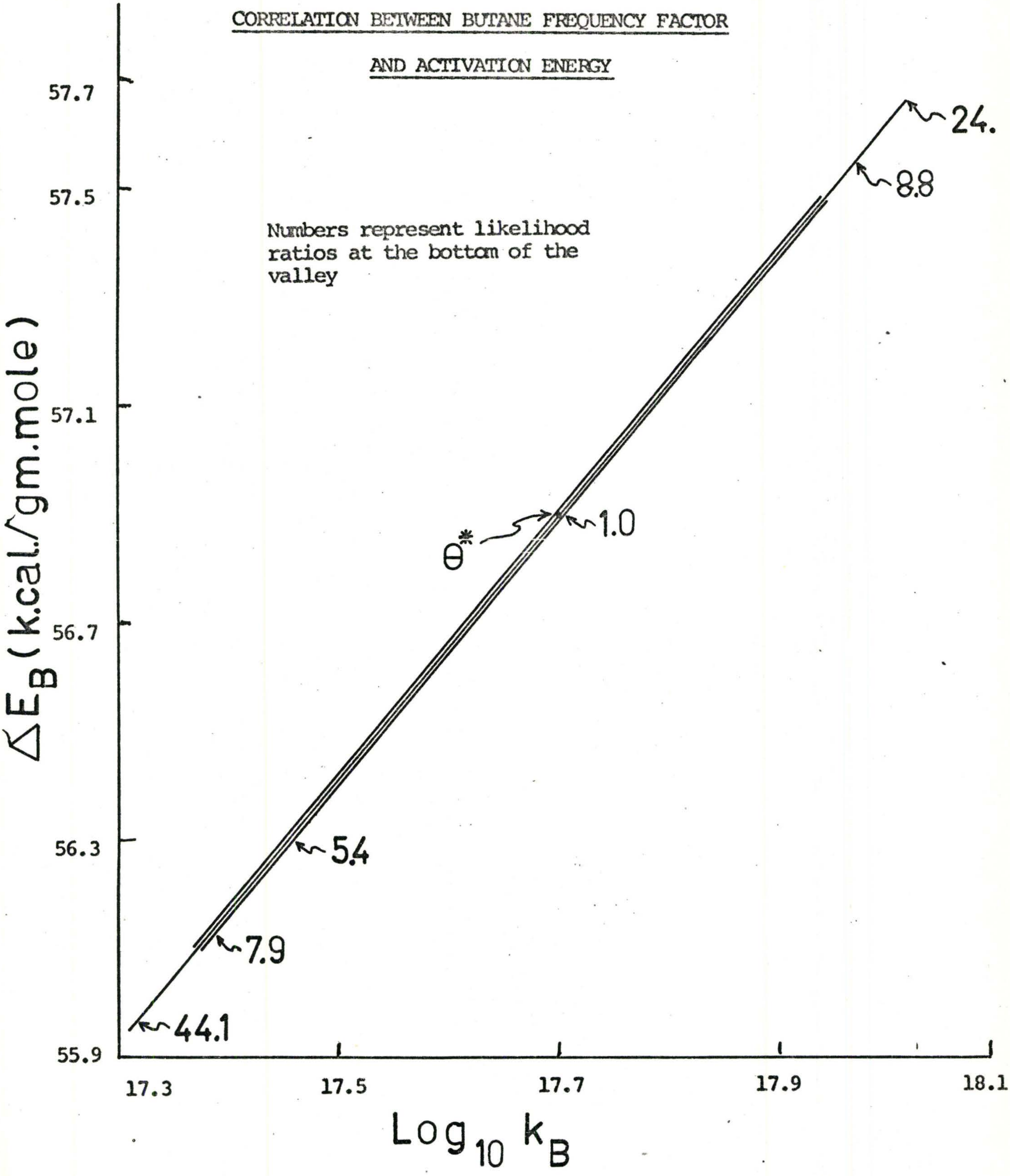
In summary, then, all three weighting matrices appear to give approximately the same activation energies of butane and the same order of magnitudes for the "confidence intervals".

(iii) CORRELATION OF THE FREQUENCY FACTOR AND THE BUTANE ACTIVATION ENERGY IN THE BUTANE RATE EXPRESSION

Because of the functional form of the expression for the Arrhenius rate constant it appears reasonable that some correlation between the frequency factor and the activation energy could occur. That is, it would appear that over a restricted range, various combinations of the frequency factor and activation energy could produce almost the same predictions. The purpose of this investigation was to examine the extent of correlation between these two parameters

FIGURE 6.2-6

CORRELATION BETWEEN BUTANE FREQUENCY FACTOR AND ACTIVATION ENERGY



Numbers represent likelihood ratios at the bottom of the valley in the butane rate expression.

To accomplish this, the likelihood ratio response surface was examined in the plane of the butane frequency factor and the butane activation energy. This surface appeared to be a valley with extremely steep sides and is shown in Figure 6.2-6. The solid line represents the locus of the bottom of the valley. This locus was found by means of grid searching and searching in one direction at a time by means of the generally accepted Golden Section search method$^{(W4)}$. The locus appears as a straight line because of the log transformation performed on the pre-exponential factor. The lines on either side of this locus, represent points on the response surface which have a likelihood ratio values of ten. These lines are extremely close to the locus of the bottom of the valley and appear to run essentially parallel to this locus until the values of the likelihood ratio at the bottom of the valley approach ten. The numbers given in Figure 6.2-6 represent values of the likelihood ratio along the locus.

It may be noted that the activation energy of butane appears significantly correlated from approximately 56.05 k.cal./gm. mole to approximately 57.60 k.cal./gm. mole with $\log_{10.} k_B$.

(iv) CORRELATION OF PARAMETERS IN THE PROPANE PART OF THE BUTANE HYDROGENOLYSIS MODEL

In following the procedures of estimating the parameters in the model for butane hydrogenolysis it was suspected that severe correlation existed between the two sets of activation energies and pre-exponential factors in the expression describing the rate of production of propane.

The purpose of this section is to check statistically this suspicion.

To accomplish this, a value of 30.00 was chosen for ΔE_{P2} (compared to the best estimate of 37.58). Then, using the best estimates of the remaining parameters, a three-variable search was performed on ΔE_{P1}, K_{P1} and K_{P2}. The best estimate values for these parameters were found to be:

ΔE_{P1} : 40.007
$\log_{10.} K_{P1}$: 10.208
$\log_{10.} K_{P2}$: 11.897

The weighted sum of squares obtained using these parameters was compared with the weighted sum of squares obtained by using the parameters given in Table 6.2-5 by means of a likelihood ratio test. The likelihood ratio was found to be 60., of course in favour of the best parameter values. In view of the large differences in parameter values (e.g. 54.334 and 40.007 for ΔE_{P1}) and since the likelihood ratio changes quickly with changes in one parameter, this relatively small likelihood ratio of 60. illustrates substantial correlation. A more detailed explanation of this observed correlation is given in Section 6.3.1.

DISCUSSION

Four different investigations have been described to examine the "confidence intervals" of the best estimate parameters in the butane cracking model. If further examination of the errors in the parameter estimates is desired, computer programs are available (see Appendix K) and further investigation may be easily carried out.

The most important observation to be made from this section is that the errors in the parameter estimates are extremely small. This means that for the experimental data used in estimating the parameters in the butane model, the parameters may be estimated extremely precisely. This precision has been checked by using three independently obtained weighting matrices which account for the errors in the observations. It is felt that this precision reflects the mathematical form of the model, i.e., it is due to the transformations inherent in the reactor and kinetic model. It means that the calculated sum of squares objective function is extremely sensitive to the suggested parameter values; therefore, these parameters must be estimated to many significant figures in order to minimize the weighted sum of squares objective function.

It is most important to realize that the extreme precision of the parameter estimates does not imply extremely accurate predictions. The extreme precision of the parameter estimates in this study is attributed more to the form of the model.

Take for example the observed value from the model:

$$y_i = e^{\theta x} + \varepsilon_i$$

Here, it may be seen that if in all cases the suggested values are of the same order of magnitude, the sensitivity of y to θ will depend upon the value of x. That is, y will be more sensitive to θ if x were equal to 20,000 rather than, say, 10. Conversely, if y values were known, the θ values would be more sensitive to the y values if x were large. This means that for, say, large x values, θ could be estimated much more precisely than if, say x was a small number. It must be realized, however that in all cases the error in the predicted value for the observation y cannot be any smaller than the error in the observation y itself. This must be true for any precision of the parameter estimate θ.

In the case of using these parameters to predict values in a different reactor system, the extremely precise parameter estimates may work against accurate predictions. Since in parameter estimation, the parameter estimates are extremely sensitive to the observations, it also follows that the values predicted will be extremely sensitive to the parameters. Thus, in using the parameter values obtained from one reactor system to predict observations in another system, the predictions may be extremely inaccurate if the true parameters in this other system are slightly different from the estimated parameters. On the other hand, in comparison, consider the situation where the parameters are estimated quite imprecisely so that large variations in the parameter values do not decrease the accuracy of the predictions significantly. In using these parameter values in another system where the true parameter values are slightly different, the model predictions should be of roughly the same accuracy as the accuracy in predicting the observations used in the parameter estimation.

These considerations have serious ramifications when one wishes to use these kinetic parameters in modeling another reactor configuration such as a fluidized bed. The question resolves itself into ascertaining whether the kinetic model alone is responsible for the sensitivity of the parameters or the conbination of a reactor model (fluid mechanics) and the chemical kinetic model.

6.3 MODEL VALIDITY

Once a model has been proposed and the parameters in it have been estimated from experimental data, there still remains the problem of testing its validity. Many tests for a model may be proposed; however, in this thesis three considerations were taken into account in checking the validity: the ability of the model to regenerate data used in the parameter estimation, the ability of the model to predict data not used in the parameter estimation and which involves extrapolation of the model over a wide range and finally, the ability of the model to predict a different type of data that was used in the parameter estimation (e.g. here the butane model was tested with data obtained from experiments with a propane feed).

In addition, the validity of the model must be considered in light of the degrees of freedom that were available when the parameters were estimated from the experimental data. This question is often discussed.

In this section, the above considerations will be discussed in turn for the butane and propane models and models for catalyst activity changes.

6.3.1 BUTANE MODEL

DEGREES OF FREEDOM

When estimating parameters, the degrees of freedom are the number of experimental data points to be fitted, minus the number of parameters used to fit the data in the models. Ten parameters were estimated in the butane model. Ten completely different experiments involving three temperatures, three flowrates and three ratios were used in the parameter estimation. Each of these experiments yielded three independent responses; that is, only three of the exit components may be said to depend entirely upon the parameters, since the feed composition and three exit mole fractions fixes the mole fractions of the remaining two components. The total number of independent responses used to estimate the ten parameters is then thirty. The degrees of freedom for fitting parameters is then twenty.

Although an apparently large number of degrees of freedom were available for fitting, some problems arose in estimating parameters in the propane part of the butane model. For example, correlation of parameters in the rate constants in the numerator and denominator of the propane rate expression was observed. This can be easily shown by considering a simple form of the propane rate expession given by equation 6.16 in section 6.1.2.

$$r_p = \frac{K - k_1 P_{C_3}^{m'} P_{H_2}^{n'}}{1 + k_2} \qquad 6.70$$

Where the reaction rate of butane, contained in K, is assumed constant.

The rate constants k_1 and k_2 both increase with temperature. Consequently, as temperature increases the numerator decreases and the denominator increases; r_p thus decreases.

It may be seen that for a given rate of decrease of the numerator with temperature, a rate of increase of the denominator may be chosen so as to maintain a constant observable rate of decrease of r_p with temperature. What this means is that over a range of parameter values, the activation energy of k_1 will be correlated with the activation energy of k_2. This was in fact observed during parameter estimation where pairs of activation energies appeared to fit the data equally well. This is a poor situation for parameter estimation, since the parameter estimates lose physical significance. The parameter estimates now depend as much on each other as on the experimental data.

This correlation of parameters occurs in attempting to include both the rates of adsorption and desorption individually in the propane model when, in fact, only a net change of propane composition in the gas phase can be observed. Correlation arises in this case, since if the change in the adsorption rate constant with temperature is estimated too high, then the change in the desorption rate constant with temperature must be estimated too high in order to predict a constant net change in the gas phase composition.

It is felt that this situation where there are essentially no degrees of freedom for fitting all of the propane parameters may not be remedied by gathering more experimental data of the same kind. The correlation between these parameters may be alleviated only by obtaining data of a different type; for example independent rate of adsorption and desorption data. These particular experimental data are difficult to obtain in a catalytic system.

In developing the kinetic model, however, the two effects of adsorption and desorption had to be included separately since these processes do in fact occur in nature. This is the important point; the model would become inadequate if both of these effects were not included. These effects may not be combined since the desorption effect depends upon the state of the surface of the catalyst (since the system is not in equalibrium), and the adsorption effect depends upon the partial pressure of the adsorbing species in the gas phase as well as the state of the surface of the catalyst.

For these reasons, adsorption and desorption terms were included in the model. The parameter values estimated in the propane model, although probably lacking physical significance, may still be used to predict experimental data. Note, however, that the functional forms of the expressions which contain these parameters are not totally empirical, but are commonly used in kinetic studies of catalytic systems.

ABILITY OF THE MODEL TO PREDICT EXPERIMENTAL OBSERVATIONS

Three aspects of the model's ability to predict observations are considered: (i) the ability of the butane model to regenerate data used in the parameter estimation, (ii) the extrapolation of the model to predict the hydrogenolysis of propane, i.e. with propane-hydrogen feed.

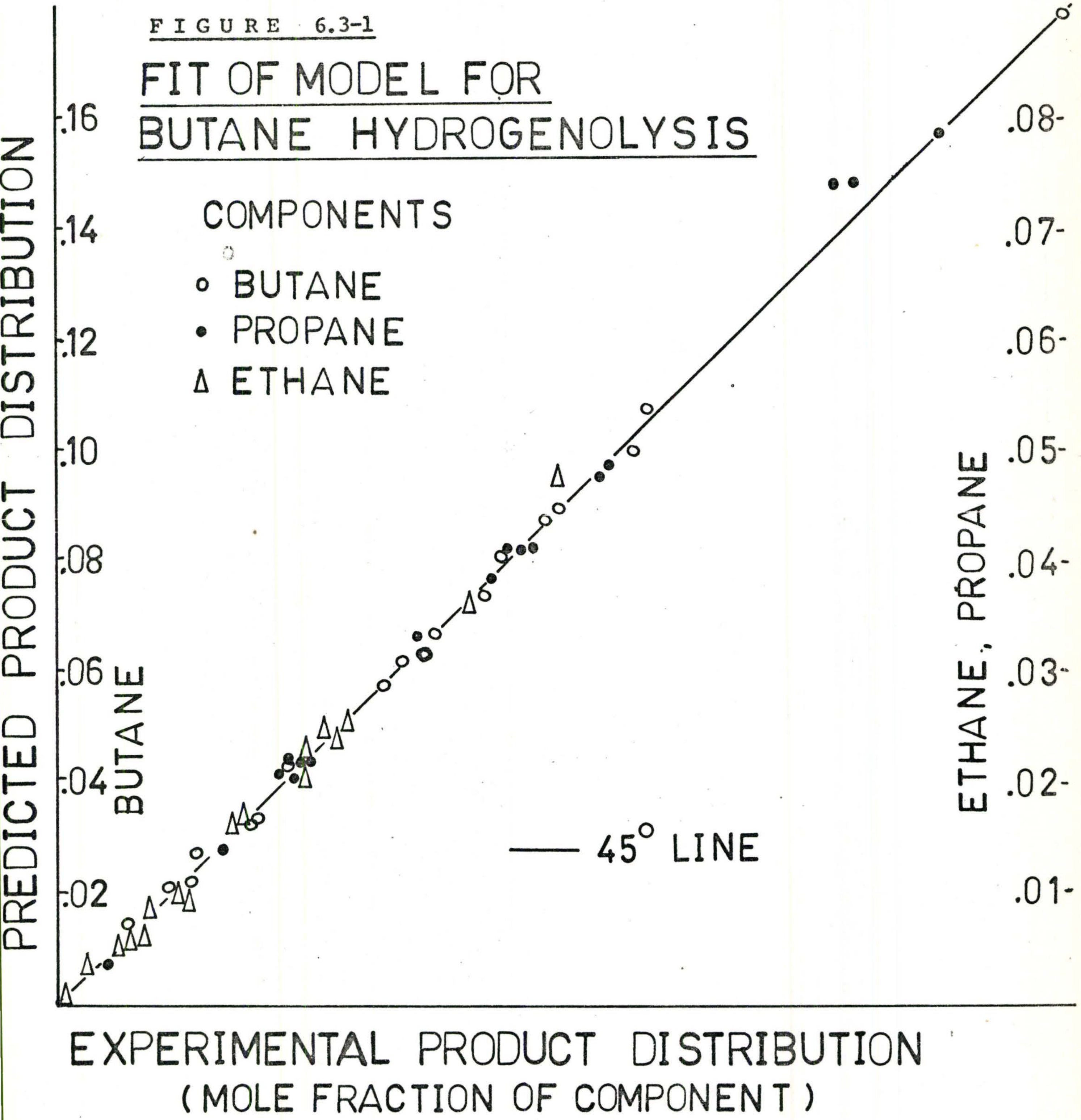


FIGURE 6.3-1

FIT OF MODEL FOR BUTANE HYDROGENOLYSIS

FIGURE 6.3-2 - FIT OF MODEL FOR BUTANE HYDROGENOLYSIS METHANE COMPONENT

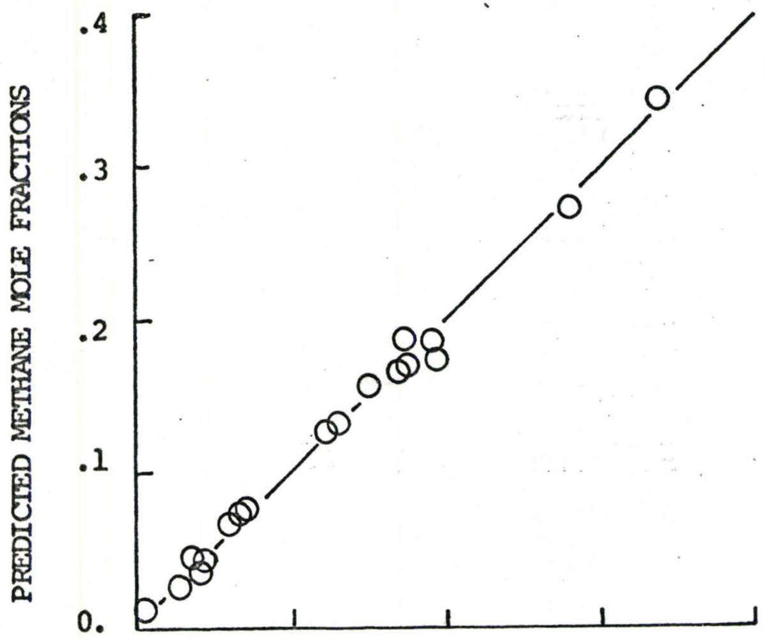


FIGURE 6.3-3 - FIT OF THE MODEL FOR BUTANE HYDROGENOLYSIS HYDROGEN COMPONENT

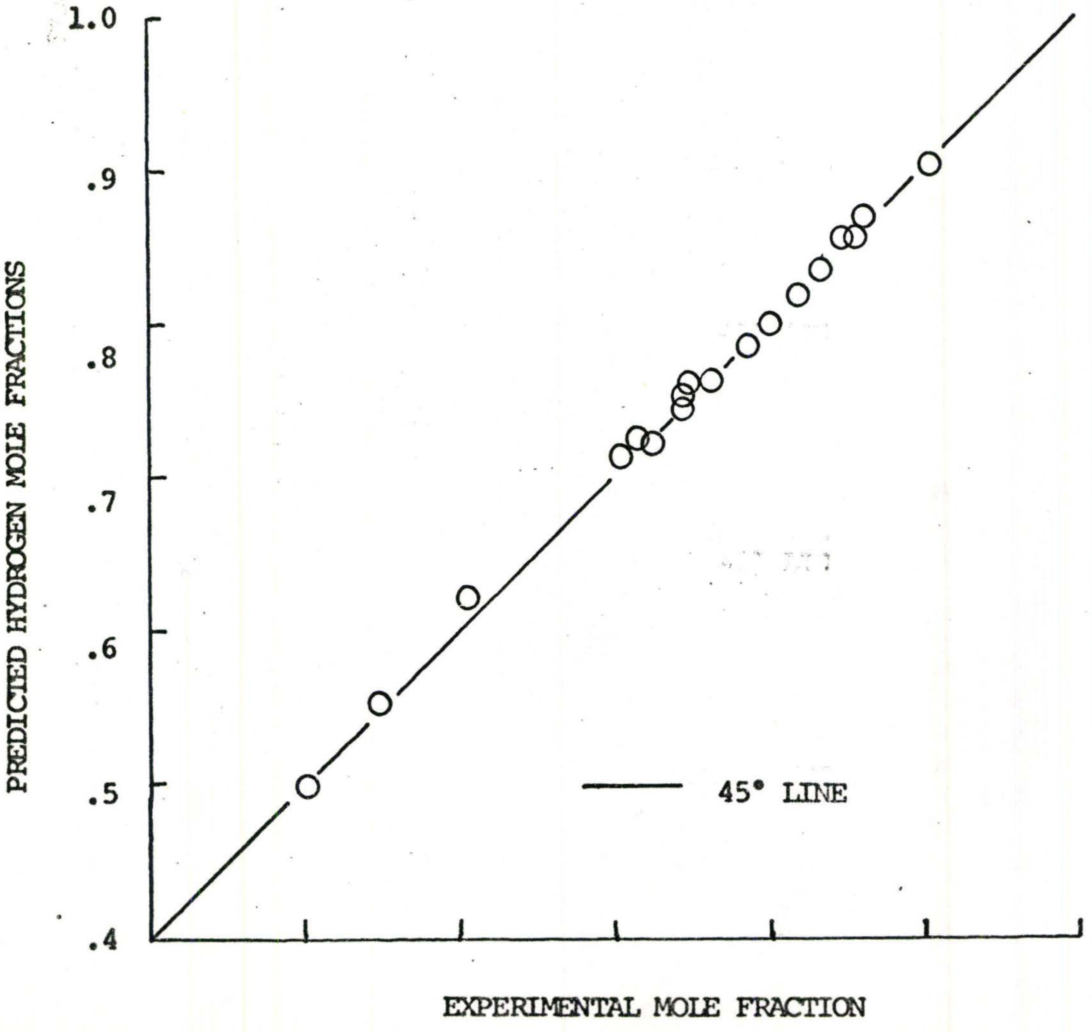


FIGURE 6.3-4

PLOT OF ETHANE MOLE FRACTION RESIDUALS

FOR HIGH CONVERSION BUTANE EXPERIMENTS

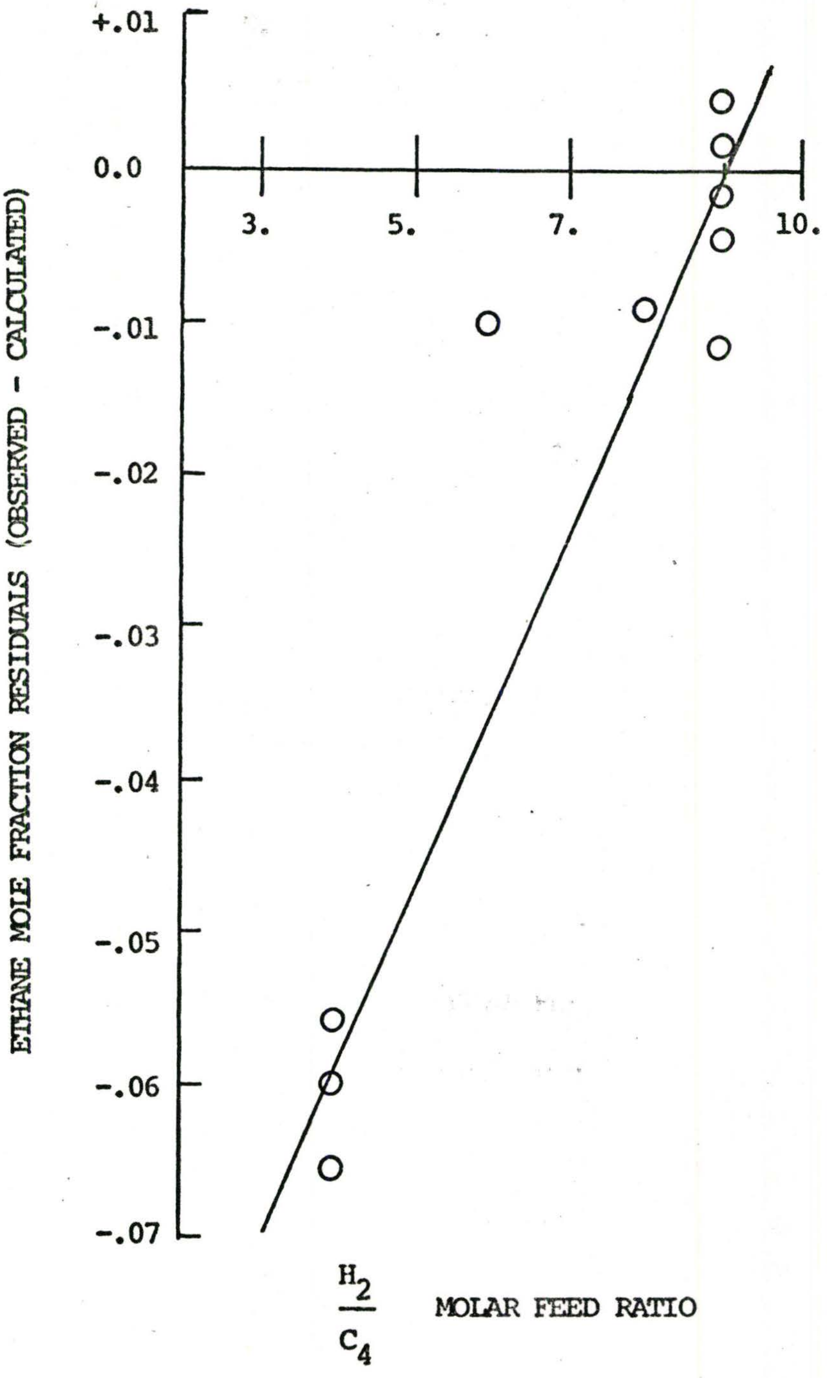


FIGURE 6.3-5

PLOT OF ETHANE MOLE FRACTION RESIDUALS FOR HIGH CONVERSION BUTANE EXPERIMENTS

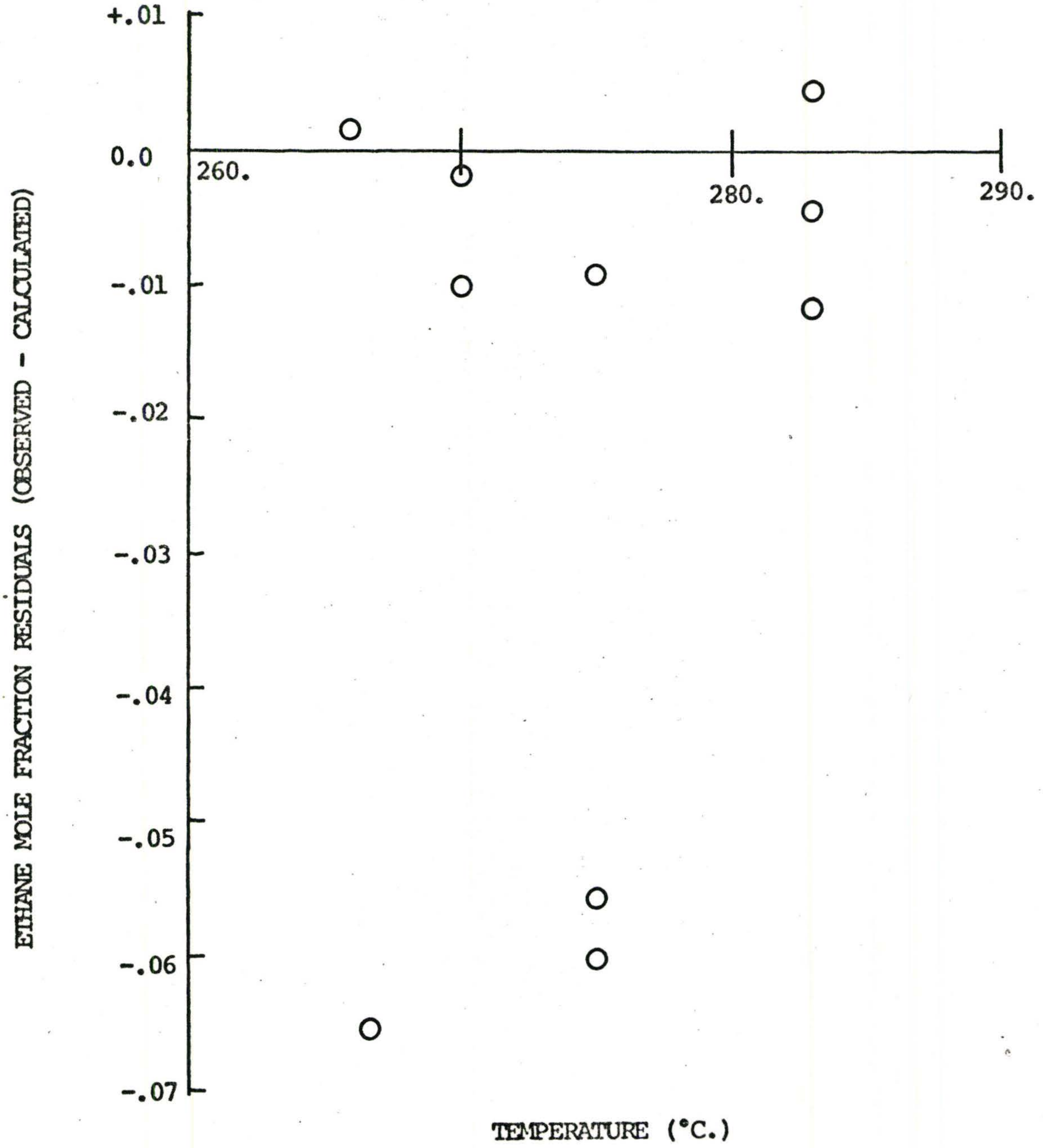


TABLE 6.3-1

PREDICTED AND EXPERIMENTAL MOLE FRACTIONS FOR HIGH CONVERSION(100%) RUNS

RUN NO.	TEMP. °C	FLOW ml./min.	RATIO H_2/C_4	REACTOR EFFLUENT MOLE FRACTIONS									
				C_1		C_2		C_3		C_4		H_2	
				EXP.	PRED.	EXP.	PRED.	EXP.	PRED.	EXP.	PRED.	EXP.	PRED.
76	266.5	1.01	9.75	.237	.234	.032	.032	.023	.023	.000	.000	.707	.709
99	267.1	1.73	3.80	.787	.639	.023	.091	.000	.004	.000	.000	.190	.266
117	270.5	1.79	9.17	.263	.258	.029	.032	.023	.023	.000	.000	.683	.686
142	270.4	1.42	6.09	.455	.430	.044	.056	.007	.007	.000	.000	.494	.507
35	274.8	0.99	3.75	.793	.680	.025	.082	.000	.000	.000	.000	.182	.239
73	275.0	1.03	8.34	.362	.333	.028	.039	.003	.006	.000	.000	.606	.622
98	275.4	1.75	3.80	.797	.674	.019	.080	.000	.000	.000	.000	.184	.246
14	283.5	1.87	8.94	.307	.306	.033	.029	.010	.012	.000	.000	.650	.652
71	283.9	1.04	8.79	.367	.340	.020	.033	.000	.001	.000	.000	.612	.626
115	282.6	1.82	8.98	.343	.327	.027	.033	.001	.003	.000	.000	.628	.638

(i) FIT OF THE MODEL WITH DATA USED IN THE PARAMETER ESTIMATION

The predicted versus experimental mole fractions of all the components in the reactor effluent are plotted in Figures 6.3-1, 2, 3.

The data plotted are the predicted and observed mole fractions for the runs used in the sum of squares objective function and these runs are given in Table 6.2-1. These runs represent a 5. to 90.% range of conversion of butane. They include three temperatures, ratios and feed flowrate levels and also five runs at standard operating conditions, but at different catalyst activities.

(ii) EXTRAPOLATION OF THE MODEL

Because of the increase in catalyst activity during the course of experimentation, several runs were available at essentially 100.% conversion of butane. The parameter estimation was performed in a temperature range of 240. to 258.°C. and the 100.% conversion runs occurred in the range of 266. to 284.°C. These experimental runs provided a rather severe test of the model. The predicted and experimental mole fractions for these high conversion runs are shown in Table 6.3-1. It is observed that the model predicts quite well even at 284°C. for high feed ratios. For low feed ratios, some deviation occurs even at a temperature as low as 267.°C. Although there is interaction among all the components in the reaction scheme, it may be seen that ethane indicates the greatest deviation between model and experiment in runs 99, 35 and 98.

Figures 6.3-4 and 6.3-5 show ethane mole fraction residuals plotted against feed ratio and temperature. The expected correlation

TABLE 6.3-2

PREDICTED AND EXPERIMENTAL MOLE FRACTIONS FOR BUTANE MODEL USING DATA FROM PROPANE EXPERIMENTS*

PROPANE RUN NO.	REACTING TEMP. (^{o}C)	EXPERIMENTAL MOLE FRACTIONS, PREDICTED MOLE FRACTIONS AND PERCENT DEVIATIONS WITH RESPECT TO THE EXPERIMENTAL VALUES									
		C_1		C_2			C_3			H_2	
1	258.3	.060	.076	.015	.017	-13%	.082	.075	+ 8%	.842	.831
4	258.5	.208	.261	.048	.059	-23%	.099	.074	+25%	.645	.606
6	258.0	.105	.142	.027	.032	-18%	.148	.132	+10%	.720	.694
8	258.2	.083	.106	.023	.024	- 4%	.072	.063	+12%	.822	.806
10	258.1	.039	.052	.011	.012	- 9%	.084	.079	+ 6%	.866	.857
14	270.6	.216	.225	.040	.038	+ 5%	.022	.020	+ 9%	.722	.717
18	269.3	.107	.115	.022	.020	+ 9%	.051	.050	+ 2%	.820	.816
19	270.5	.341	.361	.059	.061	- 3%	.050	.042	+16%	.550	.536
20	271.0	.123	.134	.027	.022	+18%	.048	.047	+ 2%	.802	.797
21	257.1	.045	.063	.014	.015	- 7%	.079	.072	+ 9%	.862	.850

* The k value for these runs was chosen a priori from Figure 6.3-10 as 117.0.

with ratio is observed and the plot against temperature appears random, although displaced slightly into the negative region. At the high temperature only high ratio runs were available, while high and low ratio runs were available for all other temperatures. This may explain the group of residuals at the high temperature.

These results may be expected at low hydrogen to butane ratios because these conditions are most favourable for ethane adsorption onto the surface of the catalyst and the butane cracking model assumes that this adsorption does not occur.

(iii) ABILITY OF THE BUTANE MODEL TO PREDICT PROPANE CRACKING RESULTS

Since runs were performed using a propane feed to the reactor, it was decided to test the butane model with a propane feed. This obviously is a rather severe test of the butane model.

The predicted and experimental methane, ethane, propane and hydrogen effluent mole fractions are given in Table 6.3-2. The predictions appear reasonable. Predictions of methane are in general higher than observed, which suggests that more reaction of all components was predicted to occur than was observed.

6.3.2 PROPANE MODEL

DEGREES OF FREEDOM

Eight different experimental design points with two independent responses (ethane and methane) per experiment were used to estimate six parameters. The number of degrees of freedom available for fitting is then ten.

ABILITY OF THE MODEL TO PREDICT EXPERIMENTAL OBSERVATIONS

Predicted versus experimental mole fractions of all the components in the reactor effluent for all the propane runs, except the one 96.% conversion run, are shown in Figures 6.3-6, 7, 8. These experimental points represent a 19. to 82.% range of propane conversions. The one run at 96.% conversion was not included in the analysis since it was felt that the conversion was sufficiently close to 100.%, that the experimental mole fractions would have little weight in the sum of squares objective function. After the parameters were estimated, the model was tested by comparing predicted and observed results for this high conversion run. The experimental and predicted mole fractions are:

	C_1	C_2	C_3	H_2
Experimental	.480	.043	.008	.470
Predicted	.399	.079	.011	.512

This high conversion run was performed at a low hydrogen to propane feed ratio. It may be seen that for this run, just as in

FIGURE 6.3-6

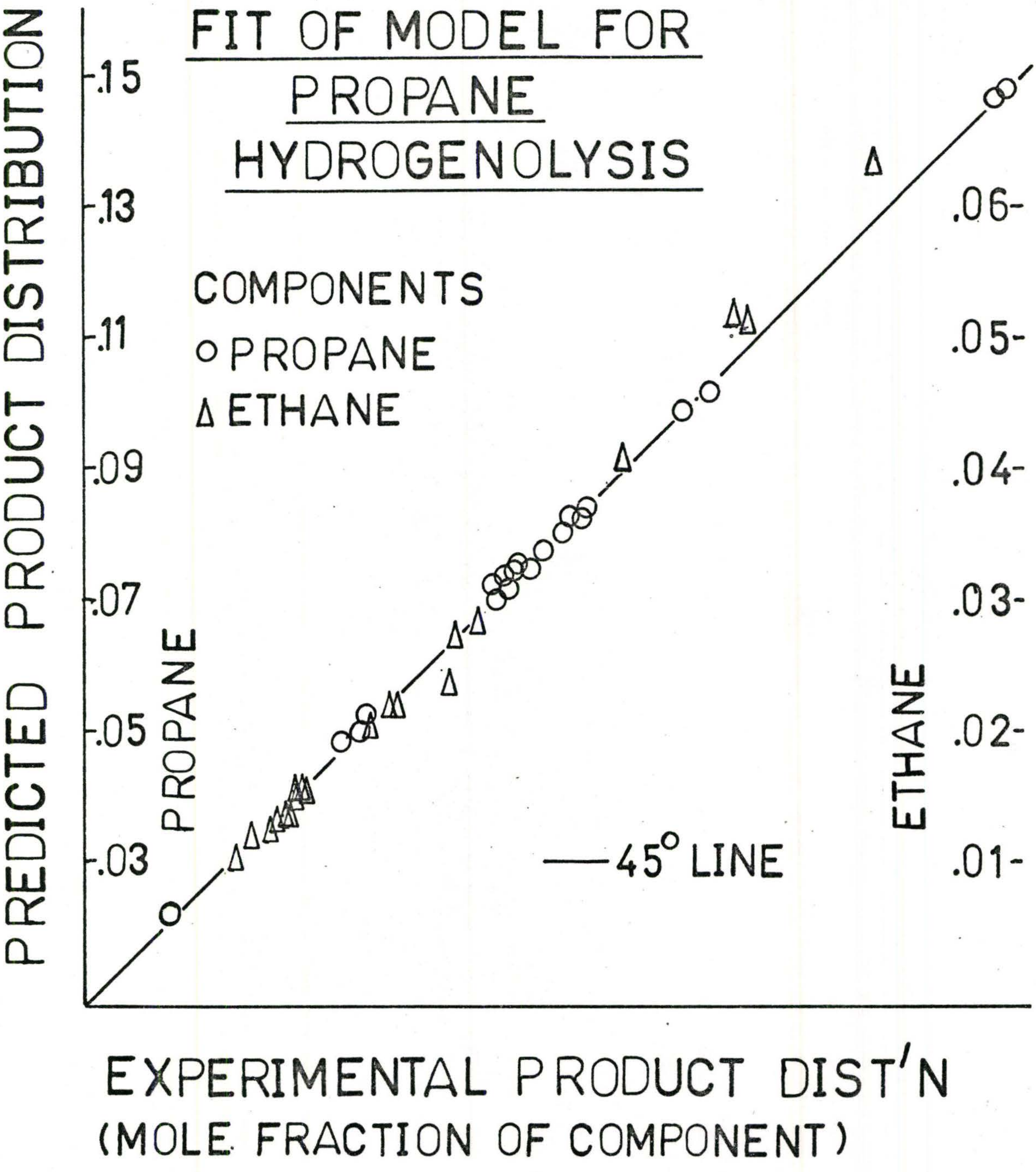

FIT OF MODEL FOR
PROPANE
HYDROGENOLYSIS
COMPONENTS
○ PROPANE
△ ETHANE
PREDICTED PRODUCT DISTRIBUTION
.15
.13
.11
.09
.07
.05
.03
PROPANE
ETHANE
.06
.05
.04
.03
.02
.01
—45° LINE
EXPERIMENTAL PRODUCT DIST'N
(MOLE FRACTION OF COMPONENT)

FIGURE 6.3-7 - FIT OF MODEL FOR PROPANE HYDROGENOLYSIS METHANE COMPONENT

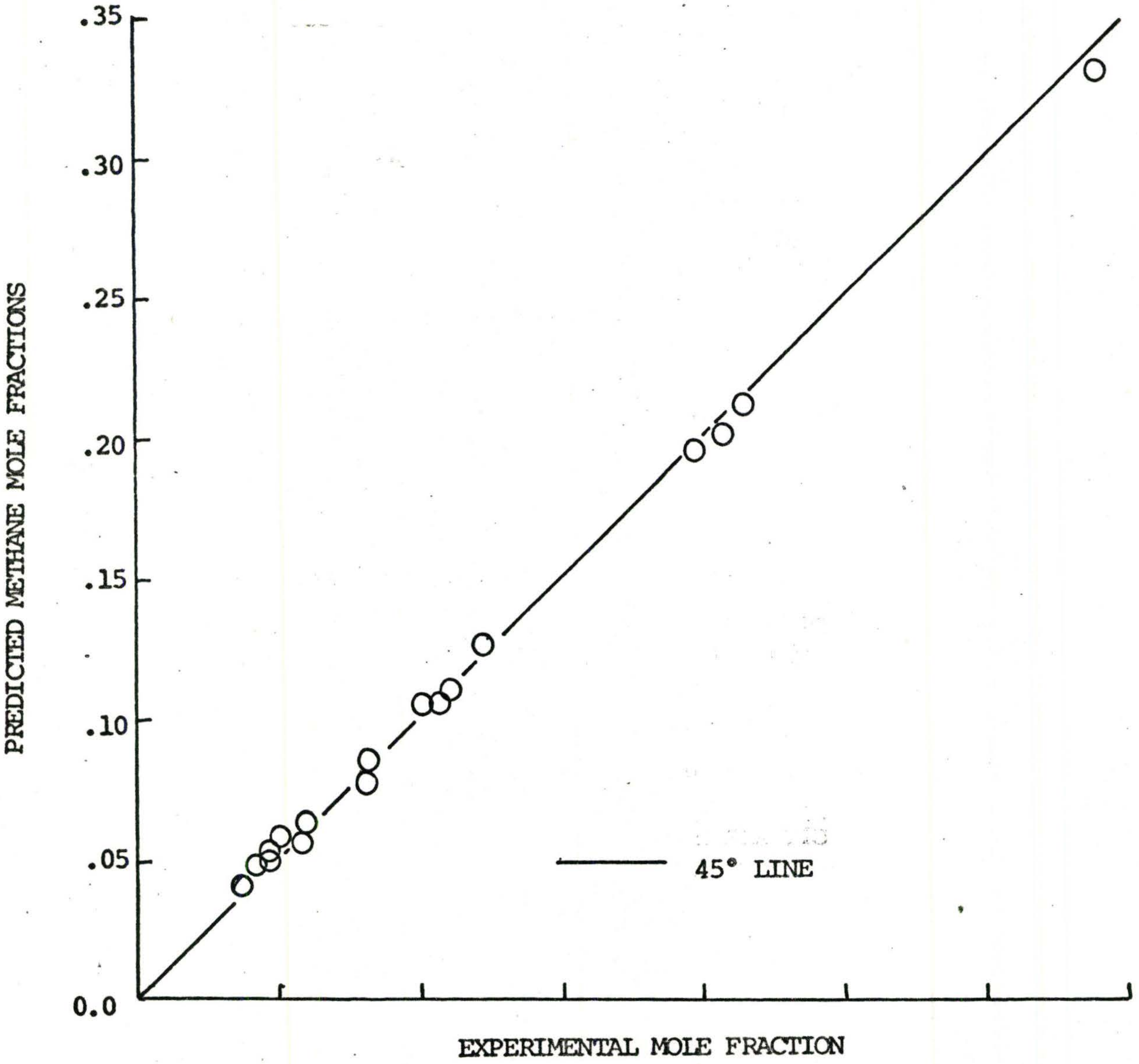
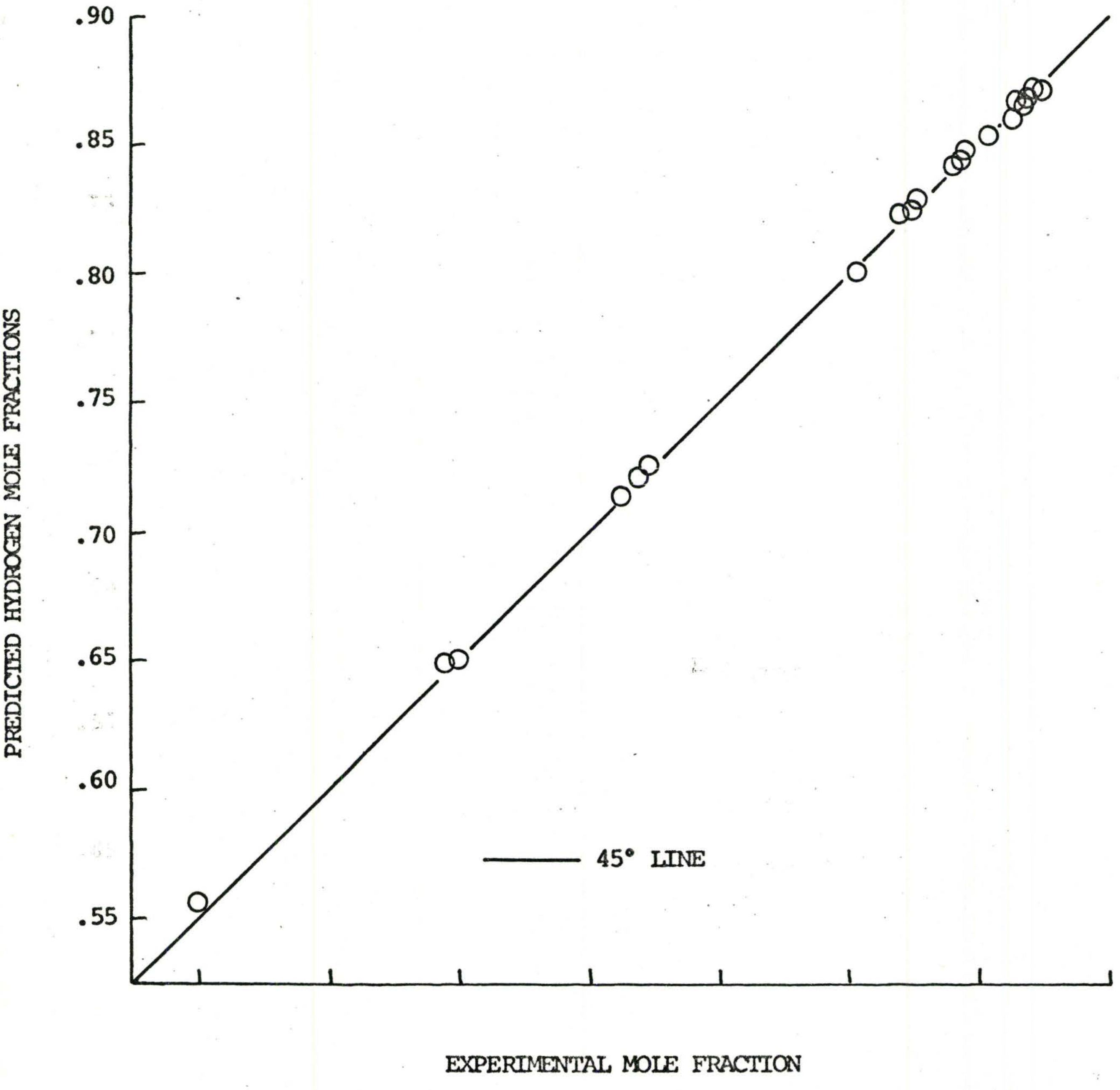


FIGURE 6.3-8 - FIT OF MODEL FOR PROPANE HYDROGENOLYSIS HYDROGEN COMPONENT



analagous runs in the butane experiments, the ethane mole fraction is predicted much to high. In the propane hydrogenolysis model, just as in the butane model, the adsorption of ethane onto the surface was assumed not be occur. It is felt that, in fact, ethane does adsorb at the high temperature level and the low feed ratio level, thus accounting for the low experimental mole fraction. The high temperature level here is 270.°C. It is interesting to note that from Table 6.3-1 the largest deviations in predicted and calculated ethane mole fractions in the butane experiments were first observed at 266.°C. as well as 270.°C.

6.3.3 MODELS FOR CATALYST ACTIVITY CHANGE

DEGREES OF FREEDOM

Catalyst activities are available for nineteen butane experiments. Since one value is needed as an initial value in each of the models to predict the changing activity, eighteen data points are available for fitting.

There are three parameters in the model which assumes a constant maximum activity and four parameters in the model which assumes the maximum activity is a function of the temperature at which the catalyst has been reduced. Therefore, there are fifteen and fourteen degrees of freedom in each model, respectively.

PREDICTING ABILITY

Figure 6.3-9 gives the temperature history of the reactor over the entire time covering these experiments; these data were used in the calculation of the models. Figure 6.3-10 shows the experimental and predicted catalyst activities for both models as a function of time. Previous to this time the catalyst was reduced at a maximum temperature of 265.°C. It may be observed that the curve predicted by the model assuming varying maximum catalyst activity has horizontal sections which correspond to times at which no reduction of catalyst is calculated to take place. This is because the temperature is low enough so that: $k(T - T_0) - c < 0$ and there is no driving force for reaction. The model assuming a maximum catalyst activity predicts a curve that continually rises , since the best estimate of the maximum catalyst activity is greater than any experimental activity so that there always

FIGURE 6.3-9

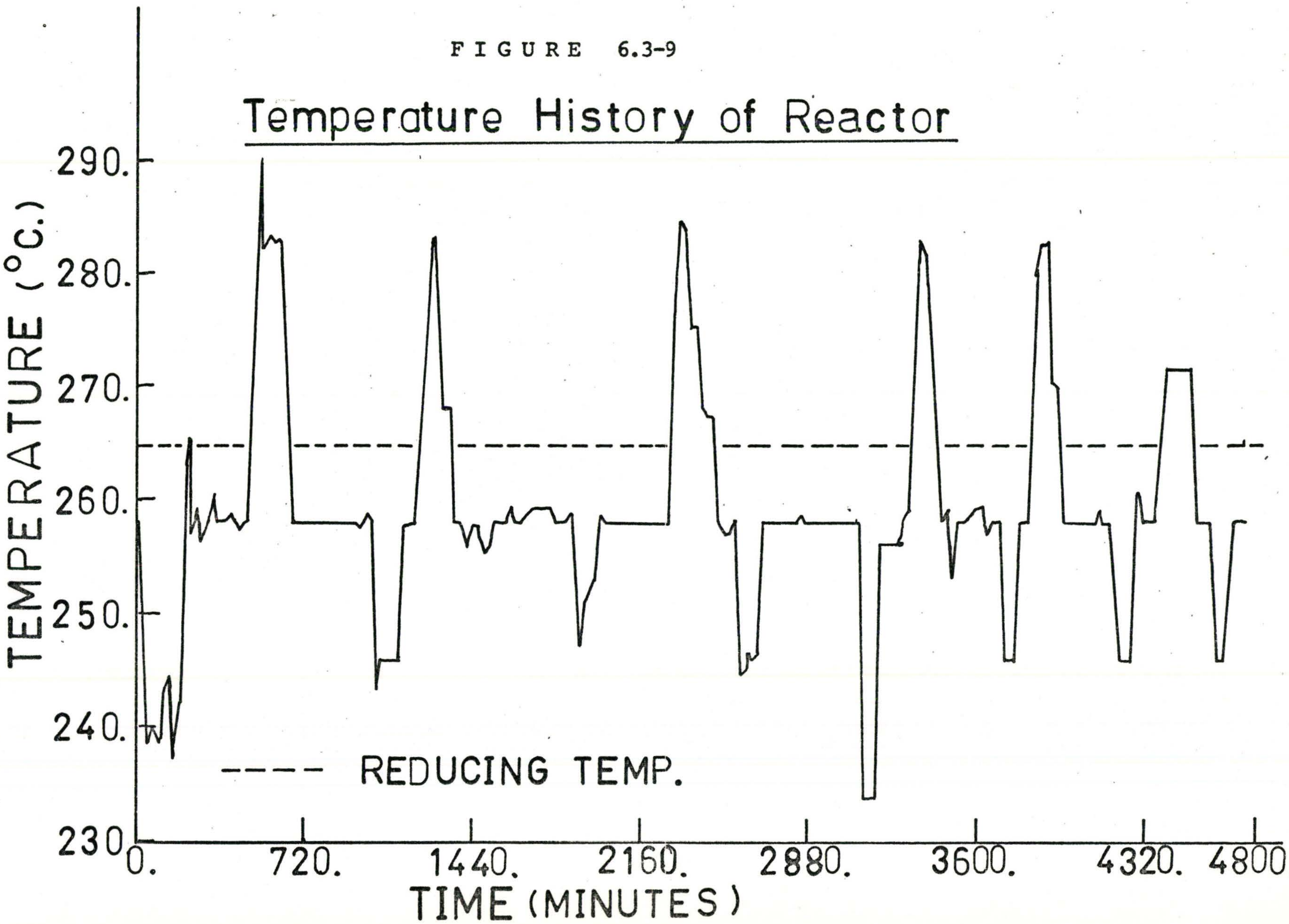
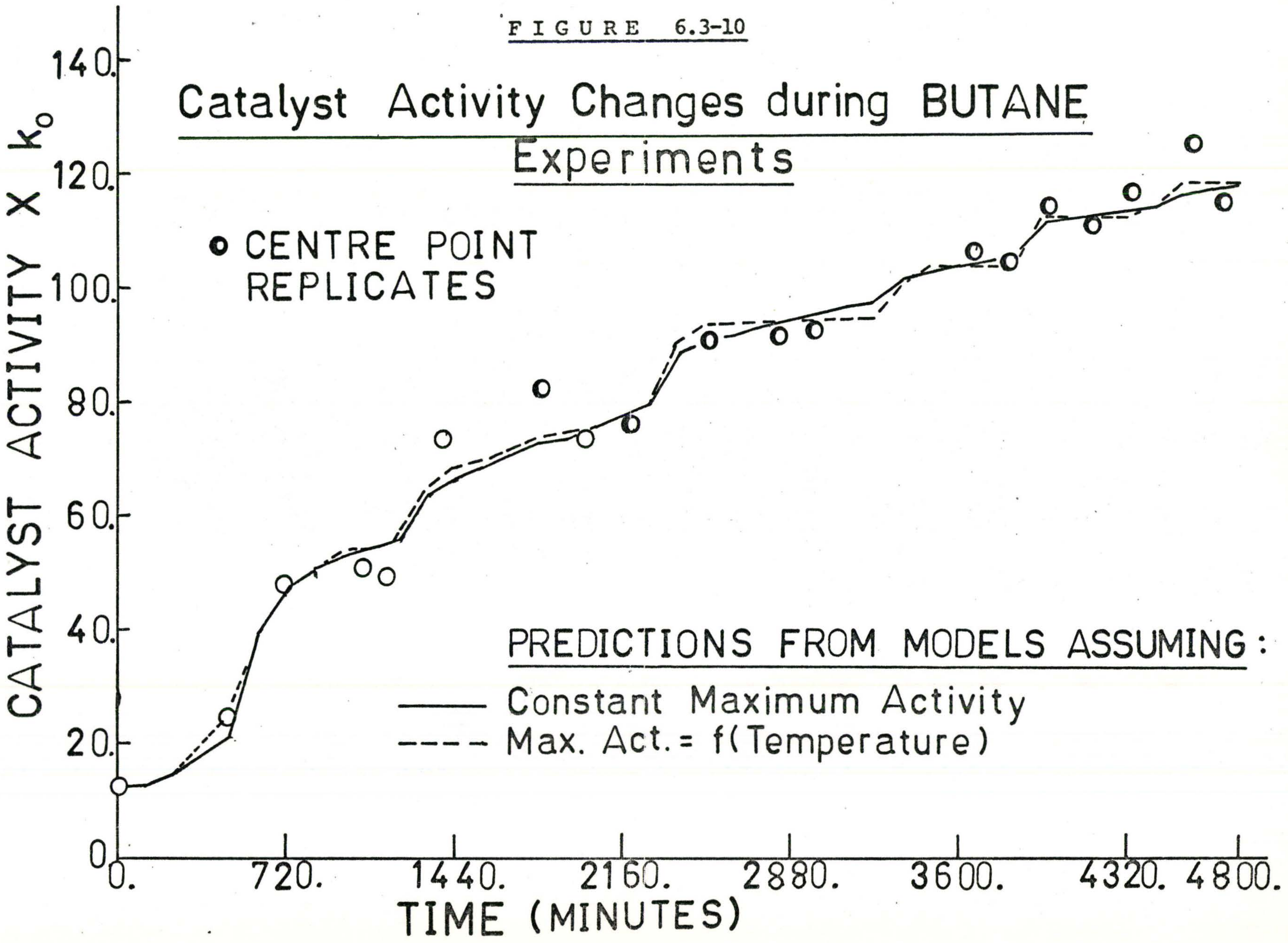

Temperature History of Reactor
TEMPERATURE (°C.)
290.
280.
270.
260.
250.
240.
230
0.
720.
1440.
2160.
2880.
3600.
4320.
4800.
TIME (MINUTES)
---- REDUCING TEMP.

FIGURE 6.3-10



Catalyst Activity Changes during BUTANE Experiments exists a positive and non-zero driving force for reaction. In both of the predicted curves sudden jumps or rises in catalyst activity occur at high temperatures as expected because of the Arrhenius form of the rate constant used.

An F ratio test* at 95.% confidence level and fifteen and fourteen degrees of freedom was performed to test whether one model predicts significantly better than the other. F was calculated as the ratio of the sum of squares of differences between the observed and computed values for the two models taking into account degrees of freedom (i.e. ratio of the mean squared errors).

$$F = \frac{\text{Sum of squares for model 1/d.f. for model 1}}{\text{Sum of squares for model 2/d.f. for model 2}}$$

The calculated F was 1.09 and the tabulated F value was 2.55. This F test is not strictly applicable here since, because of the non-linear form of the model, the errors in the predicted values need not be either equal or normally distributed for each predicted point. Also from the manner in which the experimental k values were computed, it is expected that these k values also have non-normally distributed and unequal variances. However, the computed F value here is so small with respect to the tabulated value that it seems reasonable to say that one model does not appear to predict better than the other.

Some interesting observations may, however, be made from the best estimates for the parameters for the model assuming that the maximum catalyst activity and thus, the driving for reduction at a certain activity level, depends upon the reducing temperature. This

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* See Draper and Smith (D5) page 282.

assumption is consistent with the observations of Schuit and Van Reijen (S5) who indicated that the percent reduction of the catalyst increased with the reducing temperature. Schuit and Van Reijen also quote an activation energy of -20. kcal./mole for the reduction of nickel oxide; this compares with the best estimate activation energy found from this study, -17.4. The simpler model (constant maximum catalyst activity) suggests an activation energy more than twice that reported by Schuit and Van Reijen.

7. SUMMARY AND CONCLUSIONS

In this section, the conclusions and contributions to knowledge are summarized.

(i) KINETIC MODELLING

Kinetic models have been proposed and tested experimentally to describe the hydrogenolysis of n-butane and propane over a nickel-on silica gel catalyst. These models take into account the activity of the catalyst and predict the entire product distribution of components involved in the reaction. Derivations are also given for the Cimino, Boudart and Taylor-type and Hougen and Watson-type expressions to describe this reaction.

Various validity tests have been proposed and carried out to test the ability of the models to predict experimental data. The butane cracking model holds up quite well in predicting the data used to estimate the kinetic parameters, in predicting data for which the model had to be extrapolated over twice the temperature range used in the parameter estimation and in predicting product distributions when the butane model was used with data from propane feed experiments. It was found that both the butane and the propane models broke down at high temperatures, and low hydrogen-to-hydrocarbon feed ratios. This inadequacy may be easily explained in terms of the assumption relating to ethane readsorption.

Models have also been proposed to describe the changes in catalyst activity observed during the butane cracking experiments. It is interesting to note that the activation energy found for the model, which was felt to best describe the physical situation, was in reasonable agreement with the activation energy reported in the literature for the reduction of nickel oxide.

(ii) PARAMETER ESTIMATION STRATEGY

A parameter estimation strategy, which involves application of non-linear least squares theory, has been proposed. It was found to work quite well even though the kinetic and reactor model required the estimation of a relatively large number of parameters in mathematical formulations which involved numerically integrating a set of non-linear, coupled ordinary differential equations. Moreover, there were multiple observed and calculated data at each experimental operating condition; large catalyst activity changes occurred during the course of the experiments; and the sensitivity of the predictions and hence, the weighted sum of squares objective function, differed extremely for the various parameters.

(iii) PARAMETER ESTIMATES

The parameters which were estimated from the observed experimental data may be compared to the literature values presented in Table 3.1-1. It may be seen that the estimated values of the exponents on the partial pressure of hydrogen agreed quite well with values reported in the literature. The activation energy for butane cracking (56.900 k.cal./gm. mole) appears high while that for propane (49.183) appears to show better agreement.

(iv) ERROR ANALYSES

Three independent or different variance-covariance matrices are evaluated to account for errors in the observed mole fraction. The most sophisticated of these is the covariance matrix for the three independent responses; methane, ethane and propane, which was found analytically. These three matrices were used, along with the likelihood ratio test, to estimate errors in the estimated parameters in the butane cracking model. These errors were found to be extremely small (e.g. $\Delta E_B = 56.900 (\pm 0.008)$ k.cal./gm. mole). This means that for the experimental design performed and the observation obtained from these experiments, the parameters may be estimated quite precisely. It is felt that this precision is a characteristic of the functional form of the butane cracking model. Because of this form, a simple experimental design with a very few experiments is all that is necessary to obtain precise parameter estimates. This ability to determine precise parameter estimates may be useful in a fundamental study, but may be detrimental if a simulation model of this or another reactor scheme is to be formulated. The use of the likelihood ratio test was also applied to examine correlations among parameters.

(v) EXPERIMENTAL DATA

Experimental data were obtained and plotted to show the product distribution that may be expected in cracking butane over a 10% nickel on silica gel catalyst.

(vi) APPLICATION OF BUTANE KINETIC MODEL TO FLUIDIZED BED MODELLING

The butane cracking model was incorporated into two fluidized bed models and sensitivity analyses were performed. These analyses showed the importance of determining the catalyst activity in the fluidized bed and the importance of the bubble-emulsion interchange factor in deterimining the conversion of butane and the product distribution.

(vii) CRITERION FOR DESIGNING EXPERIMENTS FOR MODEL DISCRIMINATION

A modification was proposed to the experimental design criterion, proposed by Roth, to obtain data most efficiently for model discrimination. This modification realizes that the true parameter values in a model are not usually known, and this must be taken into account if the experiments, in the long run, are to be most efficient.

8. RECOMMENDATIONS FOR FUTURE WORK

Recommendations for future work which arise directly out of this study are presented with respect to both the experimental and computational programs in turn.

(i) EXPERIMENTAL WORK

In the experiments described in this thesis, temperature variations were observed along the length of the packed bed reactor. Although it was found that these temperature variations would have little effect on the parameter estimates, there was no way of knowing whether temperatures at other points in the reactor far exceeded the observed variations. It is felt that major temperature excursions could cause significant errors in the estimated parameters. It is therefore proposed that experiments be performed in which the catalyst is diluted with; for example, glass or Vycor beads, to eliminate these temperature variation effects. Such experiments would also give an idea of the reproducability of the parameter estimates.

In the kinetic model, a term has been included for catalyst activity. From sensitivity analyses on the fluidized bed models it may be observed that this parameter is important in predicting the reactor performance. It is recommended that a method be found to remove catalyst directly from the fluidized bed reactor to the small packed bed reactor without introducing oxygen. This reactor could then be used to characterize the catalyst activity in the fluidized bed and thus, better relate this work to the overall simulation program.

(ii) COMPUTATIONAL WORK

Because of the way in which the butane and propane cracking models break down at high temperatures and low feed ratios, it is highly suspected that in these regions, contrary to the assumptions made in the models, the ethane readsorbs and cracks on the catalyst surface. It is therefore recommended that if studies are to be made at high temperatures and low feed ratios, an effort should be made to include a term for the adsorption of ethane in the butane cracking model. This term would be analagous to that used in the expression to describe the rate of production of propane in the butane hydrogenolysis model.

The proposed modification for the Roth criterion for designing experiments for model discrimination involves "integrating out" the effects of the parameters. This involves multiple integration, which when carried out numerically, could involve large computer times. It is recommended that an effort be made to find an efficient numerical technique to perform these integrations and thus reduct the time required.

The third and final recommendation involves a concept which will be referred to here as "nesting" of models. This term will be used to describe the situation where a number of independent models with independent responses (e.g. product distribution from a kinetic model, average bubble diameter and coalescence rates from a fluid mechanical model, residence time distribution from a mixing model, etc.) are assembled in some way to produce a single model (e.g. a fluidized bed reactor model) whose response variables depend upon the response variables of the component models. This is, of course, directly related to this simulation program where, in a fluidized bed, diffusion and bubble gas interchange models, fluid mechanical models, chemical kinetic models, etc., with their respective parameters are sought external to the actual reactor, or obtained by separate, independent experiments in the actual reactor, in an attempt to predict the reactor's performance a priori. These separate models are said to be "nested" together to form the fluidized bed model.

Given the predictions from the fluidized bed model, and experimental observations from the real reactor, the likelihood function of all of the parameters in the fluidized bed model may be formulated. It is proposed that the effect of the parameters in the various "nested" models, on the likelihood of these parameters based on observations of fluidized bed reactor effluent, be studied. The point is that the "confidence intervals" of the parameter may be different when considering the response (and experimental observations) of the one "assembled" model and the response (and its parallel observations from separate experiments) of the individual "nested" models. It is felt that the parameters should be estimated to the precision determined by the predictions of the "assembled" model, rather than the predictions (and experimental observations from separate experiments) of the "nested" model itself.

Essentially this says that there is no need to estimate a parameter in each "nested" model to very high precision by means of independent experiments, if this parameter can only be estimated to very low precision from the experimental data and the responses of the "assembled" model. These considerations require further investigation.

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APPENDIX A

LITERATURE SURVEY AND DISCUSSION OF FLUIDIZED BED MODELS

This section deals with a discussion of the various models proposed in the literature for fluidized bed catalytic reactors. The emphasis here will be on the different concepts used to describe the fluid mechanical behaviour of the bed. The fluidized bed itself has two main regions: a lower region, the bed itself, which is composed of a dense emulsion phase in which bubbles are rising upward, and an upper region, or dispersed phase region, less dense than the lower region, which consists of entrained, splattered and settling solids. The fluidized bed models are concerned with the former region.

The main difficulty in developing a steady-state fluidized bed model is in obtaining a satisfactory flow model which accounts for the bubbling (bubble sizes, shapes, velocities, etc.), mixing, coalescence and breakup phenomena, and the interchange of gas between the bubble and the emulsion phase of the fluidized bed.

Table A-1 gives a comparison of the various fluidized bed models proposed in the literature to date. Figure A-1 shows a general bubble and the regions that are referred to in Table A-1.

All models assume that the bubble rises faster than the gas percolating upward in the emulsion phase. Under these conditions a cloud phase forms around the bubble. The extent of the cloud phase is determined by the depth of penetration of the bubble gas as it circulates out of

TABLE A-1

COMPARISON OF CURRENT FLUIDIZED BED MODELS

MODEL	TOTAL PHASES	UPFLOW OR LESS-DENSE PHASE		
		PHASES	MODEL FOR SHAPE	MIXING ASSUMPTIONS
Orcutt, Davidson, Pigford (O1)	Bubble Emulsion	Bubble Void	Spherical Bubbles, no Cloud Overlap, Uniform Bubble Size and Velocity	Perfect Mixing in Bubble.
Partridge, Rowe (P3)	Bubble, Cloud Overlap, Emulsion	Bubble and Cloud Overlap	Murray Model, Size and Velocity Distributions Measured.	Perfect Mixing Between Bubble and Cloud Overlap.
Kunii, Levenspiel (K5, K6)	Bubble (Cloud Incl.) Wake, Emulsion	Bubble, Cloud Overlap, Wake	Davidson Model, Constant Bubble Size	Perfect Mixing in Bubble, Cloud and Wake Respectively
Kato, Wen (K7)	Bubble, Cloud, Emulsion.	Bubble, Spherical Cloud.	Spherical Bubbles and Cloud, Davidson Model For Diameter.	Perfect Mixing Between Bubble and Cloud.
Latham (L3)	Bubble, Wake, Emulsion.	Bubble, Wake	Davidson Model with no Cloud Overlap.	Perfect Mixing Between Bubble and Wake.
Van-Deemter (V1)	Bubble, Cloud, Emulsion.	Bubble, Cloud	Davidson Model, Volume Fractions of Phases Used.	No Perfect Mixing Between Bubble and Cloud.
May (M6) Van-Deemter (V2) Mireur and Bischoff (M5)	Bubble, Emulsion.	Bubble Void	Spherical Bubbles, no Cloud.	Perfect Mixing in Bubble Void.

TABLE A-1 CONT'D.

MODEL	DENSE PHASE		
	SOLIDS MIXING	GAS MIXING	EMULSION GAS SUPERFICIAL VELOCITY
Orcutt, Davidson, Pigford	Not Accounted For	Perfect Mixing.	$U_{m.f.}$
	Not Accounted For	Plug Flow Upwards.	$U_{m.f.}$
Partridge, Rowe	None	Plug Flow Upwards.	$U_{m.f.}$
Kunii, Levenspiel	Accounted For	Flow Reversal, Plug Flow Downwards.	Calculated
Kato, Wen	Accounted For	No Motion, Dead Space.	Assumed 0
Latham	Accounted For	Flow Reversal Plug Flow Down.	Calculated
Van-Deemter	Acounted For	Flow Reversal, Plug Flow Down.	To be Determined
May, Van-Deemter, Mireur and Bischoff	Not Accounted For	Mixing Characterized By Diffusion Coefficient.	$U_{m.f.}$

TABLE A-1 CONT'D.

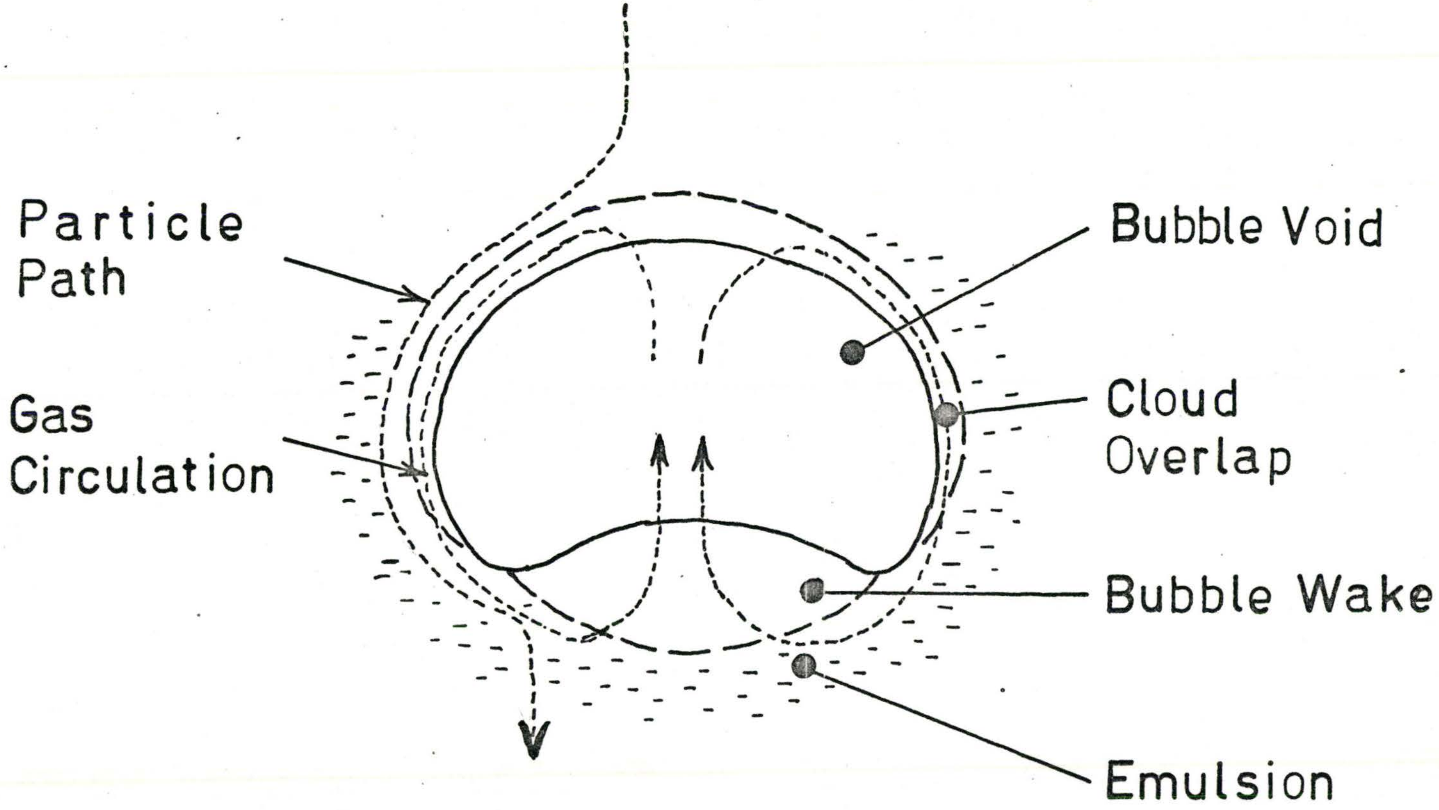
MODEL	MODEL FOR INTERCHANGE BETWEEN PHASES
Orcutt, Davidson, Pigford	Bulk Diffusion From Bubble - Davidson: $q = 3\ U_{m.f.}\ \pi D_e^2/4$ Molecular Diffusion From Bubble - Baird: $k_G = 0.975\ D_e^{-\frac{1}{4}}\ D_G^{\frac{1}{2}}\ g^{\frac{1}{4}}$
Partridge, Rowe	Mass Transfer Coeff't. for One Immerscible Liquid Rising Through Another: $h_m = D_G\ S_{h_c}\ d_c$ Where $S_{h_c} = 2.0 + 0.69\ S_c^{1/3}\ R_{e_c}^{1/2}$
Kunii, Levenspiel	Bubble to Cloud Transfer: Same as Orcutt Cloud to Emulsion: Higbie Penetration Model $K_{CE} \cong 6.78\ \left(\frac{E_{m.f.}\ D_e u_b}{d_b^3}\right)^{\frac{1}{2}}$
Kato, Wen	$F_o = 11./D_B$: - Gas Interchange per Volume of Bubble
Latham	Dimensionless Interchange Parameter $X = \frac{NQH}{U_{g_a}}$
Van-Deemter	Mass Transfer Coeff't. for Bubble-Cloud and Cloud-Emulsion Transport. Effective Mass Transfer Coeff'ts. Take Care of Wake Shedding.
May, Van-Deemter, Mireur and Bischoff	No. of Times Emulsion Gas Exchanges With Bubble Gas is Used to Characterize Gas Transfer.

TABLE A-1 CONT'D.

MODEL	ADJUSTABLE PARAMETERS
Orcutt, Davidson, Pigford	Effective Diameter of Bubbles: d_B
Partridge, Rowe	F Correlation (5): Considers Number, Sizes and Velocities of Bubbles at a Cross Section.
Kunii, Levenspiel	Effective Bubble Diameter: d_B
Kato, Wen	None.
Latham	Same as Orcutt.
Van-Deemter	Mass Transfer Coefficients, and Volume Fractions of each Phase.
May, Van-Deemter. Mireur and Bischoff	"Crossflow" Parameter and Diffusion Coefficient for Emulsion Phase.

FIGURE A-1

SCHEMATIC OF BUBBLE IN FLUIDIZED BED



the bubble and re-enters through the wake. The gas recirculates down around the edge of the bubble in the solid emulsion. Hence, the gas circulates in and out of the cloud and bubble and is transferred out of this circuit by diffusion processes. Large scale transport of this gas may also occur by cloud and wake shedding (i.e., breaking away of large sections of the cloud and wake).

The wake and emulsion phases are assumed to have the minimum fluidization voidage. No reaction is assumed to occur in the bubble void because of the absence of catalyst particles.

A model for the shape and size of the cloud overlap has been proposed by Davidson and Harrison(D4) and Murray(M4) and a comparison of these two models has been reported by Rowe, Partridge, and Lyall(R2).

Comparisons of fluidized bed model predictions with actual experimental reaction conversions are given by Orcutt et al(O1), Ellis, Partridge and Lloyd(E1), Kunii and Levenspiel(K5) and Kato and Wen(K7).

DISCUSSION - APPLICATION TO COMPUTER SIMULATION

Models assuming perfect mixing, or plug flow upwards in the emulsion phase, may readily be solved by non-linear algebraic equations and numerical initial value type solutions of non-linear ordinary differential equations.

Problems arise, however, in trying to solve the models which assume downflow of emulsion gas. For first order kinetics, as assumed in the literature, analytical solutions may be found for the differential equations developed. If the kinetics, however, are non-linear (i.e., where the mathematical expression describing the rate of reaction contains the concentration of products and/or reactants raised to powers other than one or products of concentrations of two or more components) then the model reduces to a boundary value problem with several unknown boundary conditions. These unknown boundary conditions arise from not knowing the composition, at the distributor, of the emulsion gas which is assumed to travel by plug flow from the top to the bottom of the fluidized bed reactor. At the same time, at the top of the reactor, the composition of the phases that have travelled up the reactor in plug flow are unknown. Here the exit gas and downflow emulsion gas compositions are known implicitly from the upflow phase composition and the mass balance equations over a thin slice of differential height at the top interface of the catalyst bed.

Several numerical methods may be used to solve this problem: (i) Quasilinearization and Invariant imbedding(L1), (ii) using a direct search on unknown boundary values at the bottom of the fluidized bed until mass balances are satisfied at the top of the bed, and (iii) finding the solution as a sum of the general solution and particular solution of the differential equations(K4). Any of these methods appear extremely time consuming especially within the context of the chemical reactor system to be studied. It may be that the cost of computer time would render this type of fluidized bed model of little practical value in situations where complicated kinetics including many components pertian and where the calculations involving flow reversal must be included. On the other hand, if certain realistic assumptions can be made, then analytical solutions or faster numerical solutions may be possible.

APPENDIX B

LITERATURE SURVEY AND DISCUSSION OF EXPERIMENTAL DESIGN CRITERIA FOR MODEL DISCRIMINATION

INTRODUCTION

In attempting to describe a physical situation, many mathematical models may be proposed. The predicted response of Model M_i is denoted as

$$\eta_i \ (\underline{\theta}, \underline{x}) \tag{B.1}$$

where - $\underline{\theta}$ is a vector of parameters. Usually only estimates, $\underline{\theta}^*$, are known rather than the true parameter values.

- $\underline{x}$ is a matrix of operating variables such as temperature or pressure. The number of columns of this matrix represent the number of these variables and the number of rows correspond to the number of experiments performed.

When an experiment is performed, the experimental value y_u rather than η_{iu} is observed where:

$$y_u = \eta_{iu} + \varepsilon_u \tag{B.2}$$

where - ε_u is the error for the u^{th} experiment, which, if model M_i describes the physical situation exactly, represents experimental error. This error is usually assumed to be a random event, from a normal distribution with mean zero and constant variance σ^2. The errors of each experiment are also usually assumed independent of each other.

If these assumptions for ε_u are made, the probability density function for the observations $\underline{y}$ using the model M_i, is the multivariant normal distribution. This is a function of the observations and is given by:

$$f(\underline{y}/M_i) = \left(\frac{1}{\sqrt{2\pi}\,\sigma}\right)^n \exp\left(-\frac{1}{2\sigma^2}\sum_{u=1}^{n}(y_u - \eta_{iu})^2\right) \qquad (B.3)$$

where n is the number of experiments performed,

and $f(\underline{y}/M_i)$ is the probability of making observations $\underline{y}$ given that model M_i is true.

After the n experiments have been performed, the observations $\underline{y}$ may be treated as constants and then the same expression (B.3) is the probability that model M_i is true given the experimental data and assuming the parameters are the true parameter values. The term "Likelihood" is used here when the f is a function of the model.

Thus, the likelihood of model M_i is:

$$L(\eta_i/\underline{y}) = f(\underline{y}/M_i) \qquad (B.4)$$

The experimenter may initially have a greater degree of belief in some models than in others. This may be expressed by the prior probability of model i, $P(M_i)$.

Using a Bayesian approach to model discrimination, the degree of belief in a model is examined in light of experimental data and decisions are made from this as to which model or models best describe the physical situation. Posterior probabilities may be calculated from the prior probabilities $P(M_i)$ and experimental observations $\underline{y}_u$.

This is done by means of Bayes Theorem:

$$P(\eta_i/\underline{y}_u) = \frac{P(M_i) \cdot L(\eta_i/\underline{y}_u)}{\sum_{i=1}^{m} P(M_i) \cdot L(\eta_i/\underline{y}_u)} \tag{B.5}$$

where $P(\eta_i/\underline{y}_u)$ is the probability that the data is most adequately described by model M_i of m possible models after having made the observations $\underline{y}_u$ from u experiments.

In recent years work has been done in an attempt to obtain generalized methods to direct the experiments so that the data obtained will provide the most efficient model discrimination. This Appendix will give a brief review of the criteria developed to design the most efficient experiments when they are performed sequentially.

ROTH CRITERION

Roth$^{(R3)}$ proposed that, for most efficient design for model discrimination, the operating conditions, $\underline{x}$ for the next experiment, should be chosen so as to maximize the function:

$$Z(\underline{x}) = \sum_{i=1}^{m} P(M_i) C_i \tag{B.6}$$

$$\text{where } C_i = \prod_{\substack{j=1 \\ j \neq i}}^{m} \left| \eta_j(\underline{\theta}, \underline{x}) - \eta_i(\underline{\theta}, \underline{x}) \right| \tag{B.7}$$

and m is the number of models.

ENTROPY CRITERIA

The concept of entropy was first introduced by Shannon$^{(S9)}$ in studying the amount of information that may be supplied by a communication system. Entropy is defined as:

$$S = -\sum_{i=1}^{m} \pi_i \ln \pi_i \tag{B.8}$$

where π_i is the probability associated with symbol i. The intuitive properties and mathematical properties of entropy are well dealt with by Kinchin(K12).

The most efficient experiment for model discrimination according to Box and Hill(B14,H5) is the experiment which maximizes an upper bound of the expected entropy change before and after that experiment. This upper bound reduces to their objective function:

$$D = \sum_{i=1}^{m} \sum_{j=i+1}^{m} P(M_i)P(M_j)\left(\int f_i \ln \frac{f_i}{f_j}\, dy_n + \int f_j \ln \frac{f_j}{f_i}\, dy_n\right) \tag{B.9}$$

where:

$P(M_i)$, $P(M_j)$ are the prior probabilities after (n - 1) experiments for models i and j.

f_i, f_j are the probability density functions of the nth observation (to be performed) for models i and j from equation (B.3)

$$f_i = f(\underline{y}/\eta_i) \text{ and } f_j = f(\underline{y}/\eta_j)$$

y_n is the observation after the nth experiment (which is being designed) is performed.

Box and Hill solve for D for the case of known and unknown error variance.

Reilly(R4) has actually solved for the expected entropy change rather than an upper limit by realizing that the expected entropy change, which is a function of the experimental operating conditions, may be reduced to the equivalent form:

$$R(\underline{x}) = -\frac{1}{2}(1+\ln 2\pi) - \sum_{i=1}^{m} P(M_i)\left(\frac{1}{2}\ln(\sigma^2+\sigma_i^2) + \underset{\tilde{y}_n}{E_i}\left[\ln f(y_n)\right]\right) \qquad \text{(B.10)}$$

where σ^2 is the error variance

σ_i^2 is the variance under model i and is given by

$$\sigma_i^2 = x_n^{(i)} (X_i' \cdot X_i)^{-1} x_n^{(i)} \sigma^2$$

with $x_n^{(i)}$ being the n^{th} experimental settings and X_i a matrix of partial derivatives (using model i) as described by Box and Hill, and $\underset{\tilde{y}_n}{E_i}$ is the expectation under variation in y_n assuming the i^{th} model to be correct.

Gauss-Hermite Quadrature may be modified to find the expectations of functions of normally distributed quantities.

$$\text{If } E\left(g(z)\right) = \int_z g(z) f(z) dz \qquad \text{(B.11)}$$

using Gauss-Hermite quadrature:

$$E\left(g(z)\right) = \frac{1}{\sqrt{\pi}} \sum_{i=1}^{n} P_i g(\mu + x_i \sigma \sqrt{z}) \qquad \text{(B.12)}$$

where z: $N(\mu, \sigma^2)$

g(z) is some function of Z

f(z) is the probability density function of Z and

x_i and P_i are tabulated values(LZ).

INFORMATION THEORY CRITERION

As the previous criteria were based on entropy, the following criterion is based on the Kullback-Liebler information number:

$$I(\theta,\phi,e) = \int \log \frac{f(y,\theta,e)}{f(y,\phi,e)} \, f(y,\theta,e) \, dy \qquad \text{(B.13)}$$

where e represents an experiment or experimental operating conditions

y is an experimental observation

and θ and ϕ are two hypotheses of what is true.

θ and ϕ may represent two models or two sets of parameter values.

This function is one way of representing the mean information per observation obtained from an experiment e which yields observation y when attempting to discriminate between a model described by θ and a model described by ϕ. Chernoff(C2) and Kullback and Liebler(K13) describe the properties and uses of the information number.

Chernoff considered the case of only two hypotheses about the true state of nature, θ and ϕ, and states that the most efficient experiment is the randomized experiment λ for which

$\min I(\theta,\phi,\lambda)$ is a maximum.

Bessler(B15) discusses this criterion in more detail and expands it to any number of hypotheses. He also gives several non-engineering type examples. Stone(S10) uses this measure of information in the design and comparison of regression experiments.

A good comparison of entropy and information number criteria with worked examples is given by Meeter and Pirie(M8).

OTHER METHODS

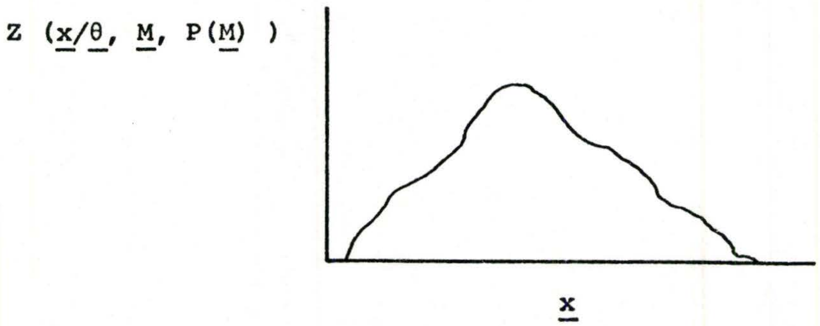
Hunter and Reiner^(H6) discuss a design criterion which may be used for only two rival models. A joint criterion for designing experiments for both parameter estimation and model discrimination is proposed by Hill, Hunter and Wichern ^(H7). Here the design criterion is a linear combination of the design criterion for parameter estimation proposed by Box and Lucas^(B3) and the design criterion for model discrimination proposed by Box and Hill^(B14).

APPENDIX C

PROPOSED MODIFICATION OF ROTH CRITERION FOR EXPERIMENTAL DESIGN FOR MODEL DISCRIMINATION WHEN THE TRUE PARAMETER VALUES ARE UNKNOWN

In most circumstances when discriminating among models the true values of the parameters are unknown, and only estimates, usually least squares estimates*, are available. It then follows that for a particular set of models, $\underline{M}$, and for any set of operating conditions, $\underline{x}$, Z, as given by equation (B.6), is a multivariate random variable whose density function depends upon the transformations of the errors in $\underline{\theta}$ inherent in the models, $\underline{M}$, and in the calculation of the function Z.

Given the true parameter values $\underline{\theta}$, the models $\underline{M}$ and prior probabilities of these models P($\underline{M}$), the true objective function may have the form:



The variable, $\underline{\theta}$, is a random variable since estimates of its value are calculated from an objective function which depends upon experimental observations, which are random variables. Since $\underline{\theta}$ is a random variable each point on the response surface Z($\underline{x}$), in independent variable space, is a random variable. Thus for different sets of best estimate parameters, $\underline{\theta}^*$, different

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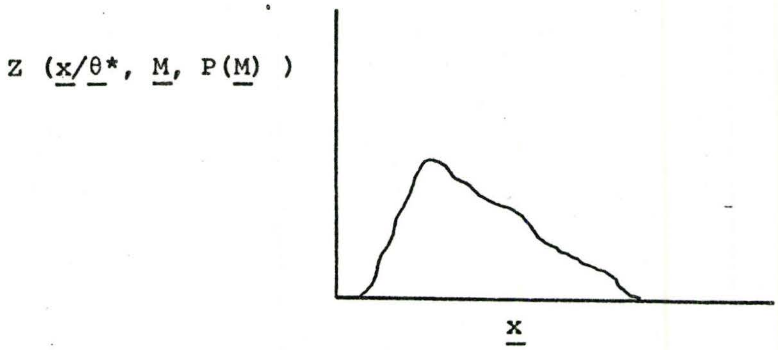
* Estimates of model parameters that minimize the sum of squares of the deviations between predicted and experimental values.

values of the objective function, Z, will be predicted at the same point in independent variable space $\underline{x}$. Thus at one set of parameter values $\underline{\theta}^*$, the observed objective function, may have the form:



It may be possible that the objective function calculated with $\underline{\theta}^*$ has a maximum at a different set of $\underline{x}$ values than the objective function calculated with the true parameter values $\underline{\theta}$. This would lead to a different and less efficient experiment. It then follows that the efficiency of the design in the long run will depend upon how well the parameters have been estimated. A "better value" for the objective function is one which takes into account all of the uncertainty due to parameter estimates.

Given the models $\underline{M}$, the prior probabilities of these models, $P(\underline{M})$, and best estimate parameter values, $\underline{\theta}^*$, the function:

$$Z\ (\underline{x}/\underline{\theta}^*,\ \underline{M},\ P(\underline{M})\ )$$

appears to behave mathematically, and may be looked upon as a likelihood function. That is, as the experimental design point $\underline{x}$ becomes more efficient with regards to producing data that would be most efficient for model discrimination, the objective function approaches a maximum. As the experimental design point $\underline{x}$ becomes less efficient, the objective function decreases. Thus, the objective function, $Z(\underline{x})$, may be looked upon as the likelihood of experimental operating conditions $\underline{x}$ producing data most efficient for model discrimination.

The "better value" for Z mentioned above comes from the marginal distribution of Z, or the distribution of Z over all possible $\underline{\theta}^*$ values in the population of parameter values with means; $\underline{\theta}$

$$L\ (\underline{x}/\underline{\theta}^*,\ \underline{M},\ P(\underline{M})\ ) = Z\ (\underline{x}/\underline{\theta}^*,\ \underline{M},\ P(\underline{M})\ ) \tag{C.1}$$

The density function for Z is then given by:

$$f\ (\underline{x}/\underline{\theta}^*,\ \underline{M},\ P(\underline{M})\ ) = \frac{L\ (\underline{x}/\underline{\theta}^*,\ \underline{M},\ P(\underline{M})\ )}{\int \underset{\underline{x}}{\cdots} \int L\ (\underline{x}/\underline{\theta}^*,\ \underline{M},\ P(\underline{M})\ )\ d\underline{x}} \tag{C.2}$$

The new criterion for experimental design involves finding the maximum of Z over all possible values of $\underline{\theta}^*$.

The objective function is given by:

$$f\ (\underline{x}/\underline{M},\ P(\underline{M})\ ) = \int \underset{\underline{\theta}}{\cdots} \int f(\underline{x}/\underline{\theta}^*,\ \underline{M},\ P(\underline{M})\ ) \cdot f(\underline{\theta}) \cdot d\underline{\theta} \tag{C.3}$$

where $f(\underline{\theta})$ is the probability density function for the parameters. If the models are linear in the parameters or if linearization techniques are employed in estimating the parameters, they may be assumed normally distributed with mean and variance either from a priori or a posteriori parameter distribution in sequential analysis.

In summary, then, if experimental operating conditions are chosen so as to maximize the objective function given by equation (C.3), more efficient information for model discrimination would be obtained, in the long run, than by using the Roth criterion since inefficiencies, due to poor parameter estimates, have been taken into account. This criterion may be more important in situations where the parameter estimates obtained are imprecise because of large error variance in the observations or because of poorly designed experiments for parameter estimation.

Although computation time may make it unfeasible, it appears reasonable that this concept could be applied to any design criterion which implicitly depends upon the parameter values and whose efficiency is influenced by the precision of these parameter estimates.

APPENDIX D

CATALYST PREPARATION

The catalyst used in this study and in the fluidized bed study was 10% nickel on silica gel. For the fluidized bed experiments which were carried out concurrently, thirty litres of catalyst were required. This represented 29 lbs. of silica gel and 3.2 lbs. nickel metal, or an equivalent 16 lbs. of nickel nitrate ($Ni(NO_3)_2.6H_2O$).

The catalyst was produced by impregnating the silica gel with an aqueous nickel nitrate solution. The nitrogen oxides were then driven off by heating the charge in an air purged furnace. The resulting nickel oxide was then reduced under hydrogen atmosphere in the reactor at 265°C for eight hours. Fisher certified N-62 nickelous nitrate crystals, obtained from Fisher Scientific Co., were used. The silica-gel carrier used, was Davidson grade 81 silica gel with a reported size range of 70. to 297. microns; this material was donated by Davidson Chemicals.

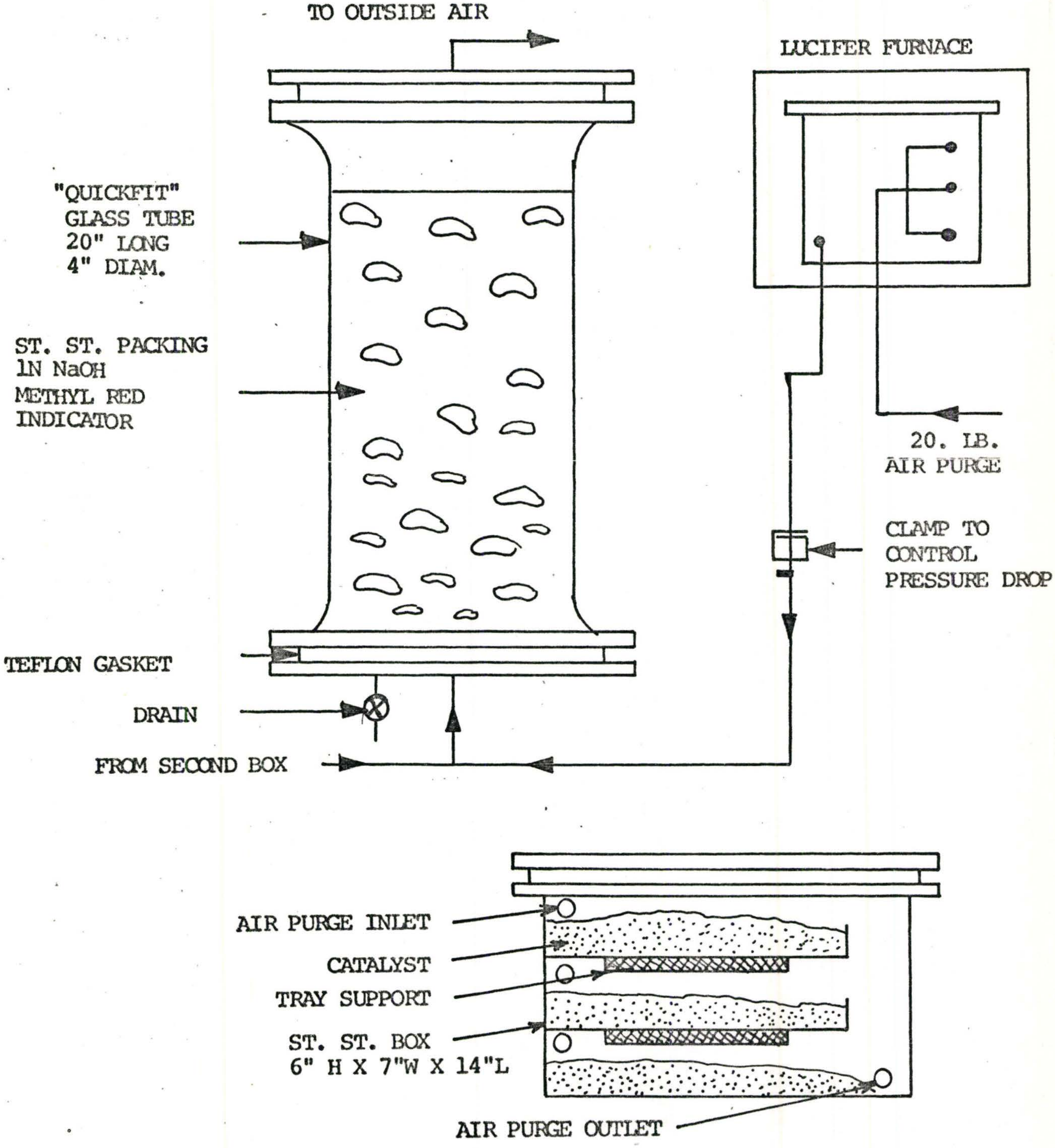
Because of the large amount of catalyst required, special apparatus was required to drive off the nitrogen oxides, mostly brown poisonous nitrogen dioxide.

This Appendix will be divided into two sections: Apparatus, and Catalyst Preparation Procedure.

D.1 Apparatus

A diagram of the apparatus is given in Figure D-1. Two airtight, type 316 stainless steel boxes which contained the catalyst were placed in

FIGURE D-1 - APPARATUS USED TO DRIVE NIGROGEN OXIDES FROM THE IMPREGNATED NICKEL ON SILICA GEL CATALYST



two Lucifer electric muffle furnaces. Each box held approximately 3½ litres of catalyst. The boxes were constantly purged with air from a 20 p.s.i.g. lab air supply; the pressure drop across the exit line from each box was monitored and regulated to ensure a reasonable purge gas flowrate through each box. The exit air, together with the poisonous nitrogen oxides, were fed into the bottom of a bubble reactor consisting of 1½ ft. of stainless steel packing. The reactor was charged with 3 litres of 1N NaOH solution. Several drops of methyl red indicator were added to the caustic solution to monitor the pH. No colour change from yellow to red was ever observed and no brown fumes were detected above the liquid in the reactor. The effluent gas from the reactor was directed by stainless steel tubing to outside air.

D.2 Procedure

The bulk density of the dry silica gel after it was dried for 8 hours at 170°C was found to be 0.43 ± .006 gm./ml. The volume of deionized water adsorbed per gram of dry silica gel was found to be .811 ± .007 ml./gm. This was found by "titrating" approximately 10. gm. of silica with deionized water until the silica gel agglomerated; this was taken to mean that the pores were filled. This "end point" was sensitive to one drop or approximately 0.05 ml. of water.

Each litre of dried support required 315 ml. of solution containing 220 gm. of nickel nitrate. For each litre of catalyst support enough deionized water was used to dissolve the required amount of nickel nitrate at room temperature (solubility of $Ni(NO_3)_2.6H_2O$ is 240 gm./100 ml. of H_2O). Heating was required since the temperature decreased as the salt dissolved. Enough deionized water was then added to the solution to obtain the required amount of total liquid volume. The silica gel was dried in a 180°C oven for eight hours prior to impregnation. The nickel solution was then added to the dried support stirring constantly by hand to distribute the liquid evenly and until all liquid was absorbed by the solid.

This green coloured material was then heated in an excess of air in an electric muffle furnace (see Figure D-1). One half hour was required to attain a temperature of 300°F. This temperature was held for 1½ hours The furnace was then held at 450°F for 1½ hours and at 690°F for eight hours.

The resulting greyish material was then placed in the fluidized bed reactor.

The catalyst used in the packed bed study was a sample taken from the fluidized bed. This sample was reduced in the packed bed at 265°C for 8 hours with a hydrogen flow of approximately 30 ml./min. The catalyst was always kept under a hydrogen atmosphere when not used. Taylor, Yates and Sinfelt(T4) observed extensive reduction of their 10% nickel on silica gel catalyst when reduced at 250°C. To ensure essentially complete reduction, the catalyst used in their kinetic studies was reduced at 370°C. The catalyst used in this study was reduced at 265°C because it was thought that the fluidized bed reactor was limited by its oil heating system to this temperature.*

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* The heating system in the fluidized bed has since been improved so now it can attain temperatures as high as 350°C.

APPENDIX E

CALIBRATION OF ANALYTICAL EQUIPMENT

E.1 Chromatograph Calibration

Analysis was required on all the components involved in the reaction. These were: methane, ethane, propane, butane and hydrogen. The calibration of the chromatograph for these components will be discussed in three sections: Calibration Apparatus, Calibration Procedure and data.

CALIBRATION APPARATUS

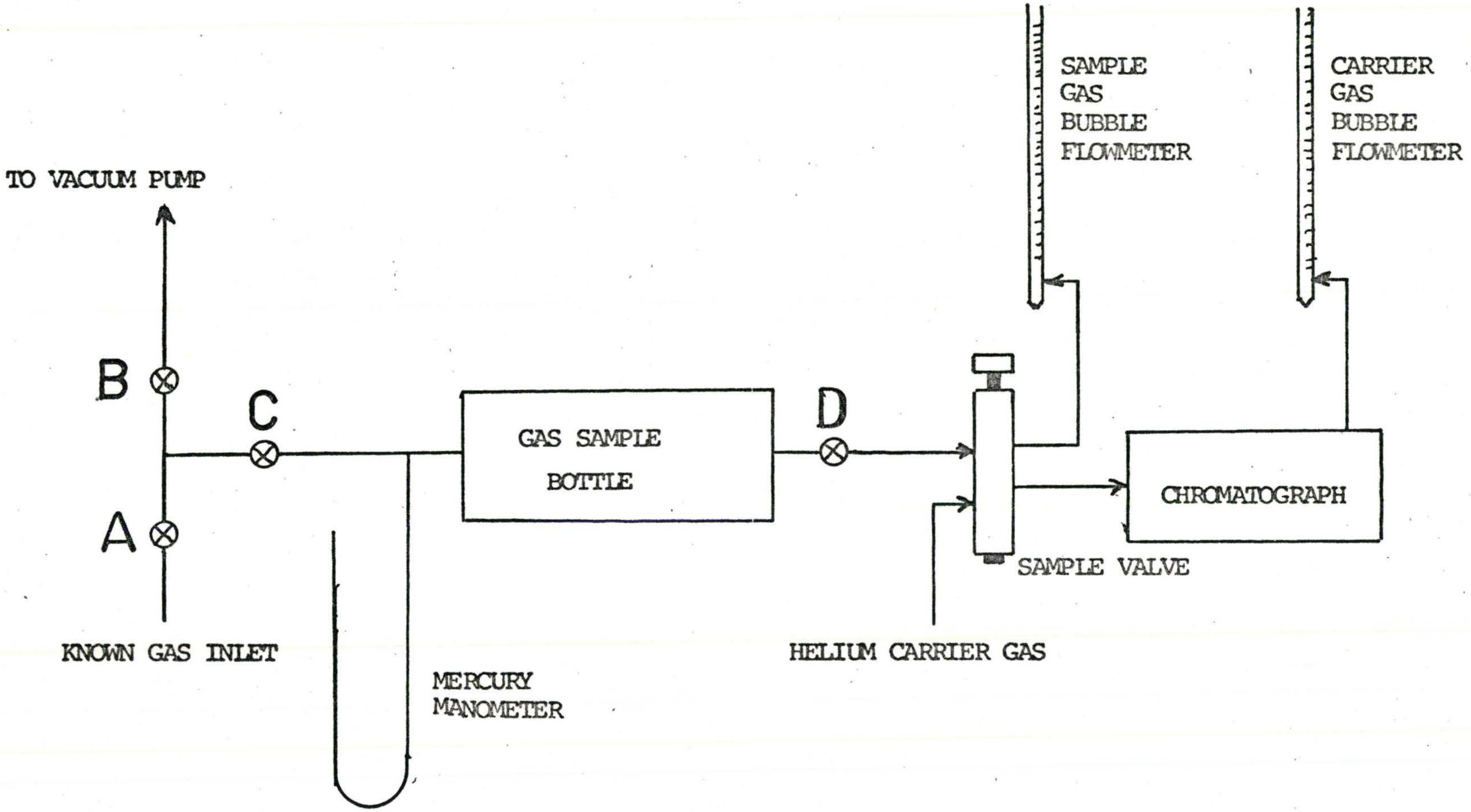
A schematic of the apparatus used is shown in Figure E-1. The known gas mixture to be analyzed was made up in a 2 ft. X 6 in. diameter sample bottle. A mercury manometer was used to measure the pressure in this bottle. Valves A and B allowed the bottle to be evacuated or filled with known gases. The known gas mixture was fed to the chromatograph sample valve through valve D.

CALIBRATION PROCEDURE

The sample bottle was first evacuated and purged at least three times with the first gas that was to be admitted.

For each known gas admitted to the sample bottle, a cylinder of the gas was attached to valve A, the lines to the sample bottle were evacuated and purged with the known gas, a portion of the gas was allowed into the bottle and its contribution to the total pressure in the bottle was measured.

FIGURE E-1 - SCHEMATIC OF CHROMATOGRAPH CALIBRATION APPARATUS



When the known gas mixture was made up, at least 15 minutes were allowed for diffusive mixing. This, and not observing any trends in composition of the replicate samples of the known gas mixture with time, gave reasonable assurance of complete gas mixing in the bottle.

The sample valve and associated lines were then purged with the gas mixture; the purge gas flowrate was measured by a bubble flowmeter. After purging, valve D was closed, producing atmospheric pressure in the sample valve, and a sample was taken. The chromatograph carrier gas flowrate was maintained at 35.0 ml./min. and the filament current was set at 200 mA.

Since the gas sample bottle could not be totally evacuated before making up a known sample, it was purged thoroughly with the first known gas to be admitted and the difference in pressure between total vacuum, as indicated by atmospheric pressure, and the actual vacuum achieved with the vacuum pump, was assumed to consist of the first known gas. To randomize the errors in measuring the contribution of each gas to the total bottle pressure, the order in which each known gas was admitted to the sample bottle for the various gas mixtures was randomized.

Since the total pressure of the gas in the sample valve was known (measured atmospheric pressure), and the composition of the gas was known (manometer measurements), the actual partial pressures of the components in the sample valve and chromatograph detector block could be calculated. These partial pressures were plotted against the areas under the corresponding chromatogram peaks to give the calibration curves. Areas were measured by a rotating ball, mechanical integrator.

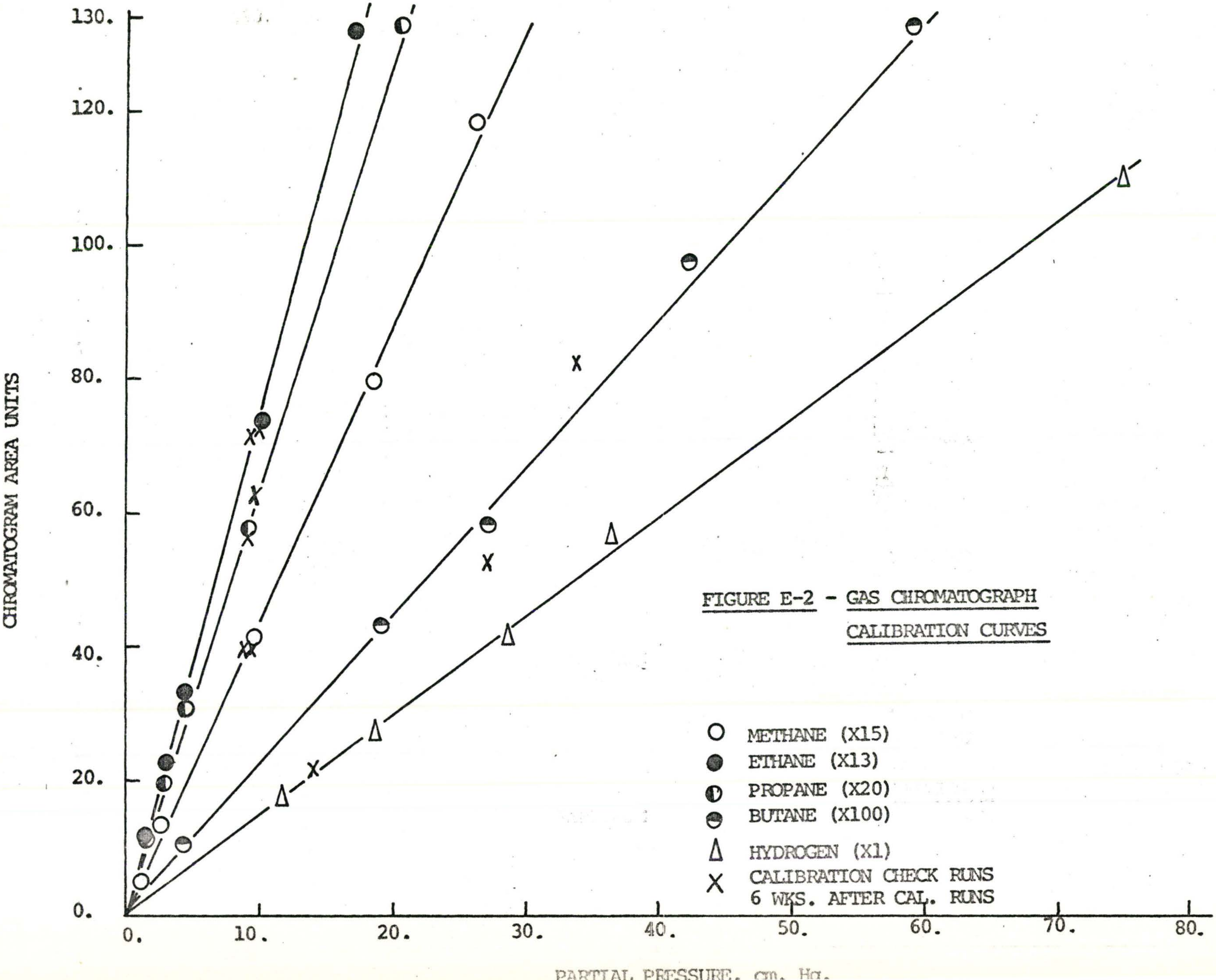


FIGURE E-2 - GAS CHROMATOGRAPH CALIBRATION CURVES

TABLE E-2

CHROMATOGRAPH CALIBRATION FACTORS

GAS COMPONENT	ATTENUATION FACTOR	CALIBRATION FACTOR $\frac{\text{mm. Hg.}}{\text{area unit}}$	95% CONFIDENCE LIMITS ON FACTOR	CONFIDENCE LIMITS AS PERCENT OF FACTOR
METHANE	x1	0.150	±.006	±4%
ETHANE	x1	0.100	±.005	±5%
PROPANE	x1	0.079	±.005	±7%
BUTANE	x1	0.068	±.004	±5%
HYDROGEN	x1	4.4	±.3	±6%

The calibration was checked six weeks after the calibration runs were performed and the results agreed very well with those established earlier.

The calibration curves obtained are shown in Figure E-2.

The calibration factors (slopes of the calibration curves) and their respective errors were calculated by the simple linear least squares formulae given by Volk$^{(V4)}$, and are listed in Table E-1.

E.2 Capilliary Flowmeter Calibration

The hydrogen and hydrocarbon "capilliary" flowmeters were calibrated with a soap-film bubble flowmeter at a constant back pressure of 1210 mm. Hg. as measured by a mercury manometer (corrections for atmospheric pressure changes were required). The hydrogen flowmeter was calibrated directly; however, the hydrocarbon flowmeter had to be calibrated by setting the hydrogen rate at a known nominal value (approximately 0.8 ml./sec.). The hydrocarbon rate was then calculated by difference since the back pressure valve could not work properly at the low hydrocarbon flowrates used (as low as 0.1 ml./sec.).

The calibrations were checked a number of times before the experiments began. During the experiments, a bubble flowmeter was used to measure the effluent rate from the reactor. Since the cracking reaction is a constant volume reaction, this was a check on the flow measurements. It was found necessary to use tygon tubing to isolate the constricted tubing flowmeters from the vibrations caused by a stirrer in order to ensure that calibrations remained constant over time.

The calibration curves for the flowmeters are given in Figures E-3

FIGURE E-3 - "CAPILLIARY" FLOWMETER CALIBRATION CURVE

HYDROCARBON FLOWMETER

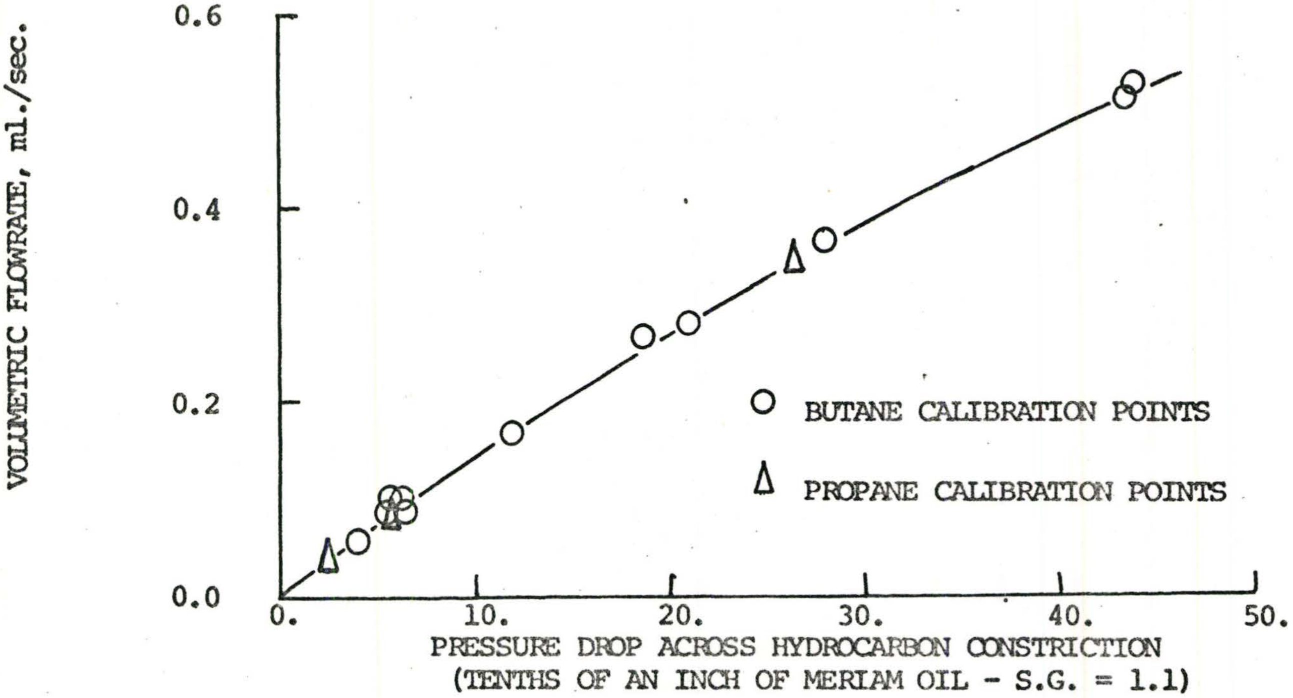
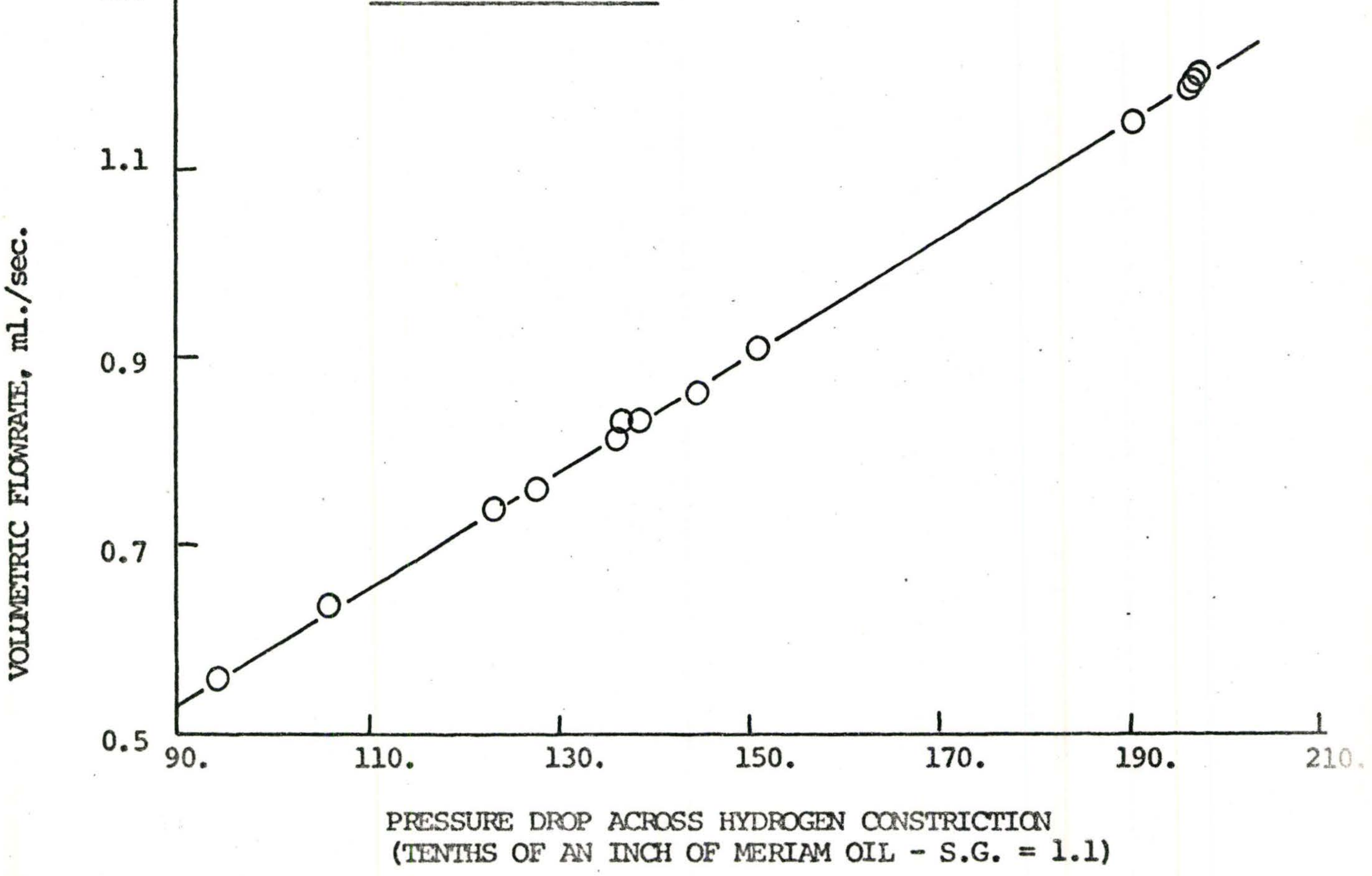


FIGURE E-4 - "CAPILLIARY" FLOWMETER CALIBRATION CURVE

HYDROGEN FLOWMETER



and E-4. The points shown were taken randomly on five different days for the hydrogen flowmeters and three different days for the butane flowmeters.

Since setting the feed flows is important in performing an experimental design, attempts were made to substantiate the flowmeter calibrations. This was done by feeding known mixtures of hydrogen and butane, as measured by the flowmeter calibrations, directly to a gas chromatograph and analyzing the mixture. It was observed that the ratio of hydrogen to butane as measured by the chromatograph was always lower than that measured by the flowmeters. This difference increased from 2% at a ratio of 2:1 to as high as 13% at a ratio of 6:1. The difference in total flow as given by the calibration curves and as measured by the bubble flowmeter at the exit of the chromatograph never exceeded 2%. It was felt that at high ratios the hydrogen rate affected the butane flowmeter calibration perhaps by diffusion of hydrogen countercurrent to the butane flow. An attempt was made to isolate the butane flowmeter constriction with 3 ft. of 1/8 in. diameter copper tubing crimped repeatedly along its length. After this modification the ratios as given by the flowmeters and chromatograph agreed to within 3% for hydrogen to butane ratios as high as 17:1.

APPENDIX F: PACKED BED REACTOR CALCULATIONS

CALCULATION OF THE HEAT OF REACTION (S6)

Assume the worst experimental conditions, i.e., a reacting temperature of 280°C. (550°K.) where the heat generated would be the greatest.

Reaction	ΔH - Heat of reaction at standard conditions (25°C.) per mole of butane reacting. Cal./gm. mole	(B.T.U./lb. mole)
$C_4 \rightarrow 4C_1$	41400.	(74500.)
$C_4 \rightarrow 2C_2$	10322.	(18600.)
$C_4 \rightarrow C_3 + C_1$	12560.	(22600.)

Assume the sample reaction:

$$4C_4 \rightarrow 8C_1 + 1C_2 + 2C_3$$

By Hess' law of constant heat summation, the standard heat of reaction at 25°C. is:

23079. cal./gm. mole of butane reacted

An additional 1000. cal./gm. mole of sensible heat is given off by cooling the reactants to standard conditions and taking the products back up to 280°C.

CALCULATION OF THE PARTICLE REYNOLDS NUMBER

Feed flowrate = 1.5 ml./sec. (constant throughout the reactor)

Reactor cross-sectional area = 0.386 cm.^{2}

Superficial feed velocity = 3.85 cm./sec.

Length of reactor = 25. cm.

Space time = 6.5 sec.

Molar flowrate $= \frac{PV}{RT} = \frac{1.0 \times 1.5}{82.06 \times 550.}$

$= 0.0000332$ gm. moles/sec.

Average molecular weight assuming 5:1 hydrogen to butane molar ratio

$$= \frac{(1. \times 5.) \times (58. \times 1.)}{6.}$$

$= 10.$ gm./gm. - mole.

Superficial mass velocity $= G$

$$= \frac{0.00332 \times 10.}{0.386}$$

$= 0.00086$ gm./(sec.) (cm.^{2})

Assume particle diameter $= d_p = 0.015$ cm.

The gas viscosity is close to $\mu = 0.00011$ poise$^{(P2)}$.

Reynolds number $= N_{Re} = \frac{G\, d_p}{\mu}$

$= 0.12$

CALCULATION OF AVERAGE MASS FLUX FROM PARTICLES

Assume most severe rate of reaction of butane at 283°C.

$$r_B = 3.22 \times 10^{17} \exp.\ (-\ 56400./1.99 \times 556.)\ P_B\ P_H^{-2}$$

$$= 0.000019\ P_B\ P_H^{-2}$$

Assume a partial pressure of butane, P_B, of 0.3 and a partial pressure of hydrogen, P_H, of 0.7

$\therefore r_B = 0.0000118$ gm. moles/(sec.) (volume of reactor)

$$\frac{\text{surface area of particle}}{\text{volume of particle}} = \frac{\pi d_p^{\,2}}{\frac{\pi d_p^{\,3}}{6.}} = \frac{6.}{d_p}$$

$$\frac{\text{volume of particle}}{\text{volume of reactor}} = (1.0 - \varepsilon)$$

$$\therefore \frac{\text{surface area of particles}}{\text{volume of reactor}} = \frac{6. \times (1. - \varepsilon)}{d_p}$$

$$= 348.\ \text{cm.}^2/\text{cm.}^3$$

Assuming $\varepsilon = 0.42$

$$\therefore \text{mass flux} = \frac{r_B}{348.}$$

$$N = 3.4 \times 10.^{-8}\ \text{gm. moles/(sec.) (cm.}^2)$$

CALCULATION OF AVERAGE HEAT FLUX FROM PARTICLES

Using the heat of reaction calculated previously for the worst case where all butane cracks to methane:

$$\text{heat flux} = N \times \Delta H$$

$$= 3.4 \times 10.^{-8} \times 42400.$$

$$Q = 0.0014\ \text{cal./(sec.) (cm.}^2)$$

j_D AND j_H VALUES FOR MASS AND HEAT TRANSFER

The factors j_D and j_H are obtained from the correlations given by Satterfield and Sherwood (S7).

Here for $N_{Re} = 0.12$

$$j_D \approx j_H \approx 40.$$

CALCULATION OF DRIVING FORCE FOR MASS TRANSFER

$$\text{Schmidt number} = N_{Sc} = \frac{\mu}{\rho \mathcal{D}}$$

$$\text{where } \rho = \frac{P}{RT} \times \text{average Mol. Wt.} = \frac{1.}{82.06 \times 550.} \times 10.$$

$$= 0.00022 \text{ gm./cm.}$$

and taking $\mathcal{D} \approx 0.3$ cm.^{2}/sec.$^{(P2)}$

$$\therefore N_{Sc} = \frac{0.00011}{0.00022 \times 0.3}$$

$$= 1.7$$

The mass transfer coefficient is calculated from the j_D factor

$$k_g = \frac{j_D G}{P(N_{Sc})^{1/3} \text{ (average mol. wt.)}}$$

$$= 0.0024 \text{ gm. moles/(sec.) (cm.}^2\text{) (atm.)}$$

Therefore the driving force required to bring the reactants to the catalyst surface must be:

$$\Delta p = \frac{N}{k_g} = \frac{3.4 \times 10.^{-8}}{.0024}$$

$$= 0.00001 \text{ atm.}$$

Thus there is no mass transfer limitation on the surface of the catalyst.

CALCULATION OF DRIVING FORCE FOR HEAT TRANSFER

$$\text{Prandth number} = N_{Pr} = \frac{C_p \mu}{k}$$

where, C_p, the heat capacities at 500°K. were obtained from reference$^{(S6)}$.

Component	Heat Capacity (cal./(gm. mole) (C.°)
methane	10.2
ethane	16.4
propane	23.4
butane	30.
hydrogen	7.

Assume an average heat capacity, C_p, of 14. cal./(gm. mole) (C.°)

The thermal conductivity is calculated in the same way, taking values from reference$^{(K12)}$.

$$k = 0.00206 \text{ cal./(sec.) (cm.) (°C.)}$$

$$N_{Pr} = \frac{14. \times 0.00011}{0.00206}$$

$$= 0.75$$

The heat transfer coefficient is calculated from j_H

$$h = \frac{j_H \, G \, C_p}{(N_{Pr})^{1/3}}$$

$$= 0.58 \text{ cal./(sec.) (cm.}^2\text{) (°C.)}$$

Therefore the driving force required to remove the heat generated is,

$$\Delta T = \frac{Q}{h} = \frac{0.0014}{0.58}$$

$$= 0.0024 \text{ °C.}$$

Thus there is essentially no temperature difference between the particle and on the reacting gas flowing by it.

CALCULATION OF THE THIELE MODULUS

The effect of the Thiele modulus:

$$\phi = L\sqrt{\frac{k_v}{\mathcal{D}_{eff.}}}$$

on the effectiveness factor, η, for a first order reaction in spherical catalyst pellets is given by Satterfield and Sherwood$^{(S7)}$.

For spheres $L = \text{radius}/3$.

$\mathcal{D}_{eff.}$ is the effective diffusivity of the reacting gas in the catalyst pores.

k_v is the first order velocity constant based on the gross volume of catalyst particle.

Note that as $\phi \longrightarrow 0, \eta \longrightarrow 1$.

For the present case:

(i) Calculate L

$$L = 1/3 \times 0.0075$$
$$= 0.0025 \text{ cm.}$$

(ii) Calculate k_v

From the rate expression for the cracking of butane and assuming the most severe conditions: (from previous calculations)

$$r_B = 0.000019\ P_B\ P_H^{-2}$$

assume $P_H = 0.7$ atm.

$$\therefore r_B = 0.000039\ P_B$$
$$= 0.000039 \times R \times T \times C_B$$
$$= 1.76\ C_B$$

where k = 1.76 1/sec. is the rate constant expressed on the basis of unit volume of reactor

$$k_v = k \times \frac{1.}{(1.-\varepsilon)} = \frac{1.76}{0.58}$$

$$= 3.04 \text{ (1./sec.) on the basis of volume of catalyst to particle.}$$

(iii) Determine $\mathcal{D}_{eff.}$

Take the worst case for effective diffusivity (Knudsen diffusion range). From Satterfield and Sherwood the Knudsen diffusion coefficient should not be lower than 0.0001 cm.^{2}/sec.*. This is the coefficient for cumene gas at 420°K. in silica alumina cracking catalyst.

assume $\mathcal{D}_{eff.}$ = 0.001 cm.^{2}?sec.

Thiele modulus $= 0.0025 \dfrac{3.04}{0.001}$

$\tilde{=}$ 0.1

For this Thiele modulus, from Satterfield and Sherwood and Bird Stewart and Lightfoot$^{(B2)}$, the effectiveness factor is essentially equal to one. This means that the reaction is not limited by pore diffusion.

CHECK THE IMPORTANCE OF AXIAL DIFFUSION

$$\text{Peclet number} = \frac{\bar{U}L}{E_{DA}}$$

where $\bar{U}$ = average superficial velocity, cm./sec.

L = characteristic length, cm.

E_{DA} = eddy diffusivity, cm.^{2}/sec.

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* Note the normal diffusion coefficient, $\mathcal{D}$, would be about 0.3 cm.^{2}/sec.

Carberry[(C3)], found that the eddy diffusivity for a He-air system approached the molecular diffusivity for Reynolds numbers less than 1.

Since in this study:

$$N_{Re} = 0.12$$

assume from reference[(P2)]

$$E_{DA} = \mathcal{D} = 0.3 \text{ cm.}^2/\text{sec.}$$

N_{Pe} based on particle diameter is:

$$N_{Pe} = N_{Re} \times N_{Sc}$$

$$= 0.12 \times 1.7$$

$$= 0.2$$

N_{Pe} based on the reactor length

$$N_{Pe} = \frac{\bar{U}L}{E_{DA}} = \frac{3.9 \times 25.}{0.3}$$

$$= 325.$$

IMPORTANCE OF AXIAL DIFFUSION TERM

From Petersen[(P4)] the steady state mass conservation equation for a packed bed catalytic reactor, taking axial components only is

$$E_{DA} \left(\frac{d^2c}{dz^2}\right) - \bar{U} \left(\frac{dc}{dz}\right) - kc = 0 \qquad \text{F.1}$$

where c = concentration of reacting component gm. moles/cm.^{3}

z = length along the reactor

k = first order reaction velocity constant based on the volume of the reactor (here a pseudo first order rate constant is used to test the assumption)

In dimensionless form the equation becomes:

$$\alpha^2 \left(\frac{d^2\Psi}{d\tau^2}\right) - \frac{d\Psi}{d\tau} - \Psi = 0$$

where $\alpha^2 = \frac{k\ E_{DA}}{\overline{U}^2}, \quad \tau = \frac{kz}{\overline{U}}, \quad \Psi = \frac{c}{c_o}$

The rate expression for butane cracking at $P_H = 0.88$ atm. and a temperature of 258°C. is:

$$r_B = 3.22 \text{ X } 10.^{17} \exp.\ (-56400./1.99 \text{ X } 531.)\ P_B\ (0.88)^{-2}$$

$$= 0.0000018\ P_B$$

$$= 0.157\ C_B$$

Thus, a pseudo first-order rate constant, k, is calculated to be 0.157.

Since the minimum volumetric flowrate is 1.0 cm.^{3}/sec.

$$\overline{U} = \frac{1.0}{.386} = 2.6 \text{ cm./sec.}$$

The maximum α^2

$$= \frac{0.157 * 0.3}{(2.6)^2}$$

$$= 0.007$$

Figures Fl, F.2 and F.3 give the most severe concentration profiles in the packed bed reactor, as predicted by a plug flow model. Since the curvature in the profiles is small, then

$$0.007 \frac{d^2\Psi}{d\tau^2} << \frac{d\Psi}{d\tau}$$

This means that the axial diffusion term should be negligible compared to the convective term and can be neglected.

FIGURE F-1 - CONCENTRATION PROFILES IN REACTOR CALCULATED FROM PACKED BED REACTOR MODEL

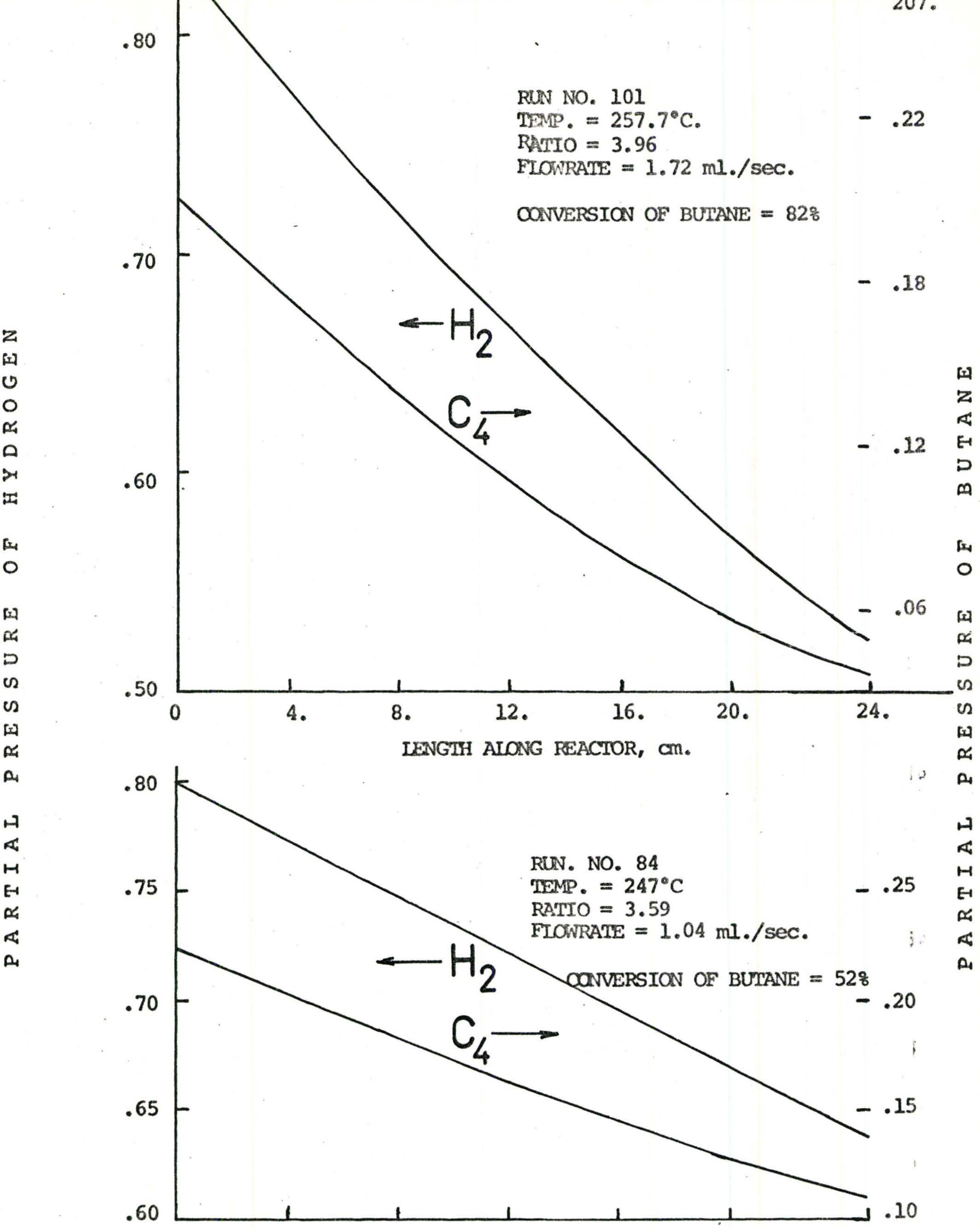
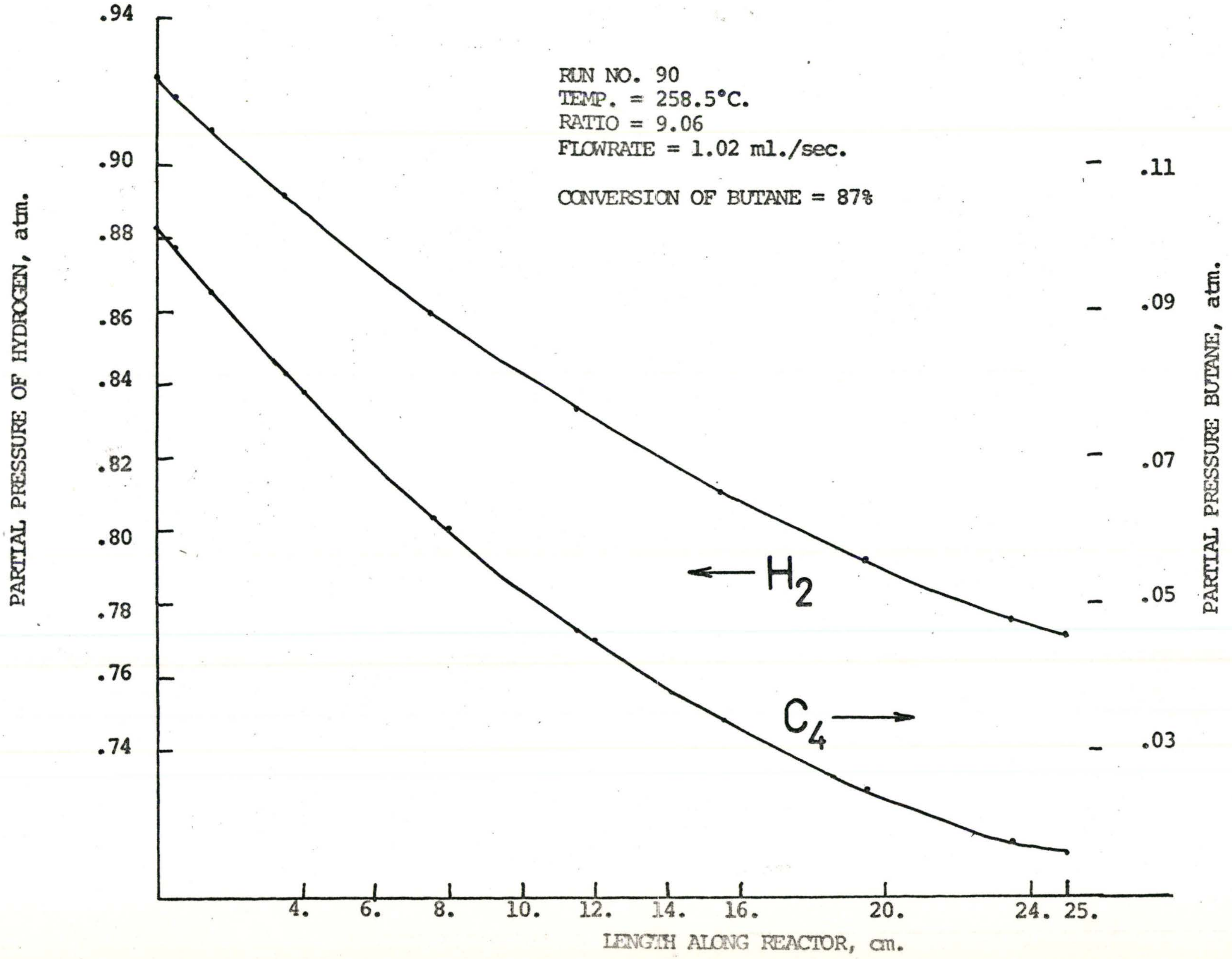


FIGURE F-2 - MOST SEVERE CONCENTRATION PROFILE OF RUNS USED IN PARAMETER ESTIMATION



RUN NO. 90
TEMP. = 258.5°C.
RATIO = 9.06
FLOWRATE = 1.02 ml./sec.

CONVERSION OF BUTANE = 87%

SAMPLE CALCULATION

Several sample concentration profiles in the packed bed reactor, as calculated from the packed bed reactor model, are shown in Figures F-1, 2 and 3.

This section will refer to the most severe of all of the profiles encountered in the runs used in parameter estimation. This profile is given in Figure F-3. A sample calculation will give orders of magnitude for the first and second derivatives in equation F.1.

Taking $\Delta z = 4.\ \text{cm.}$

$z_1 = 6.\ \text{cm.}$

$z_2 = 10.\ \text{cm.}$

Equation F.2 in terms of partial pressures:

$$0.007 \frac{d^2p}{dz^2} - 2.6 \frac{dp}{dz} = 0.157\ P \qquad \text{F.3}$$

$$\left.\frac{\Delta p}{\Delta z}\right|_{z_1} = \frac{0.838 - 0.800}{4.} = 0.0095$$

$$\left.\frac{\Delta p}{\Delta z}\right|_{z_2} = 0.0055$$

$$\left.\frac{\Delta^2 p}{\Delta z^2}\right|_{z = 8.\ \text{cm.}} = 0.001$$

in this case P = 0.06

reaction term: 0.006 X 0.157 = 0.01

first derivative term: 2.6 X 0.0075 = 0.02

second derivative term: 0.007 X 0.001 = 0.000007

APPENDIX G: PRIMARY EXPERIMENTAL DATA

This appendix gives, for the butane and propane cracking experiments:

the measured operating conditions, i.e. feed flowrate, ratio and temperature

and the reactor effluent analyses, i.e. exit mole fractions and selectivity of the products of reaction.

TABLE G-1

EXPERIMENTAL DESIGN RESULTS FOR BUTANE CRACKING

CONVERSION OF BUTANE

(ONE OF SEVERAL REPLICATES SHOWN FOR EACH EXPERIMENT)

EXPERIMENTAL LEVELS TEMPERATURE FLOWRATE RATIO	RUN NO.	AVERAGE REACTOR TEMP. DEG.C.	FEED FLOWRATE ML./SEC.	FEED RATIO H2/C4	CONVERSION OF BUTANE PERCENT
M	4	258.7	1.38	7.14	15.7
TL FL RH*	5	239.7	0.89	9.97	5.0
M*	9	258.7	1.61	6.36	27.4
TH FH RH	14	283.5	1.87	8.94	99.8
M	17	258.6	1.45	7.04	50.1
TM FH RH*	21	258.8	1.85	8.81	40.4
M*	25	258.7	1.43	7.08	53.5
TL FH RL*	27	246.1	1.86	3.95	14.0
M	30	258.7	1.48	7.37	50.4
TH FL RL	35	274.8	.992	3.75	100.
M	38	258.6	1.45	7.84	66.2
TM FL RL	43	258.2	1.01	4.08	96.9
M	50	258.6	1.49	7.08	72.3
TL FH RH*	54	245.7	1.80	8.24	19.4
M*	57	258.5	1.44	7.13	67.2
TM FH RL*	64	258.7	1.85	3.89	68.6
M	66	258.6	1.46	6.99	68.9
TH FL RH	70	283.7	1.04	8.60	99.9
	73	275.0	1.03	8.34	99.9
	76	266.5	1.01	9.75	99.9
M	80	258.6	1.44	7.15	76.3
TL FL RL*	82	246.2	1.01	3.73	49.7
M*	86	259.2	1.39	7.67	79.4
TM FL RH*	90	258.5	1.02	9.06	87.3
M	93	258.1	1.45	6.63	76.3
TH FH RL*	97	281.0	1.77	3.79	100.
	98	275.4	1.75	3.80	100.
	99	267.1	1.73	3.80	100.
	100	258.9	1.72	3.85	94.5
M*	105	258.1	1.44	7.08	79.9
TL FL RH*	109	245.9	1.03	7.81	41.2
M	112	258.5	1.45	6.71	82.1
TH FH RH	115	282.6	1.81	8.98	99.9
	117	270.5	1.79	9.17	99.7
M*	119	258.5	1.37	8.88	82.0
TM FH RH*	125	258.1	1.85	8.84	66.5
M	126	258.9	1.41	8.05	83.9
TL FM RH	133	245.9	1.63	8.66	27.3
M	135	258.2	1.42	7.50	83.4
POINT B	140	270.5	1.41	5.98	99.8
M	146	258.4	1.44	6.75	87.0
TL FH RH*	149	245.2	1.78	8.24	27.6
M	150	257.9	1.43	6.97	82.4

TABLE G-2

PROPANE CRACKING EXPERIMENTS
EXPERIMENTAL OPERATING CONDITIONS

RUN NO.	FEED FLOWRATE ML./SEC.	FEED RATIO H2/C3	REACTOR TEMPERATURES TOP TO BOTTOM DEG. CENTIGRADE				AVERAGE TEMPERATURE DEG. C.
			1	2	3	4	
1	1.40	7.93	258.7	258.7	257.2	258.5	258.3
2	1.40	8.01	258.2	258.2	258.2	257.5	258.1
3	1.40	8.01	259.2	259.0	258.8	258.2	258.8
4	0.99	3.99	259.0	258.7	258.5	257.8	258.5
5	0.99	3.95	258.5	258.4	258.0	257.3	258.0
6	1.80	3.98	258.5	258.2	258.0	257.3	258.0
7	1.81	3.93	259.0	258.7	258.2	257.8	258.4
8	1.00	7.72	258.5	258.5	258.2	257.8	258.2
9	1.00	7.95	258.5	258.2	258.2	257.3	258.1
10	1.84	8.57	258.2	258.2	258.2	257.5	258.1
11	1.38	9.29	258.7	258.7	258.2	257.7	257.4
12	1.38	9.32	258.2	258.2	258.2	257.3	258.0
14	1.01	7.29	271.0	270.7	270.5	270.0	270.5
15	1.01	4.10	270.2	269.5	268.7	268.5	269.3
16	1.38	9.57	258.2	258.2	258.0	257.5	258.0
17	1.38	9.61	258.5	258.4	258.0	258.0	258.2
18	1.77	8.88	270.2	268.0	269.5	269.3	269.3
19	1.76	3.93	271.4	270.3	270.3	270.1	270.5
20	1.79	8.39	271.5	271.2	271.0	270.5	271.0
21	1.37	8.71	257.3	257.3	257.0	256.8	257.1
22	1.38	8.62	259.0	259.5	259.0	258.7	259.0

TABLE G-3

PROPANE CRACKING EXPERIMENTS
REACTOR PRODUCT ANALYSES

RUN NO.	PRODUCT MOLE FRACTIONS				SELECTIVITY		CONVERSION OF PROPANE
	C1	C2	C3	H2	S1	S2	
1	0.0594	0.0145	0.0825	0.8422	2.01	0.493	26.34
2	0.0562	0.0159	0.0816	0.8450	1.91	0.544	26.47
3	0.0610	0.0155	0.0803	0.8421	1.99	0.505	27.63
4	0.2077	0.0481	0.0989	0.6452	2.05	0.475	50.59
5	0.1990	0.0491	0.1032	0.6486	2.01	0.496	48.98
6	0.1049	0.0268	0.1477	0.7199	1.99	0.507	26.34
7	0.1108	0.0290	0.1469	0.7130	1.97	0.515	27.70
8	0.0828	0.0227	0.0720	0.8222	1.94	0.530	37.22
9	0.0822	0.0209	0.0703	0.8261	1.99	0.506	37.03
10	0.0394	0.0106	0.0843	0.8657	1.95	0.526	19.33
11	0.0499	0.0135	0.0716	0.8645	1.95	0.526	26.36
12	0.0465	0.0148	0.0715	0.8665	1.83	0.583	26.20
14	0.2163	0.0403	0.0217	0.7217	2.18	0.407	82.02
15	0.4797	0.0429	0.0078	0.4696	2.54	0.227	96.00
16	0.0459	0.0116	0.0717	0.8702	1.99	0.503	24.31
17	0.0451	0.0127	0.0708	0.8709	1.92	0.540	24.95
18	0.1069	0.0225	0.0505	0.8199	2.11	0.445	50.07
19	0.3410	0.0590	0.0500	0.5500	2.23	0.386	75.40
20	0.1228	0.0269	0.0477	0.8026	2.08	0.457	55.24
21	0.0455	0.0139	0.0785	0.8616	1.86	0.569	23.72
22	0.0552	0.0151	0.0755	0.8539	1.94	0.530	27.36

TABLE G-4

BUTANE CRACKING EXPERIMENTS
EXPERIMENTAL OPERATING CONDITIONS

RUN NO.	FEED FLOWRATE ML./SEC.	FEED RATIO H2/C4	REACTOR TEMPERATURES TOP TO BOTTOM DEG. CENTIGRADE				AVERAGE TEMPERATURE DEG. C
			1	2	3	4	
1	1.40	6.10	258.0	258.2	258.0	257.8	258.0
2	1.43	5.53	258.5	259.7	258.7	258.7	258.9
3	1.43	5.59	258.5	259.5	258.5	258.5	258.7
4	1.39	7.14	258.5	259.5	258.5	258.5	258.7
5	.89	9.97	239.6	239.9	239.6	239.6	239.7
6	1.14	8.53	244.8	245.3	244.8	244.2	244.7
8	1.50	6.20	258.5	258.9	258.7	258.5	258.6
9	1.61	6.36	258.5	259.5	258.5	258.5	258.7
10	1.49	6.31	258.5	259.7	258.5	258.5	258.8
12	1.85	8.19	284.7	284.6	283.3	283.2	284.0
13	1.93	8.80	284.4	284.4	282.7	282.3	280.5
14	1.87	8.94	284.4	284.2	283.0	282.5	283.5
17	1.45	7.04	259.0	259.5	258.5	257.6	258.6
18	1.46	5.87	259.2	259.7	258.5	257.8	258.8
19	1.84	*.08	259.0	259.7	258.2	257.6	258.6
20	1.85	9.34	258.7	259.5	258.2	257.6	258.5
21	1.85	8.81	259.2	259.7	258.4	257.8	258.8
22	1.84	9.39	258.5	259.7	258.2	258.2	258.7
23	1.44	6.72	258.7	259.7	259.0	257.8	258.8
24	1.44	6.71	258.2	259.2	258.2	257.3	258.2
25	1.44	7.08	258.9	259.5	258.2	258.2	258.7
26	1.87	3.78	246.0	246.7	245.9	245.5	246.0
27	1.86	3.95	246.0	246.7	246.0	245.5	246.1
29	2.00	3.82	282.9	282.9	282.2	281.8	282.4
30	1.48	7.37	282.7	283.2	282.0	281.5	282.4
31	1.47	7.63	282.5	283.2	282.0	281.6	282.3
32	1.47	7.47	283.3	284.0	282.7	282.5	283.1
33	1.51	7.91	282.7	283.5	282.7	282.1	282.8
35	.99	3.75	275.1	275.1	274.9	273.9	274.8
38	1.45	7.84	259.0	259.2	258.7	257.5	258.6
39	1.44	7.26	257.6	257.6	257.5	256.3	257.3
40	1.43	7.62	258.2	258.2	258.2	257.0	257.9
42	1.00	4.19	259.2	259.0	257.5	257.0	258.2
43	1.01	4.08	259.2	259.0	257.5	257.0	258.2
44	1.00	4.13	258.7	258.7	257.0	256.5	257.8

TABLE G-4 CONTINUED

45	1.46	7.55	259.2	259.5	258.2	257.6	258.6
46	1.47	7.41	260.2	260.7	259.2	258.9	259.7
47	1.44	7.61	260.2	259.5	259.2	257.4	259.1
48	1.48	7.37	260.0	258.7	259.0	257.0	258.7
49	1.44	7.60	259.8	259.2	259.2	257.0	258.8
50	1.49	7.08	259.5	258.9	258.9	257.4	258.6
51	1.48	7.34	258.9	258.9	258.9	257.4	258.5
52	1.61	7.23	259.0	258.7	258.7	257.3	258.4
53	1.81	8.23	246.0	246.0	246.0	245.0	245.8
54	1.80	8.24	246.0	246.0	246.0	245.0	245.8
56	1.43	7.20	259.0	258.7	258.2	257.6	258.4
57	1.44	7.13	259.2	259.0	258.2	257.6	258.5
58	1.45	6.80	259.2	259.0	258.0	257.6	258.5
60	1.45	6.68	259.2	259.0	258.2	257.6	258.5
61	1.45	6.51	259.1	258.9	258.2	257.6	258.5
63	1.85	3.89	259.5	259.0	258.2	257.4	258.5
64	1.85	3.89	259.7	259.2	258.2	257.5	258.7
65	1.85	3.76	259.7	259.0	258.2	257.5	258.6
66	1.46	7.00	259.5	259.0	258.0	258.0	258.6
67	1.45	6.44	259.2	259.0	258.2	257.8	258.5
68	1.45	6.62	259.2	259.0	258.2	257.6	258.5
69	1.04	7.48	284.4	284.2	283.5	283.0	283.8
70	1.04	8.60	284.7	284.2	283.3	282.7	283.7
71	1.04	8.79	284.7	284.4	283.7	283.0	284.0
73	1.03	8.34	276.4	275.4	274.4	273.9	275.0
75	1.03	8.08	267.8	267.1	266.2	265.8	266.7
76	1.01	9.75	267.4	266.8	265.8	265.8	266.5
77	1.44	8.11	257.6	257.5	256.5	256.3	257.0
78	1.41	7.31	258.0	257.8	257.0	256.5	257.3
79	1.42	7.84	258.0	258.0	257.0	256.3	257.3
80	1.44	7.15	259.2	259.0	258.2	258.0	258.6
82	1.01	3.73	246.7	246.7	246.0	245.5	246.2
83	1.03	3.68	247.5	247.5	246.0	245.8	246.7
84	1.04	3.58	247.2	247.2	246.2	246.0	246.7
85	1.43	8.85	258.7	258.7	257.8	258.3	258.4
86	1.39	7.67	259.7	259.5	258.5	258.2	259.2
87	1.01	9.42	260.0	259.7	258.7	258.2	259.2
88	1.00	9.25	258.2	258.2	257.5	257.0	257.8
89	1.02	9.15	258.5	258.5	257.8	257.4	258.0
90	1.02	9.06	259.1	259.0	258.2	257.6	258.5
91	1.02	8.65	258.9	258.9	258.0	257.6	258.3
92	1.46	6.20	259.0	258.9	258.0	257.5	258.3
93	1.45	6.63	258.9	258.6	257.8	257.3	258.1
94	1.40	7.84	257.5	257.5	257.0	256.8	257.2
95	1.41	8.29	258.0	257.8	257.8	257.3	257.7
96	1.41	8.11	259.2	259.0	259.0	258.2	258.9

TABLE G-4 CONTINUED

97	1.77	3.79	281.5	281.0	281.3	280.3	281.0
98	1.75	3.80	276.1	275.6	275.4	274.4	275.4
99	1.73	3.80	268.5	266.8	266.8	266.3	267.1
100	1.72	3.85	260.0	259.5	258.5	258.0	259.0
101	1.72	3.96	259.2	258.2	257.0	256.3	257.7
102	1.39	8.26	258.2	258.2	257.8	257.5	257.9
104	1.44	6.84	259.2	258.7	258.2	257.8	258.5
105	1.44	7.09	258.9	258.2	258.0	257.3	258.1
106	1.44	6.66	258.9	258.7	258.2	257.8	258.4
107	1.04	7.72	246.0	246.0	246.0	246.0	246.0
108	1.03	7.60	246.0	246.0	246.0	246.0	246.0
109	1.03	7.81	246.0	246.0	246.0	246.0	246.0
111	1.44	6.62	259.1	258.9	258.2	257.8	258.5
112	1.45	6.71	259.1	258.7	258.2	257.8	258.5
113	1.82	8.61	284.3	283.2	282.7	282.0	283.1
115	1.82	8.98	284.0	282.7	282.0	281.6	282.6
116	1.78	8.40	272.0	270.5	270.2	269.6	270.6
117	1.79	9.17	271.7	270.5	270.2	269.5	270.5
118	1.38	8.89	258.0	258.0	257.6	257.3	257.7
119	1.37	8.88	258.9	258.9	258.2	258.0	258.5
120	1.40	8.93	258.9	258.5	258.2	258.0	258.4
121	1.40	8.99	258.7	258.5	258.2	257.8	258.3
123	1.84	8.77	258.9	258.2	258.2	257.8	258.3
124	1.84	8.83	258.7	258.2	258.0	257.5	258.1
125	1.85	8.84	258.5	258.2	258.0	257.6	258.1
126	1.41	8.05	259.5	259.2	258.7	258.2	258.9
127	1.41	8.11	258.0	257.8	257.3	256.9	257.5
128	1.39	9.13	258.0	258.0	257.5	257.3	257.7
129	1.39	9.36	258.2	258.2	257.8	257.3	257.9
130	1.65	8.86	246.7	246.7	246.1	246.0	246.4
131	1.65	8.77	246.0	245.8	245.5	245.3	245.6
132	1.64	8.64	246.7	246.5	246.2	246.0	246.4
133	1.63	8.66	246.0	246.0	245.8	245.8	245.9
134	1.41	8.19	258.5	258.2	257.8	257.3	257.9
135	1.42	7.50	258.7	258.5	258.0	257.8	258.2
136	1.41	7.52	258.4	258.2	257.6	257.0	257.8
137	1.43	6.06	272.7	270.5	270.0	269.8	270.7
139	1.41	5.99	272.7	270.5	269.8	269.3	270.5
140	1.41	5.98	272.7	270.5	269.8	269.3	270.5
141	1.41	6.36	272.7	270.0	269.5	269.0	270.3
142	1.42	6.09	272.7	270.0	269.5	269.3	270.4

TABLE G-4 CONTINUED

145	1.61	6.19	258.7	258.7	257.8	257.5	258.2
146	1.44	6.75	259.0	259.0	257.8	257.8	258.4
147	1.78	7.81	245.4	245.4	245.0	245.0	245.2
148	1.78	7.70	245.3	245.5	245.0	244.9	245.2
149	1.78	8.24	245.4	245.4	245.0	245.0	245.2
150	1.43	6.97	258.2	258.2	257.8	257.4	257.9
151	1.42	7.54	258.6	258.4	258.2	257.6	258.2
152	1.42	7.52	258.2	258.2	257.8	257.0	257.8

TABLE G-5

BUTANE CRACKING EXPERIMENTS
REACTOR PRODUCT ANALYSES

RUN NO.	PRODUCT MOLE FRACTIONS C1	C2	C3	C4	H2	SELECTIVITY S1	S2	S3	CONVERSION OF BUTANE
1	.0182	.0302	.0073	.1158	.8285	.72	1.203	.290	17.8
2	.0333	.0052	.0137	.1321	.8158	1.57	.244	.647	13.8
3	.0345	.0050	.0143	.1299	.8163	1.58	.228	.656	14.4
4	.0305	.0041	.0128	.1036	.8490	1.58	.212	.664	15.7
5	.0028	.0005	.0048	.0866	.9054	.60	.106	1.062	5.0
6	.0025	.0007	.0026	.1020	.8922	.85	.238	.890	2.8
8	.0627	.0082	.0233	.1016	.8042	1.68	.220	.625	26.8
9	.0601	.0100	.0231	.0987	.8083	1.61	.267	.618	27.4
10	.0619	.0118	.0242	.0973	.8048	1.57	.298	.612	28.9
12	.3300	.0356	.0113	0.0000	.6231	3.03	.328	.104	100.0
13	.3138	.0307	.0106	.0002	.6446	3.08	.302	.104	99.8
14	.3067	.0331	.0096	.0002	.6504	3.05	.330	.096	99.8
17	.1099	.0151	.0365	.0620	.7765	1.76	.242	.585	50.2
18	.1249	.0235	.0425	.0708	.7383	1.67	.314	.568	51.4
19	.0631	.0081	.0234	.0529	.8525	1.69	.218	.625	41.4
20	.0597	.0100	.0228	.0597	.8478	1.61	.269	.616	38.3
21	.0679	.0111	.0249	.0608	.8354	1.65	.270	.604	40.4
22	.0639	.0113	.0243	.0565	.8441	1.60	.283	.610	41.4
23	.1340	.0159	.0404	.0578	.7519	1.87	.221	.563	55.4
24	.1308	.0185	.0413	.0567	.7526	1.79	.254	.567	56.3
25	.1203	.0153	.0380	.0575	.7689	1.82	.232	.573	53.5
26	.0448	.0067	.0215	.1785	.7484	1.46	.219	.700	14.7
27	.0414	.0057	.0202	.1736	.7592	1.46	.202	.711	14.0
29	.0411	.0075	.0210	.1775	.7529	1.38	.253	.704	14.4
30	.1017	.0157	.0360	.0592	.7874	1.69	.260	.597	50.4
31	.0968	.0152	.0339	.0587	.7955	1.69	.265	.592	49.3
32	.1050	.0151	.0428	.0522	.7849	1.59	.229	.649	55.8

TABLE G-5 CONTINUED

33	.0981	.0155	.0336	.0547	.7981	1.71	.270	.584	51.2
35	.7933	.0246	0.0000	0.0000	.1820	3.77	.117	0.000	100.0
38	.1383	.0187	.0413	.0382	.7635	1.85	.250	.551	66.2
39	.1314	.0206	.0419	.0465	.7595	1.76	.276	.562	61.6
40	.1341	.0197	.0415	.0416	.7631	1.80	.265	.557	64.2
42	.4484	.0565	.0614	.0062	.4276	2.41	.303	.329	96.8
43	.4486	.0642	.0620	.0060	.4192	2.35	.336	.325	96.9
44	.4364	.0629	.0631	.0072	.4304	2.32	.335	.336	96.3
45	.1389	.0153	.0421	.0430	.7607	1.88	.207	.569	63.2
46	.1479	.0218	.0429	.0389	.7485	1.85	.272	.536	67.3
47	.1488	.0220	.0430	.0357	.7505	1.85	.273	.535	69.3
48	.1623	.0215	.0451	.0343	.7368	1.91	.253	.530	71.3
49	.1516	.0238	.0439	.0336	.7472	1.83	.288	.530	71.1
50	.1598	.0294	.0464	.0342	.7302	1.79	.329	.519	72.3
51	.1691	.0224	.0455	.0323	.7306	1.93	.256	.520	73.1
52	.1636	.0238	.0461	.0341	.7323	1.87	.273	.527	71.9
53	.0281	.0028	.0146	.0889	.8655	1.45	.146	.753	17.9
54	.0286	.0056	.0148	.0872	.8638	1.36	.266	.703	19.5
56	.1496	.0206	.0442	.0410	.7445	1.85	.255	.547	66.3
57	.1568	.0184	.0457	.0403	.7388	1.90	.223	.553	67.2
58	.1653	.0196	.0473	.0416	.7263	1.91	.226	.546	67.6
60	.1713	.0201	.0485	.0410	.7191	1.92	.225	.543	68.5
61	.1668	.0220	.0490	.0436	.7185	1.86	.246	.548	67.2
63	.2811	.0356	.0703	.0638	.5492	2.00	.253	.499	68.8
64	.2806	.0362	.0694	.0642	.5497	2.00	.258	.495	68.6
65	.2913	.0360	.0719	.0652	.5356	2.01	.249	.497	68.9
66	.1620	.0209	.0471	.0388	.7312	1.88	.243	.546	69.0
67	.1755	.0239	.0504	.0408	.7094	1.87	.255	.539	69.7
68	.1706	.0220	.0485	.0413	.7176	1.89	.244	.539	68.6
69	.4385	.0163	.0001	.0001	.5450	3.72	.138	.001	99.9
70	.3728	.0215	.0001	.0001	.6054	3.58	.207	.001	99.9
71	.3673	.0205	.0001	0.0000	.6122	3.60	.200	.001	100.0
73	.3623	.0285	.0028	.0001	.6063	3.39	.267	.026	99.9
75	.2960	.0381	.0224	.0002	.6433	2.69	.347	.204	99.8
76	.2372	.0320	.0235	.0001	.7072	2.55	.345	.253	99.9

TABLE G-5 CONTINUED

77	.1307	.0175	.0415	.0372	.7732	1.80	.241	.572	66.1
78	.1460	.0275	.0468	.0349	.7447	1.71	.323	.548	71.0
79	.1428	.0202	.0437	.0346	.7588	1.82	.257	.556	69.4
80	.1809	.0231	.0492	.0290	.7178	1.93	.247	.525	76.3
82	.1760	.0237	.0658	.1063	.6282	1.67	.225	.625	49.7
83	.1778	.0239	.0667	.1074	.6241	1.67	.225	.627	49.8
84	.1967	.0239	.0701	.1044	.6049	1.73	.210	.617	52.1
85	.1322	.0216	.0405	.0273	.7785	1.78	.291	.546	73.1
86	.1749	.0249	.0471	.0238	.7293	1.91	.272	.515	79.4
87	.1739	.0245	.0408	.0096	.7511	2.01	.284	.472	89.9
88	.1623	.0237	.0420	.0137	.7583	1.93	.282	.500	86.0
89	.1698	.0216	.0425	.0134	.7527	1.99	.254	.499	86.4
90	.1750	.0223	.0425	.0127	.7476	2.02	.257	.490	87.3
91	.1747	.0288	.0435	.0130	.7400	1.93	.318	.479	87.5
92	.2160	.0271	.0549	.0302	.6718	1.99	.250	.505	78.3
93	.1913	.0256	.0524	.0311	.6995	1.91	.256	.524	76.3
94	.1479	.0203	.0447	.0325	.7546	1.83	.252	.554	71.3
95	.1426	.0180	.0427	.0309	.7657	1.86	.235	.557	71.3
96	.1579	.0233	.0443	.0253	.7491	1.87	.276	.525	76.9
97	.8202	.0073	0.0000	0.0000	.1725	3.93	.035	0.000	100.0
98	.7969	.0185	0.0000	0.0000	.1846	3.82	.089	0.000	100.0
99	.7871	.0227	0.0000	0.0000	.1902	3.78	.109	0.000	100.0
100	.4512	.0576	.0709	.0113	.4090	2.32	.296	.364	94.5
101	.3402	.0447	.0780	.0357	.5014	2.05	.269	.470	82.3
102	.1603	.0223	.0459	.0224	.7492	1.87	.260	.536	79.2
104	.2064	.0264	.0530	.0229	.6912	1.97	.252	.507	82.0
105	.1925	.0250	.0508	.0248	.7068	1.95	.253	.515	79.9
106	.2089	.0289	.0536	.0237	.6849	1.95	.270	.502	81.9
107	.0656	.0130	.0313	.0683	.8218	1.41	.280	.676	40.4
108	.0723	.0102	.0334	.0681	.8160	1.50	.212	.692	41.5
109	.0686	.0108	.0322	.0667	.8216	1.47	.231	.690	41.2
111	.2097	.0310	.0537	.0231	.6825	1.94	.286	.496	82.4
112	.2127	.0260	.0537	.0232	.6843	2.00	.244	.505	82.1
113	.3817	.0157	.0009	.0001	.6015	3.67	.151	.009	99.9
115	.3435	.0269	.0011	.0001	.6284	3.43	.269	.011	99.9

TABLE G-5 CONTINUED

116	.2828	.0375	.0226	0.0000	.6571	2.66	.352	.213	100.0
117	.2635	.0294	.0233	.0002	.6836	2.69	.300	.238	99.7
118	.1521	.0198	.0424	.0214	.7643	1.91	.248	.532	78.8
119	.1615	.0204	.0432	.0182	.7566	1.95	.246	.520	82.0
120	.1498	.0217	.0424	.0206	.7656	1.87	.271	.530	79.6
121	.1516	.0218	.0421	.0196	.7648	1.89	.272	.524	80.4
123	.1240	.0168	.0392	.0336	.7864	1.80	.244	.570	67.2
124	.1210	.0166	.0389	.0340	.7895	1.79	.245	.574	66.5
125	.1224	.0160	.0387	.0340	.7889	1.81	.236	.573	66.5
126	.1786	.0263	.0465	.0178	.7308	1.93	.283	.502	83.9
127	.1634	.0206	.0461	.0240	.7459	1.91	.241	.538	78.2
128	.1380	.0230	.0415	.0216	.7759	1.79	.298	.538	78.1
129	.1412	.0197	.0407	.0208	.7775	1.87	.261	.538	78.4
130	.0407	.0067	.0206	.0725	.8595	1.41	.231	.710	28.5
131	.0382	.0064	.0195	.0750	.8609	1.39	.234	.712	26.7
132	.0492	.0027	.0215	.0739	.8526	1.65	.092	.721	28.7
133	.0396	.0064	.0202	.0753	.8585	1.40	.228	.715	27.3
134	.1683	.0233	.0453	.0211	.7419	1.92	.266	.517	80.6
135	.1910	.0269	.0493	.0195	.7133	1.95	.274	.502	83.4
136	.1808	.0284	.0490	.0212	.7207	1.88	.295	.510	81.9
137	.4521	.0485	.0054	.0002	.4937	3.20	.343	.038	99.8
139	.4673	.0442	.0054	.0002	.4829	3.27	.309	.038	99.9
140	.4646	.0455	.0056	.0002	.4841	3.25	.318	.039	99.9
141	.4274	.0455	.0080	.0003	.5189	3.15	.335	.059	99.8
142	.4555	.0440	.0067	.0002	.4937	3.23	.312	.048	99.9
145	.2425	.0350	.0573	.0179	.6473	2.00	.289	.473	87.1
146	.2335	.0273	.0537	.0168	.6688	2.08	.243	.478	87.0
147	.0415	.0056	.0211	.0845	.8473	1.43	.194	.727	25.6
148	.0442	.0052	.0215	.0853	.8439	1.49	.174	.722	25.9
149	.0431	.0056	.0216	.0784	.8512	1.45	.189	.726	27.6
150	.2010	.0267	.0530	.0220	.6972	1.94	.258	.513	82.4
151	.1873	.0240	.0496	.0212	.7180	1.95	.250	.517	81.9
152	.1802	.0243	.0494	.0232	.7230	1.91	.258	.524	80.2

APPENDIX H ANALYSIS OF ERRORS

This Appendix gives two methods of analyzing the errors in the observed mole fractions in the packed bed reactor effluent. In analyzing errors one is interested in finding the covariance matrix $\underline{V}$ for the vector of observations $\underline{y}$. The inverse of the covariance matrix, $\underline{V}^{-1}$, may be used in the non-linear regression analysis to calculate the confidence contours of the parameters.

In this work eighteen experimental runs were used in the parameter estimation. Five responses, of which three are independent, were observed for each run. That is, the rate equations for two components, in this case, methane and hydrogen, may be written as a linear combination of the remaining three components. Thus, strictly speaking, for estimating parameters and obtaining confidence regions for these parameters, only three independent components may be considered, since all the information about the system is given by these components. Thus the covariance matrix will be developed in terms of three components, methane, ethane and propane.

Errors will be assumed independent between runs and covariances will only be considered among the responses of a single run. This assumes that the errors in the responses of one run do not influence the errors in the responses of another run. Thus, the covariance matrix for all of the (18 x 3) responses has the form shown in Figure H-1.

Since the errors are independent among runs the likelihood

FIGURE H-1

Form of the Covariance Matrix for the Observed Responses In the Butane Cracking Experiments

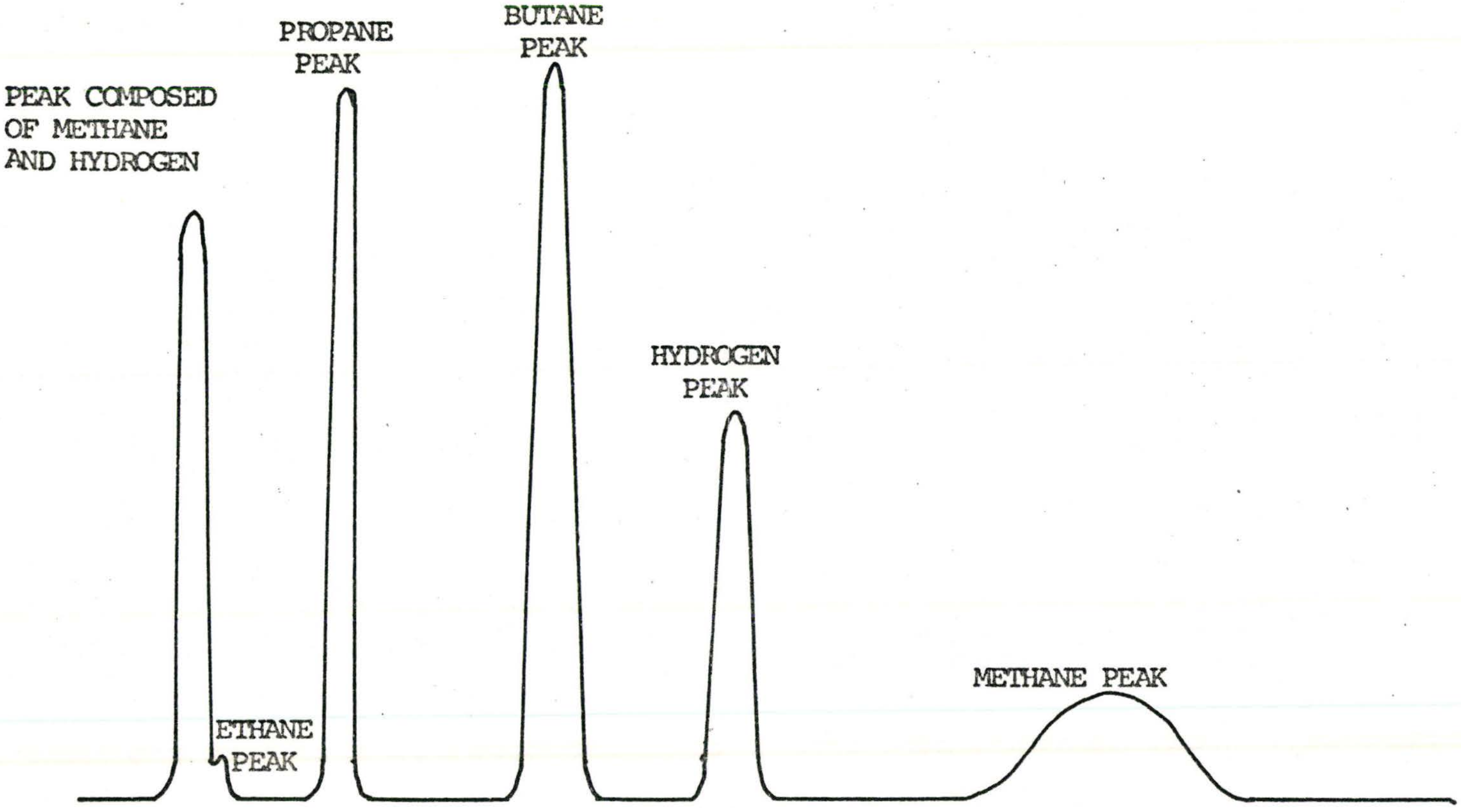
$$\underline{V} = \begin{bmatrix}
\nu_1^{(1)} & cov_{12}^{(1)} & cov_{13}^{(1)} & 0 & 0 & 0 & 0 & & & \\
cov_{12}^{(1)} & \nu_2^{(1)} & cov_{23}^{(1)} & 0 & 0 & 0 & 0 & & & \\
cov_{13}^{(1)} & cov_{23}^{(1)} & \nu_3^{(1)} & 0 & 0 & 0 & 0 & & & \\
0 & 0 & 0 & \nu_1^{(2)} & cov_{12}^{(2)} & cov_{13}^{(2)} & 0 & & & \\
0 & 0 & 0 & cov_{12}^{(2)} & \nu_2^{(2)} & cov_{23}^{(2)} & 0 & & & \\
0 & 0 & 0 & cov_{13}^{(2)} & cov_{23}^{(1)} & \nu_3^{(2)} & 0 & & & \\
0 & 0 & 0 & 0 & 0 & 0 & \ddots & 0 & 0 & 0 \\
 & & & & & & 0 & \nu_1^{(18)} & cov_{12}^{(18)} & cov_{13}^{(18)} \\
 & & & & & & 0 & cov_{12}^{(18)} & \nu_2^{(18)} & cov_{23}^{(18)} \\
 & & & & & & 0 & cov_{13}^{(18)} & cov_{23}^{(18)} & \nu_3^{(18)}
\end{bmatrix}$$

where:

$$\nu_i^{(u)} = E\{[y_{ui} - E(y_{ui})][y_{ui} - E(y_{ui})]\} \quad \underline{\text{and}} \quad cov_j^{(u)} = E\{[y_{ui} - E(y_{ui})][y_{uj} - E(y_{uj})]\}$$

for the i^{th} and j^{th} components in the u^{th} experiment.

FIGURE H-2 - TYPICAL CHROMATOGRAM OF REACTOR EFFLUENT



function for the (18 x 3) observations is the product of the likelihood function for the observations in a run. For this reason, the following two sections will be concerned with finding the covariance matrix for the observations within a run. In the first section of this Appendix the covariance matrices will be calculated by analytical methods and in the second section the covariance will be calculated using statistical methods.

H.1 Analytical Formulation of the Covariance Matrix

A typical chromatogram showing the reactor effluent analysis is given in Figure H-2.

Let the components be labelled:

Component 1 - methane
Component 2 - ethane
Component 3 - propane
Component 4 - butane
Component 5 - hydrogen

Let the areas (as given by the distance the integrator pen moves) be represented by:

A_1 - area under the methane peak
A_3 - area under the propane peak
A_4 - area under the butane peak

A_5 - area under the hydrogen peak
A_2 - area under the first two peaks. This area contains the contributions of the methane, ethane and hydrogen components.

From calibration factors shown in Appendix E.1, the partial pressure for component u is calculated from:

$$P_u = C_u A_u \qquad u = 1,2, \ldots 5. \tag{H.1}$$

where C_u = the calibration factor at an attenuation of 1.

A_u is the area under the peak due to component i at an attenuation of 1.

Note

$$P_2 = C_2 (A_2 - A_1 - A_5) \tag{H.2}$$

The mole fraction of component u is now calculated from:

$$F_u = \frac{P_u}{\sum_{u=1}^{5} P_u} \tag{H.3}$$

The analytical forms of the mole fractions of methane, ethane and propane are given by:

$$F_1 = \frac{C_1 A_1}{T} \tag{H.4}$$

$$F_2 = \frac{C_2 (A_2 - A_1 - A_5)}{T} \tag{H.5}$$

$$F_3 = \frac{C_3 A_3}{T} \tag{H.6}$$

where

$$T = C_1A_1 + C_2(A_2 - A_1 - A_5) + C_3A_3 + C_4A_4 + C_5A_5 \tag{H.7}$$

A_i are the areas which are random variables; C_i are constants.

Thus the mole fractions F_u are random variables, and by the formula for the propagation of errors (DS,J1,P1,V4,W1) the errors in F_u may be expressed in terms of the errors in A_i by:

$$\varepsilon F_u \approx \frac{\partial F_u}{\partial A_1}\,\varepsilon A_1 + \frac{\partial F_u}{\partial A_2}\,\varepsilon A_2 + \frac{\partial F_u}{\partial A_3}\,\varepsilon A_3 + \frac{\partial F_u}{\partial A_4}\,\varepsilon A_4 \qquad \text{H.8}$$

where ε represents the "error or standard deviation in", so that εF_u represents the error in the value F_u.

A_5 is not included since there are only four independent areas.

The problem now becomes one of finding the errors in the areas. These errors arise not only from measurement errors but also from inaccurate settings of the independent variables.

In the packed bed reactor, temperature variations were observed. Isothermal conditions were, however, assumed in the packed bed reactor model. Thus in estimating the parameters in the kinetic model, uncertainty must be added because of the temperature gradients. In taking replicates and assuming the temperature is perfectly set at a single value, good replication may be observed but these are only replicates of the situation which exists in the reactor and thus can cause uncertainty in the observed data. Similar arguments pertain to the other independent variables. Therefore, the parameter estimates are subject to uncertainty because of variations from the stated settings of the independent variables.

In this analysis the reactor temperature is treated as a random variable with mean value given by the average reactor temperature, and the standard deviation being one quarter of the difference between the highest and lowest reactor temperatures, ΔT_{max}, measured by thermocouples. This assumes that the observed ΔT_{max} is the widest temperature variation that occurs in the reactor and, at the 95% confidence limits, is composed of four standard deviations. The temperature variance may then be represented by:

$$\sigma_T^2 = [\frac{1}{4}\ \Delta T_{max}]^2 \qquad \text{H.9}$$

This assumes that most of the reactor is at the average reactor temperature and that, within the temperature variations observed, the higher and lower temperature regions about the mean temperature have a linear effect on rate. That is, increasing the reaction temperature Δt°C. above the mean increases the rate by the same amount as the rate is decreased by decreasing the temperature Δt°C. below the mean.

In the same way, errors are assumed in the settings of feed flowrate and ratio. These errors are assumed to be 3 percent so that 3 percent of the variable value is approximately 2σ.

Thus the variances in flowrate and feed ratio settings are:

$$\sigma_R^2 = (\frac{0.03 \text{ x } R}{2})^2 \qquad \text{H.10}$$

and

$$\sigma_F^2 = (\frac{0.03 \text{ x } F}{2})^2 \qquad \text{H.11}$$

where F and R are the values of the flowrate and ratio settings respectively.

The error in measurement of the areas is called the pen error and this error is assumed to be approximately 5% so that the variance in pen or measurement error is:

$$\sigma_{P_i}^2 = (\frac{0.05\ A_i}{2})^2 \qquad \text{H.12}$$

for the i^{th} area.

The area A_i may now be considered a function of the pen movements, temperature, flowrate and the feed ratio, and by propagation of errors, the error in area A_i is given by:

$$\varepsilon A_i \approx \frac{\partial A_i}{\partial P} \varepsilon P + \frac{\partial A_i}{\partial T} \varepsilon T + \frac{\partial A_i}{\partial F} \varepsilon F + \frac{\partial A_i}{\partial R} \varepsilon R \qquad \text{H.13}$$

These component errors are assumed to be independent. That is, for example, slight variations in feed flow do not cause systematic variations in the temperature. This assumption may not be exactly correct but these effects are felt to be quite small. To investigate these effects, since they would be difficult to measure experimentally, a quite sophisticated model would have to be developed that could predict the effects of interaction of feed flow, feed ratio and the temperature profile in the reactor.

The variance matrix for the observations may now be found from equations H.8 and H.13 (R4).

Let the pen, temperature, flowrate, and ratio variables be denoted by the variables V_1, V_2, V_3 and V_4.

The error in the mole fraction u is:

$$\varepsilon F_u \approx \frac{\partial F_u}{\partial A_1} \varepsilon A_1 + \ldots\ldots + \frac{\partial F_u}{\partial A_k} \varepsilon A_k \qquad \text{H.14}$$

In this case u = 1, ..5; p = 3; k = 4.

The error in the area, i, is:

$$\varepsilon A_i \approx \frac{\partial A_i}{\partial V_1} \varepsilon V_1 + \ldots\ldots + \frac{\partial A_i}{\partial V_j} \varepsilon V_j \qquad \text{H.15}$$

$$i = 1, \ldots, k$$

In this case, $j = 4$.

Substituting the set of equations represented by H.15 into equation H.14:

$$\begin{aligned}\varepsilon F_u \approx\ & \frac{\partial F_u}{\partial A_1}\left[\frac{\partial A_1}{\partial V_1}\,\varepsilon V_1 + \frac{\partial A_1}{\partial V_2}\,\varepsilon V_2 + \ldots + \frac{\partial A_1}{\partial V_j}\,\varepsilon V_j\right] \\ & + \frac{\partial F_u}{\partial A_2}\left[\frac{\partial A_2}{\partial V_1}\,\varepsilon V_1 + \frac{\partial A_2}{\partial V_2}\,\varepsilon V_2 + \ldots + \frac{\partial A_2}{\partial V_j}\,\varepsilon V_j\right] \\ & + \frac{\partial F_u}{\partial A_k}\left[\frac{\partial A_k}{\partial V_1}\,\varepsilon V_1 + \frac{\partial A_k}{\partial V_2}\,\varepsilon V_2 + \ldots + \frac{\partial A_k}{\partial V_j}\,\varepsilon V_j\right]\end{aligned} \qquad \text{H.16}$$

Multiplying and rearranging equation H.16 we get:

$$\begin{aligned}\varepsilon F_u \approx\ & \left[\frac{\partial F_u}{\partial A_1}\,\frac{\partial A_1}{\partial V_1} + \frac{\partial F_u}{\partial A_2}\,\frac{\partial A_2}{\partial V_1} + \ldots + \frac{\partial F_u}{\partial A_k}\,\frac{\partial A_k}{\partial V_1}\right]\varepsilon V_1 \\ & + \left[\frac{\partial F_u}{\partial A_1}\,\frac{\partial A_1}{\partial V_2} + \frac{\partial F_u}{\partial A_2}\,\frac{\partial A_2}{\partial V_2} + \ldots + \frac{\partial F_u}{\partial A_k}\,\frac{\partial A_k}{\partial V_2}\right]\varepsilon V_2 \\ & + \left[\frac{\partial F_u}{\partial A_1}\,\frac{\partial A_1}{\partial V_j} + \frac{\partial F_u}{\partial A_2}\,\frac{\partial A_2}{\partial V_j} + \ldots + \frac{\partial F_u}{\partial A_k}\,\frac{\partial A_k}{\partial V_j}\right]\varepsilon V_j\end{aligned} \qquad \text{H.17}$$

Now let

$$K_{ui} = \frac{\partial F_u}{\partial A_1}\,\frac{\partial A_1}{\partial V_i} + \frac{\partial F_u}{\partial A_2}\,\frac{\partial A_2}{\partial V_i} + \ldots + \frac{\partial F_u}{\partial A_k}\,\frac{\partial A_k}{\partial V_i} \qquad \text{H.18}$$

Then:

$$\varepsilon F_u \simeq K_{u_1}\,\varepsilon V_1 + K_{u_2}\,\varepsilon V_2 + \ldots. + K_{u_j}\,\varepsilon V_j \qquad \text{H.19}$$

Similarly for component ν:

$$\varepsilon F_\nu \simeq K_{\nu_1}\,\varepsilon V_1 + K_{\nu_2}\,\varepsilon V_2 + \ldots. + K_{\nu_j}\,\varepsilon V_j \qquad \text{H.20}$$

From the definition of covariance:

$$\begin{aligned} \operatorname{cov}(F_u, F_\nu) &= \operatorname{cov}(\varepsilon F_u, \varepsilon F_\nu) \\ &= E(\varepsilon F_u, \varepsilon F_\nu) - E[\varepsilon F_u]\,E\,[\varepsilon F_\nu] \end{aligned} \qquad \text{H.21}$$

By multiplying H.19 and H.20

$$E(\varepsilon F_u, \varepsilon F_\nu) = E[K_{u_1} K_{\nu_1} (\varepsilon V_1)^2 + K_{u_2} K_{\nu_2} (\varepsilon V_2)^2 + K_{u_j} K_{\nu_j} (\varepsilon V_j)^2 + \text{all cross product terms, } \varepsilon V_q \times \varepsilon V_r\text{, where q is not equal to r}] \qquad \text{H.22}$$

Since V_i are assumed normally distributed random variables

$$E[\varepsilon V_i] = 0 \text{ for } i = 1, 2, .., j \qquad \text{H.23}$$

Since V_q and V_r are also assumed independent

$$E[\varepsilon V_q \cdot \varepsilon V_r] = 0 \qquad \text{H.24}$$

Note also

$$(\varepsilon V_i)^2 = \sigma^2_{V_i} \qquad \text{H.25}$$

Taking expectations in equation H.21 and noting equation H.24 and H.25:

$$E(\varepsilon F_u \; \varepsilon F_\nu) = K_{u_1} \, K_{\nu_1} \, \sigma^2_{V_j} + K_{u_2} \, K_{\nu_2} \, \sigma^2_{V_2} + \ldots$$

$$+ K_{u_j} \, K_{\nu_j} \, \sigma^2_{V_j} \qquad \text{H.26}$$

Taking expectations in equation H.19 and H.20 and noting H.23:

$$E[\varepsilon F_u] \; E\,[\varepsilon F_\nu] = 0 \qquad \text{H.27}$$

Therefore from equation H.21, H.26 and H.27 we obtain:

$$\operatorname{cov}(F_u, F_\nu) = K_{u_1} \, K_{\nu_1} \, \sigma^2_{V_1} + K_{u_2} \, K_{\nu_2} \, \sigma^2_{V_2} + \ldots$$

$$+ K_{u_j} \, K_{\nu_j} \, \sigma^2_{V_j} \qquad \text{H.28}$$

and

$$\operatorname{Var}(F_u) = K^2_{u_1} \, \sigma^2_{V_1} + K^2_{u_2} \, \sigma^2_{V_2} + \ldots + K^2_{u_j} \, \sigma^2_{V_j} \qquad \text{H.29}$$

Thus, from H.28, H.29 and H.18 it may be seen that the variance matrix for the vector of observations $\underline{y}$ is given by:

$$\operatorname{var}\,(\underline{y}) = \underline{K} \; \underline{V} \; \underline{K}' \qquad \text{H.30}$$

where $\underline{K}$ is a p x j matrix whose elements are K_{u_i} and

$\underline{V}$ is a diagonal matrix with elements

FIGURE H-3

The Jacobian Matrix R
(Partial Derivatives of Mole Fractions with Respect to Area)

$$NUM = \begin{bmatrix} C_1[C_2A_2 + C_3A_3 + C_4A_4 + A_5(C_5 - C_2)] & - C_1C_2A_1 & - C_1C_3A_1 & - C_1C_4A_1 \\ C_2(-C_3A_3 - C_4A_4 - C_5A_5 - C_1A_2) & C_2(C_1A_1 + C_3A_3 + C_4A_4 + C_5A_5) & C_2C_3(A_1-A_2+A_5) & C_2C_4(A_1-A_2+A_5) \\ - C_3A_3\ (C_1 - C_2) & - C_3A_3C_2 & C_3[A_1(C_1-C_2) + C_2A_2 + C_4A_4 + A_5(C_5-C_2)] & - C_3C_4A_3 \end{bmatrix}$$

and $\underline{R} = \{\frac{R_{NUM}}{T^2}\}$

where $T = C_1A_1 + C_2(A_2-A_1-A_5) + C_3A_3 + C_4A_4 + C_5A_5$

$$V = \text{Diag}\ \{\sigma^2_{V_1},\ \sigma^2_{V_2}\ ,\ \ldots,\ \sigma^2_{V_j}\ \} \qquad \text{H.31}$$

Now let

$$\underline{R} = \left[\frac{\partial F_i}{\partial A_j}\right] \quad \text{and} \quad \underline{S} = \left[\frac{\partial A_i}{\partial V_j}\right] \qquad \text{H.32}$$

Where R and S are pxk and kxj derivative matrices respectively.

Since from H.18

$$\underline{K} = \underline{R}\ \underline{S} \qquad \text{H.33}$$

Substitute into H.30

$$\text{var}\ (\underline{y}) = R\ S\ V\ S'\ R' \qquad \text{H.34}$$

In this study R is a 3 x 4 matrix

S is a 4 x 4 matrix

V is a 4 x 4 diagonal matrix

The Jacobian matrix R may be evaluated analytically from equations H.4, H.5 and H.6. The elements of this matrix are shown in Figure H-3.

The Jacobian matrix S must be evaluated numerically for each run, the temperature, ratio and flowrate in the packed bed reactor model.

Also note that since there is a direct relationship between the measurement error and the pen movement

$$\frac{\partial A_i}{\partial V_1} = \frac{\partial A_i}{\partial P} = 0 \qquad \text{H.35}$$

TABLE H-1

ANALYTICAL VARIANCE MATRICES FOR RUNS USED IN BUTANE PARAMETER ESTIMATION

RUN NO.	VARIANCE MATRIX FOR METHANE, ETHANE, AND PROPANE MOLE FRACTIONS (elements X 10.^{8})		
5.	1.8	3.1	1.5
	3.1	28.4	5.6
	1.5	5.6	1.7
26.	433.5	73.8	183.6
		31.5	32.9
			79.1
53.	135.1	40.4	60.2
		30.5	20.1
			27.6
84.	4924.	65.6	1164.
		94.5	164.3
			30.8
109.	362.4	105.4	161.7
		44.8	48.6
			72.6
133.	148.2	56.4	72.1
		37.9	28.5
			35.3
149.	165.7	59.1	79.5
		35.1	29.3
			38.6
21.	2139.	227.9	411.9
		60.4	58.6
			89.4

TABLE H-1 CONT'D

64.	22281.	2020.	383.1
		198.6	70.2
			134.4
90.	3334.	434.8	139.3
		74.3	50.8
			95.5
101.	74898.	-5009.	-11111.
			1118.
			1962.
125.	1668.	253.6	311.4
		57.0	63.2
			81.4
8.	766.0	115.0	198.3
		38.6	36.6
			56.0
23.	5630.	536.8	788.9
		74.4	95.4
			141.2
60.	4915.	527.0	533.2
		74.0	81.5
			110.6
86.	3779.	464.4	241.8
		79.8	65.1
			99.4
105.	4931.	567.0	275.7
		84.1	65.8
			105.1
121.	2158.	329.6	281.5
		70.1	66.1
			81.2

TABLE H-2

INVERSE OF VARIANCE MATRICES FOR RUNS USED IN BUTANE PARAMETER ESTIMATION

RUN NO.	ELEMENTS OF INVERSE VARIANCE MATRIX FOR METHANE, ETHANE AND PROPANE MOLE FRACTIONS (elements X $10.^{-4}$)		
5.	2341200.	504061.	-3836312.
	504061.	109489.	-829547.
	-3836312.	-829547.	6304297.
26.	1359.	202.	-3235.
		592.	-714.
			7926.
53.	4156.	934.	-9781.
		840.	-2659.
			23722.
84.	27.2	-129.	-34.3
		2070.	-617.
			491.
109.	7396.	1805.	-17691.
		1259.	-4866.
			42820.
133	13843.	1689.	-29652.
		878.	-4160.
			64237.
149.	5870.	580.	-12541.
		832.	-1827.
			27500.
21.	61.6	118.	-361.
		680.	-988.
			2423.

TABLE H-2 CONT'D

64.	13.8	-155. 1800.	41.6 -500. 217.
90.	26.4	-201. 1746.	68.4 -634. 342.
101.	1.02	-1.71 15.5	6.77 -18.5 54.0
125.	21.8	-32.5 1319.	-58.1 -900. 1044.
8.	201.	200. 882.	-843. -1285. 4002.
23.	8.18	-3.38 1000.	-43.4 -656. 756.
60.	9.50	-91.4 1594.	21.5 -733. 526.
86.	14.9	-123. 1279.	44.1 -539. 347.
105.	17.3	-159. 1694.	54.2 -644. 357.
121	17.8	-110. 1302.	28.1 -678. 578.

TABLE H-3

ANALYTICAL VARIANCE MATRICES IN WHICH MAXIMUM OBSERVED TEMPERATURE VARIATION IN REACTOR WAS MULTIPLIED BY TEN

RUN NO.	VARIANCE MATRIX FOR METHANE, ETHANE AND PROPANE MOLE FRACTIONS (elements x 10^8)		
5	14.2	4.2	7.9
	4.2	28.5	6.2
	4.2	7.9	4.9
26	28505.	2633.	10932.
		264.8	1013.
			4195.
53	7035.	667.8	2673.
		87.6	257.7
			1017.
84	307451.	35502.	54103.
		4109.	6262.
			9571.
109	362.4	105.4	161.7
		44.8	48.6
			72.6
133	775.5	114.5	282.3
		43.3	48.0
			105.7
149	2402.	269.0	875.5
		54.8	104.0
			321.9
21	173383.	11732.	27789.
		833.2	1898.
			4466.
64	1854432.	154317.	-26995.
		12858.	-2205.
			544.

TABLE H-3 CONT'D

90	165041.	13156.	-18355.
		1075.	-1404.
			2211.
101	6719775.	-457030.	-1104253.
		32175.	75480.
			181794.
125	61873.	4826.	2941.
		404.	263.
			196.
8	42237.	3091.	8053.
		252.	600.
			1544.
23	443064.	32607.	45517.
		2426.	3375.
			4715.
60	323023.	25306.	12025.
		2004.	976.
			526.
86	189255.	14245.	-13322.
		1104.	-943.
			1091.
105	297468.	23945.	-13668.
		1952.	-1048.
			770.
121	76059.	5936.	-3272.
		495.	-203.
			252.

TABLE H-4

Standard Deviations of Mole Fraction Responses for Runs Used in Parameter Estimation

Run No.	Standard Deviations in Mole Fraction				
	C_1	C_2	C_3	C_4	H_2
5	.0007	.0001	.0007	.003	.02
26	.002	.0007	.0007	.004	.007
53	.0003	.002	.0002	.001	.002
84	.015	.0002	.005	.002	.008
109	.007	.002	.0015	.0015	.01
133	.007	.003	.005	.002	.008
149	.002	.0003	.0004	.005	.007
21	.005	.003	.001	.002	.01
64	.007	.001	.003	.002	.008
90	.007	.006	.002	.002	.01
101	.002	.003	.004	.002	.002
125	.003	.0008	.001	.001	.002
8	.002	.002	.001	.007	.004
23	.007	.002	.002	.0007	.007
60	.02	.003	.003	.0007	.02
86	.02	.003	.004	.003	.03
105	.02	.003	.03	.002	.05
121	.007	.001	.0007	.007	.007

Using the formula given by equation H.34 and the variances given by H.9, H.10, H.11 and H.12 the covariance matrices for methane, ethane and propane were calculated for each of the 18 runs used in the parameter estimation. These variance matrices are given in Table H-1. The inverse of these matrices are given in Table H-2. The sensitivity of these matrices to the temperature variance was checked by multiplying all of the maximum temperature differences by 10. The resulting covariance matrices are shown in Table H-3.

H.2 Statistical Formulation of the Covariance Matrix

In this section of the Appendix, a variance matrix for each of the 18 runs used in parameter estimation will be calculated using the replicated experiments at each of the 18 settings of independent variables. This was done in order to obtain a check of the confidence contours obtained using the covariance matrices derived in the first part of this Appendix.

In this section no covariance will be assumed to exist among the various responses in one experimental run. Thus the covariance matrices will be diagonal matrices whose elements are the variance estimates of the responses.

From the replicates available at each experimental run, an estimate of the standard deviation for each of the five mole fraction responses was obtained. These are shown in Table H-4.

The variance matrices for each of the experimental runs will have the form shown below. Run number five is used as an example.

TABLE H-5

DIAGONAL ELEMENTS OF VARIANCE MATRICES CALCULATED STATISTICALLY

RUN NO.	VARIANCE (x 10^8)				
	C_1	C_2	C_3	C_4	H_2
5	49.	1.	49.	900.	40000.
26	400.	49.	49.	1600.	4900.
53	9.	400.	4.	100.	400.
84	2250.	4.	2500.	400.	6400.
109	2900.	400.	225.	225.	10000.
133	4900.	900.	2500.	400.	6400.
149	400.	9.	16.	2500.	4900.
21	2500.	900.	100.	400.	10000.
64	4900.	100.	900.	400.	6400.
90	4900.	3600.	400.	400.	10000.
101	400.	900.	1600.	400.	400.
125	900	64.	100.	100.	400.
8	400.	400.	100.	4900.	1600.
23	4900.	400.	400.	49.	4900.
60	40000.	900.	900.	49.	40000.
86	40000.	900.	1600.	900.	90000.
105	40000.	900.	90000.	400.	250000.
121	4900.	100.	49.	4900.	4900.

TABLE H-5 CONT'D

INVERSE OF VARIANCE ELEMENTS

RUN NO.	$(\text{VARIANCE})^{-1}$ $(\times 10^{-4})$				
	C_1	C_2	C_3	C_4	H_2
5	204.	10000.	204.	11.1	.25
26	25.	204.	204.	6.25	2.0
53	1111.	25.	2500.	100.	25.
84	0.44	2500.	4.0	25.0	1.56
109	2.04	25.	44.4	44.4	1.0
133	2.04	11.1	4.0	25.0	1.56
149	25.	1111.	625.	4.0	2.04
21	4.0	11.1	100.	25.0	1.0
64	2.04	100.	11.1	25.0	1.56
90	2.04	2.8	25.0	25.0	1.0
101	25.0	11.1	6.25	25.0	25.0
125	11.1	156.	100.	100.	25.0
8	25.0	25.	100.	2.04	6.25
23	2.04	25.	25.	204.	2.04
60	.25	11.1	11.1	204.	.25
86	.25	11.1	6.2	11.1	.11
105	.25	11.1	0.11	25.0	.04
121	2.0	100.	204.	2.0	2.04

$$\underline{V} = \begin{bmatrix} (0.0007)^2 & 0 & 0 & 0 & 0 \\ 0 & (0.0001)^2 & 0 & 0 & 0 \\ 0 & 0 & (0.0007)^2 & 0 & 0 \\ 0 & 0 & 0 & (0.03)^2 & 0 \\ 0 & 0 & 0 & 0 & (0.02)^2 \end{bmatrix}$$

In comparing this matrix with those derived in the first half of this Appendix, the first three rows and columns of the above matrix should be considered. Table H-5 gives the elements of $\underline{V}$ and $\underline{V}^{-1}$ for the eighteen runs used in parameter estimation.

APPENDIX I DEVELOPMENT OF MODELS WHICH DESCRIBE THE CHEMICAL KINETICS

The first part of this Appendix will be concerned with the development of the same type of rate expression for butane hydrogenolysis as that proposed by Cimino, Boudart and Taylor$^{(C1)}$ to describe the hydrogenolysis of ethane. In the second part of this Appendix, the Hougen-Watson formulations are presented to describe the processes in the hydrogenolysis of butane shown in Figure 6.1-1.

I.1 Development of Formulations via the Cimino - Boudart - Taylor Approach

Butane, upon or after adsorption loses hydrogen atoms according to the process:

$$C_4H_{10} \rightleftharpoons (C_4H_f)_a + (\frac{10-f}{2})\ H_2 \qquad \text{I.1}$$

It is assumed that the adsorbed hydrocarbon reacts with gaseous hydrogen in the reaction step according to the process.

$$(C_4H_f)_a + H_2 \rightarrow \begin{array}{l}\text{Methane, ethane and propane}\\ \text{adsorbed species}\end{array} \qquad \text{I.2}$$

Assume that the process represented by equation I.1 is in equilibrium. Equating the rates of adsorption and desorption:

$$k_a\ P_B\ (1-\Theta) = k_d\ P_H^{(\frac{10-f}{2})}\ \Theta \qquad \text{I.3}$$

where k_a = rate constant for adsorption

$= k_a \exp(-\Delta E_d/RT)$

k_d = rate constant for desorption

$k_d' \exp(-\Delta E_d/RT)$

$\Delta E_a, \Delta E_d$ = activation energies for adsorption and desorption respectively.

Θ = fraction of surface covered with adsorbed butane species.

P_B, P_H = partial pressures of butane and hydrogen respectively.

Solve for Θ in equation I.3:

$$\Theta = \frac{\alpha\beta}{1 + \alpha\beta} \tag{I.4}$$

where $\alpha = k_a/k_d$

$$\beta = P_B/P_H{}^{[(10-f)/2]}$$

Consider β over a restricted range of pressures

$$\text{if} \quad \beta >> 1 \text{ then } \Theta \simeq \alpha^0\beta^0 \tag{I.5}$$

$$\text{if} \quad \beta << 1 \text{ then } \Theta \simeq \alpha^1\beta^1 \tag{I.6}$$

Thus over any restricted range of pressures:

$$\Theta \propto \alpha^x\beta^x \tag{I.7}$$

where $\Theta < x < 1$.

A proportionality is used in I.7 because, although the expression:

$$\Theta = \alpha^x \beta^x$$

for an appropriate value of x, predicts the same trends as I.4, over a restricted pressure range the values of Θ will not be predicted the same. The proportionality factor is included to compensate for this.

Thus

$$\Theta = a\ \alpha^x \beta^x \qquad \text{I.8}$$

where "a" actually depends upon x.

This proportionality is not clearly stated in either the original paper by Taylor et.al.(C1) or in a later development by Bond(B17).

Assuming the rate of cracking of butane is the slow step, and that the adsorbed butane molecules react with the gaseous hydrogen molecules, the rate of reaction of butane may be described by $r \propto \Theta P_H$

$$\text{i.e.} \quad r \propto a\ \alpha^x P_B{}^x P_H{}^{\{1 - x[(10-f)/2]\}} \qquad \text{I.9}$$

Therefore

$$r = K\ a\ \alpha^x P_B{}^x P_H{}^n \qquad \text{I.10}$$

where K = rate constant for reaction on the surface of the catalyst

$= k_r \exp(-\Delta E_r/RT)$

ΔE_r = activation energy for reaction in the surface

$n = 1 - x[(10-f)/2]$

Thus equation I.10 may be written simply:

$$r = K_r P_B^{\,x} P_H^{\,n} \tag{I.11}$$

where $K_r = ak_rk_ak_d \exp\{[-\Delta E_r + x\,(\Delta E_d - \Delta E_a)]/RT\}$.

The simple rate expression, or the power rate law expressed in I.11 is used to describe the rate of butane and propane hydrogenolysis in section 6.1.1 and 6.1.2 of this thesis.

I.2 Development of Formulations via the Hougen-Watson Approach

In this section the Hougen Watson equations describing all the rate processes shown in Figure 6.1-1 will be given.

Let the components be represented as:

Component 1 - methane
Component 2 - ethane
Component 3 - propane
Component 4 - butane
Component 5 - hydrogen

Let k_{ai} = rate constant at constant temperature for adsorption of component i.

k_{di} = rate constant at constant temperature for desorption of component i.

k_{ri} = rate constant at constant temperature for reaction of hydrocarbon component i.

P_i = partial pressure of component i in the gas phase.

Θ_i = fraction of active surface sites covered by component i.

Θ_L = fraction of surface sites empty and available for adsorption.

F = fraction of the butane adsorbed species that reacts to propane adsorbed species.

FIGURE I-1

Hougen Watson Type Equations for Butane Hydrogenolysis

EQUATIONS:

$$\begin{bmatrix} 0 & 0 & 0 & (-k_{d_4}-k_{r_4}) & 0 & k_{a_4}P_4 \\ 0 & 0 & (k_{r_3}-k_{d_3}) & -Fk_{r_4} & 0 & k_{a_3}P_3 \\ 0 & (k_{r_2}-k_{d_2}) & -k_{r_3} & 2(F-1)k_{r_4} & 0 & k_{a_2}P_2 \\ -k_{d_1} & -2k_{r_2} & -k_{r_3} & -Fk_{r_4} & 0 & k_{a_1}P_1 \\ 0 & -k_{r_2} & -k_{r_3} & -k_{r_4} & -k_{d_5} & k_{a_5}P_5 \\ 1.0 & 1.0 & 1.0 & 1.0 & 1.0 & 1.0 \end{bmatrix} \begin{bmatrix} \Theta_1 \\ \Theta_2 \\ \Theta_3 \\ \Theta_4 \\ \Theta_5 \\ \Theta_L \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

SOLUTION: $\underline{\underline{A}}\ \underline{\Theta} = \underline{b}$

$$\underline{\Theta} = \underline{\underline{A}}^{-1}\ \underline{b}$$

The rate of adsorption and desorption of component i are represented by the forms, respectively

$$k_{ai} P_i \Theta_L$$

$$k_{di} \Theta_i$$

Assume that the inhibitory effect on reaction by hydrogen is taken into account by the adsorption terms and that hydrogen is present in sufficient excess on the surface so as not to influence the rates of reaction on the surface. The rate of reaction of component i on the surface is then given by:

$$k_{ri} \Theta_i$$

Pseudo-steady state is assumed on the surface of the catalyst so that Θ_i does not change with time.

i.e. $$\frac{d\Theta_i}{dt} = 0 \qquad \text{I.12}$$

Equating for each component the net rate of adsorption to the rate of reaction on the surface, a linear set of equations in Θ may be formulated. The matrix form of these equations is shown in Figure I-1. Given the rate constants and F, Θ_i may be calculated for each component.

Working through the schematic in Figure 6.1-1 and knowing Θ_i, the rates of appearance, r_i, of the components are given by:

$$r_4 = -k_{r_4}\Theta_4 \qquad \text{I.13}$$

$$r_3 = -F_{r_4} - k_{r_3}\Theta_3 \qquad \text{I.14}$$

$$r_2 = -r_4(2-F) - r_3 - k_{r_2}\Theta_2 \qquad \text{I.15}$$

$$r_1 = -4r_4 - 3r_3 - 2r_2 \qquad \text{I.16}$$

$$r_5 = 3r_4 + 2r_3 + r_2 \qquad \text{I.17}$$

The equations may be solved by solving the matrix of equations:

$$\begin{bmatrix} 1 & 0 & 0 \\ F & -1 & 0 \\ (2-F) & -1 & -1 \end{bmatrix}\begin{bmatrix} r_4 \\ r_3 \\ r_2 \end{bmatrix} = \begin{bmatrix} -k_{r_4}\Theta_4 \\ k_{r_3}\Theta_3 \\ k_{r_2}\Theta_2 \end{bmatrix}$$

Thus the rates of reaction may be calculated for each component given F, five adsorption constants and five desorption constants, k_{di}. These rate constants apply for one temperature and if the Arrhenius rate law is used to account for changes with temperature, as many parameters (activation energies) again are required.

The monomolecular rates of reaction arise since the hydrogen is assumed to be in sufficient excess on the surface of the catalyst so as not to affect the rates of reaction in an appreciably different way from one set of reacting conditions to another. This effect of hydrogen would thus be included in the reaction rate constant and would be assumed constant.

The inverse reaction rate dependence on hydrogen partial pressure would appear through the adsorption rate constants. That is, the hydrogen constant would be such as to inhibit the adsorption of the hydrocarbons. This inverse dependence could also perhaps be included in the Θ values in the above matrix solution for the rates, however, the inverse dependence would also be taken into account in the calculation of these Θ values from Figure I-1.

APPENDIX J APPLICATION OF THE BUTANE CRACKING KINETICS TO FLUIDIZED BED MODELLING USING THE MODELS OF ORCUTT, DAVIDSON AND PIGFORD(01)

This Appendix is divided into two sections. The first section gives derivations of the fluidized bed models first proposed by Orcutt, Davidson and Pigford(01) in which the butane cracking kinetics are incorporated. The second section gives a sensitivity analysis of these models to study the effects of catalytic activity and the mass transfer rate between bubble and emulsion phase on conversion of butane and selectivity, assuming that the kinetics are perfectly known.

J.1 Fluidized Bed Modelling

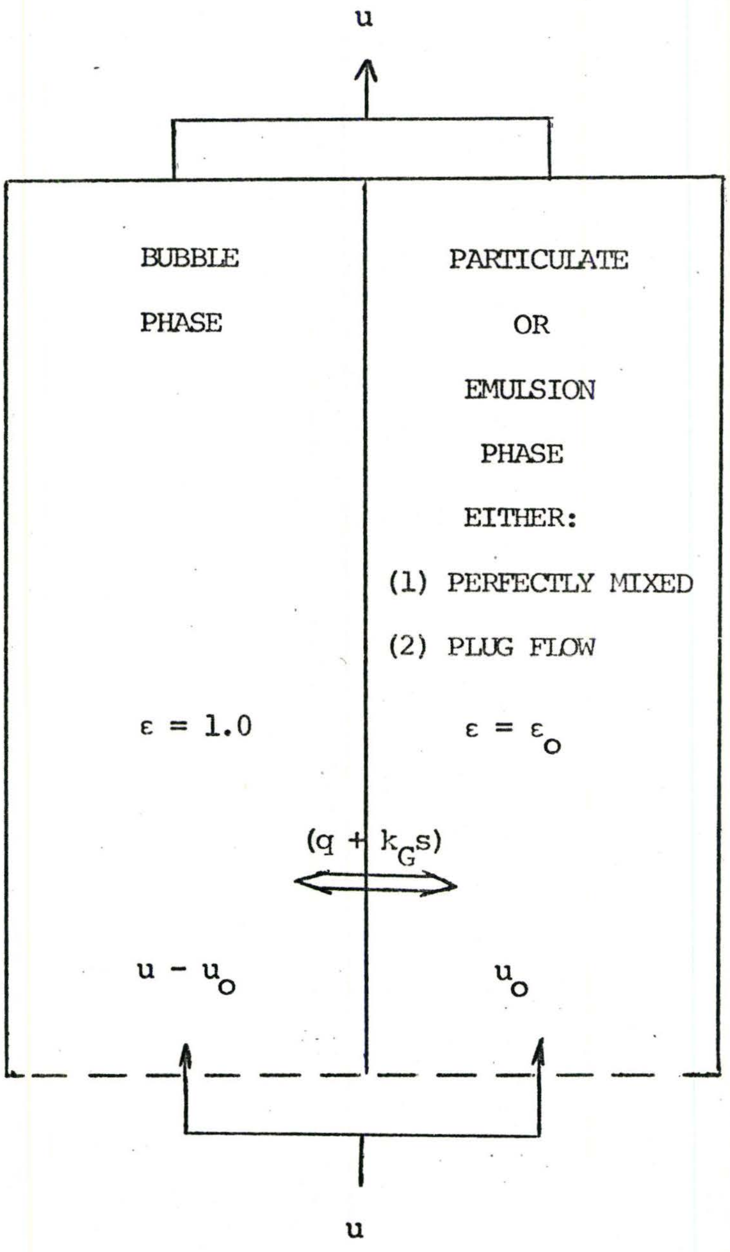
In this section two models for fluidized bed chemical reactors first proposed by Orcutt et al. will be described. These models assume that the bed is composed of two phases: the bubble phase in which there are no particles and, therefore, no reaction, and the particulate or emulsion phase which is uniform and has a voidage equal to that at minimum fluidization. All reaction, therefore, occurs in the emulsion phase. The bubbles are assumed spherical and of uniform size; they rise through the emulsion phase at the same velocity, exchanging gas with the emulsion phase by means of molecular diffusion and bulk flow. Finally, it is assumed that all gas over that required to maintain the emulsion phase in a fluidized state, forms the bubble phase.

The two theoretical models differ in the mixing assumptions in

FIGURE J-1

TWO PHASE MODEL PROPOSED BY

ORCUTT, DAVIDSON AND PIGFORD (O1)



ε_o - Minimum fluidization voidage

u_o - Minimum fluidization velocity

u - Feed superficial velocity

q - Bulk flow interchange

$k_G s$- Diffusive flow interchange

the emulsion phase. In one model, perfect mixing is assumed and in the other, plug flow is assumed. A schematic diagram showing flows and phases is given in Figure J-1.

In the next two sub-sections, mathematical developments of these models are given. These differ from the developments given by Davidson and Harrison$^{(D4)}$ only in that the equations are more general in order to incorporate the relatively complicated kinetics. In this treatment, partial pressures of components, rather than concentrations, are the dependent variables.

J.1.1 Model Assuming Perfect Mixing in the Dense Phase

MASS BALANCE ON BUBBLE PHASE

The material balance for any component over a differential height is

$$Q(P_p-P_b) = U_A V \frac{dP_b}{dy} \qquad J.1$$

Integrating equation (J.1)

$$P_b = P_p + (P_o-P_p)\exp\{-Qy/U_A V\} \qquad J.2$$

At the top of the bed the partial pressure of any component is:

$$P_b = P_p + (P_o-P_p)\ \exp\ (-x) \qquad J.3$$

where:

$$X = \frac{QH}{U_A V} \qquad J.4$$

MASS BALANCE ON EMULSION PHASE

The flow of any component from emulsion into bubble is given by

$$NQ \overset{H}{\underset{o}{}} C_b \, dy = NQ \overset{H}{\underset{o}{}} (P_b/RT) dy$$

substituting equation (J.2) and integrating; this flow is

$$\frac{NQ}{RT} [P_p H + (P_o P_p)(\frac{U_A V}{Q}) (1. - \exp(-X)] \qquad J.5$$

Flow of any component into bubble from emulsion:

$$NQHC_p = \frac{NQHP_p}{RT} \qquad J.6$$

∴ Net flow into the emulsion phase is equation J.5 minus J.6

$$\frac{(P_o - P_p)}{RT} . NVU_A . (1. - \exp(-X)) \qquad J.7$$

The feed flowrate of any component into the emulsion phase is:

$$U_o C_o = \frac{U_o P_o}{RT} \qquad J.8$$

The exit flowrate of any component from the emulsion phase is:

$$U_o C_p = \frac{U_o P_p}{RT} \qquad J.9$$

Hence, the net flowrate of any component into the emulsion phase is:

$$\frac{U_o}{RT} (P_o - P_p) \qquad J.10$$

The rate of <u>disappearance</u> of any component due to reaction is:

$$r_V H(1. - NV) \qquad \text{J.11}$$

Writing a total mass balance on the emulsion phase

$$\boxed{\begin{matrix}\text{Net Flow In}\\ \text{From Bubbles}\end{matrix}} + \boxed{\begin{matrix}\text{Net Flow In}\\ \text{From Feed}\end{matrix}} = \boxed{\begin{matrix}\text{Rate of disappearance}\\ \text{Due to Reaction}\end{matrix}}$$

adding J.7 and J.10 and equating to equation J.11 yields

$$(P_o-P_p).NVU_A.(1.-\exp(-X)) + (P_o-P_p)U_o = r_V HRT(1.-NV) \qquad \text{J.12}$$

Substituting $\beta = 1. - U_o/U$ into equation J.12 gives

$$(P_o-P_p)\ \gamma = r_V \qquad \text{J.13}$$

where

$$\gamma = \frac{U}{RTH_o}(1. - \beta\ .\ \exp(-X)) \qquad \text{J.14}$$

KINETIC RATE EQUATIONS

The pre-exponential factors for the butane cracking term and propane adsorption term were evaluated with the units:

$$\frac{\text{Moles}}{\text{(sec.) (volume packed bed reactor (P.B.))}}$$

The units required for r_V in J.13 are:

$$\frac{\text{Moles}}{\text{(sec.) (volume emulsion phase (E.P.))}}$$

Thus, a correction must be applied to take into account the difference in voidage between the packed bed and the emulsion phase of the fluidized bed.

Now

$$\frac{\text{Moles}}{(\text{sec.})\ (V_{E.P.})} = \frac{\text{Moles}}{(\text{sec.})\ (V_{P.B.})} \times \frac{(1-\varepsilon_o)\ \text{volume catalyst}/V_{E.P.}}{(1-\varepsilon_{P.B.})\ \text{volume catalyst}/V_{P.B.}}$$

Assume $\varepsilon_o = 0.45$

$\varepsilon_{P.B.} = 0.4$

Therefore

$$\frac{\text{Moles}}{(\text{sec.})\ (V_{E.P.})} = 0.9 \times \frac{\text{Moles}}{(\text{sec.})\ (V_{P.B.})}$$

The kinetic rate expressions then become:

BUTANE

$$r_{VB} = +(0.9)(k/k_o)(k_b)(P^m_{c_3})(P^n_{H_2}) \qquad \text{J.15}$$

PROPANE

$$r_{VP} = -\left[\frac{(0.9)(r_{VB}) - (0.9)(k/k_o)(K_{p1})\ P^{m'}_{c_3}\ P^{n'}_{H_2}}{(1.+K_p)}\right] \qquad \text{J.16}$$

ETHANE

$$r_{VE} = -\left[\frac{1.1\ r_{VB} - r_{VP}}{1.+K_E}\right] \qquad \text{J.17}$$

METHANE

$$r_{VM} = -[4 \times r_{VB} - 3 \times r_{VP} - 2 \times r_{VE}] \qquad \text{J.18}$$

HYDROGEN

$$r_{VH} = +[3 \times r_{VB} - 2 \times r_{VP} - r_{VE}] \qquad \text{J.19}$$

METHOD OF SOLUTION

Since exponents of the hydrocarbons are reported in literature as being very close to 1.0 and to simplify calculation, assume m and m′ are equal to 1.0. Substitute r_{VB} into equation J.13 and solve for P_{C_4}

$$P_{C_4} = \frac{P^{o}_{C4}\ \gamma}{(0.9)(k/k_o)k_B\ P^{n}_{H_2} + \gamma} \qquad J.20$$

since $P^{o}_{C_3} = 0$, substitute r_{VP} into J.13 and solve for P_{C_3}

$$P_{C_3} = \frac{0.9\ r_{VB}}{[(0.9)(k/k_o)(k_p)\ P^{n'}_{H_2} + \gamma\ .\ (1.+K_p)} \qquad J.21$$

Similarly for ethane and methane:

$$P_{C_2} = \frac{(1.1\ r_{VB} - r_{VP})}{\gamma\ .\ (1.\ + K_E)} \qquad J.22$$

$$P_{C_1} = \frac{4 \times r_{VB} - 3 \times r_{VP} - 2 \times r_{VE}}{\gamma} \qquad J.22$$

Substitute r_{VH} into equation J.13 and solve for P_{H_2}

$$P_{H_2} = \frac{(P^{o}_{H_2}\ \gamma - 3 \times r_{VB} + 2 \times r_{VP} + r_{VE})}{\gamma} \qquad J.24$$

The emulsion phase partial pressures are calculated by selecting P_{H_2}, solving equations J.20 to J.24 inclusive to find a calculated P_{H_2}. A binary search routine was used to select the P_{H_2}

to be substituted into J.20 and the objective was to make the selected value equal to the calculated value in J.24. Once the emulsion partial pressures were obtained in this way, the exit bubble partial pressures were obtained directly from equation J.3.

J.1.2 Model Assuming Plug Flow in Dense Phase

BUBBLE PHASE DIFFERENTIAL EQUATION:

By a mass balance in the bubble phase over a differential height of the reactor:

$$(U-U_o)\ A\Delta C_b = QNA\ \Delta\ y\ (C_p-C_b) \qquad J.25$$

From continuity of gas flow, flow through bubbles is:

$$NVU_A = U - U_o \qquad J.26$$

letting

$$X = \frac{QH}{U_A V} \qquad J.27$$

and taking limits as

$$\Delta y \rightarrow 0$$

and converting to partial pressures:

$$\frac{dC_b}{dy} = \frac{X}{H}\ (C_p - C_b) \qquad J.28$$

EMULSION PHASE DIFFERENTIAL EQUATION:

From a mass balance on each component in the emulsion phase over a differential height of reactor:

$$U_o A \Delta C_p = - QNA\ \Delta y\ (C_p - C_b) - r_V (1.-NV)\ HA \frac{\Delta y}{H} \qquad \text{J.29}$$

where r_V is the rate of disappearance of a component.

Since

$$U_o = U(1 - \beta) \qquad \text{J.30}$$

and since bubble volume is assumed to cause bed expansion

$$NVH = H - H_o \qquad \text{J.31}$$

then

$$(1-NV) = H_o/H \qquad \text{J.32}$$

Let

$$Q = \frac{XU_A V}{H} \qquad \text{J.33}$$

and for equations J.26 and J.29

$$U_A = \frac{U\beta}{NV} \qquad \text{J.34}$$

Substituting equations J.30, J.32, J.33 and J.34 in turn into equation J.29, converting to partial pressures and taking limits as $\Delta y \rightarrow 0$ we obtain

$$\frac{dP_p}{dy} = - [\frac{H_o RT}{UH(1-\beta)}]\ r_v - [\frac{\beta X}{H(1-\beta)}]\ (P_p - P_b) \qquad \text{J.35}$$

METHOD OF SOLUTION

For each component in the reaction scheme, there exist two differential equations, J.28 and J.35, which describe the rates of change of the partial pressure of each component with height. With the five

TABLE J-1

PARAMETERS USED IN SENSITIVITY ANALYSES OF FLUIDIZED BED MODELS

KINETIC PARAMETERS:

ΔE_B = 56.454 (k.cal./gm. mole)
ΔE_{P1} = 54.397 "
ΔE_{P2} = 37.514 "
ΔE_E = 16.751 "
$\log_{10} k_B$ = 17.507 (moles/sec.vol.reactor atm.$^{-0.7}$)
$\log_{10} K_{P1}$ = 16.097 "
$\log_{10} K_{P2}$ = 15.043 (dimensionless)
$\log_{10} k_E$ = 6.984 "
n = 1.7
n' = 2.45

FLUIDIZED BED PARAMETERS AND OPERATING CONDITIONS:

Minimum Fluidization Velocity = 0.88 cm./sec.
Feed Superficial Velocity = 8.8 cm./sec.
Initial Bed Height = 90 cm.
Expanded Bed Height = 100 cm.
Feed Hydrogen to Butane Ratio = 7.0

FOR SENSITIVITY WITH X:

Operating temperature = 255.0°C.
Catalyst activity (k/k_o) = 250.

FOR SENSITIVITY WITH CATALYST ACTIVITY:

Operating temperature = 270°C.

FIGURE J-2

SENSITIVITY ANALYSIS ON INTERCHANGE PARAMETER

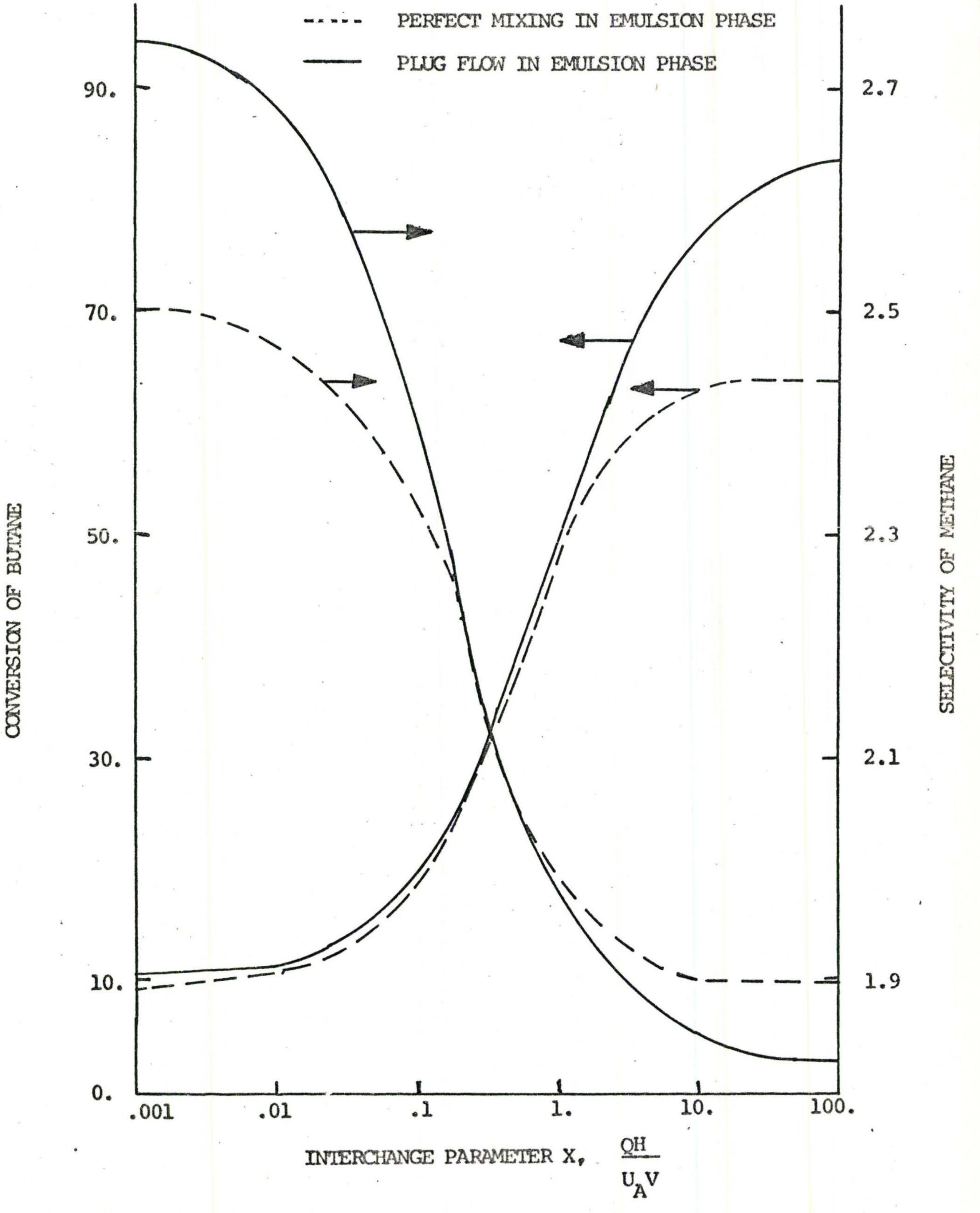


FIGURE J-3

SENSITIVITY ANALYSIS ON INTERCHANGE PARAMETER

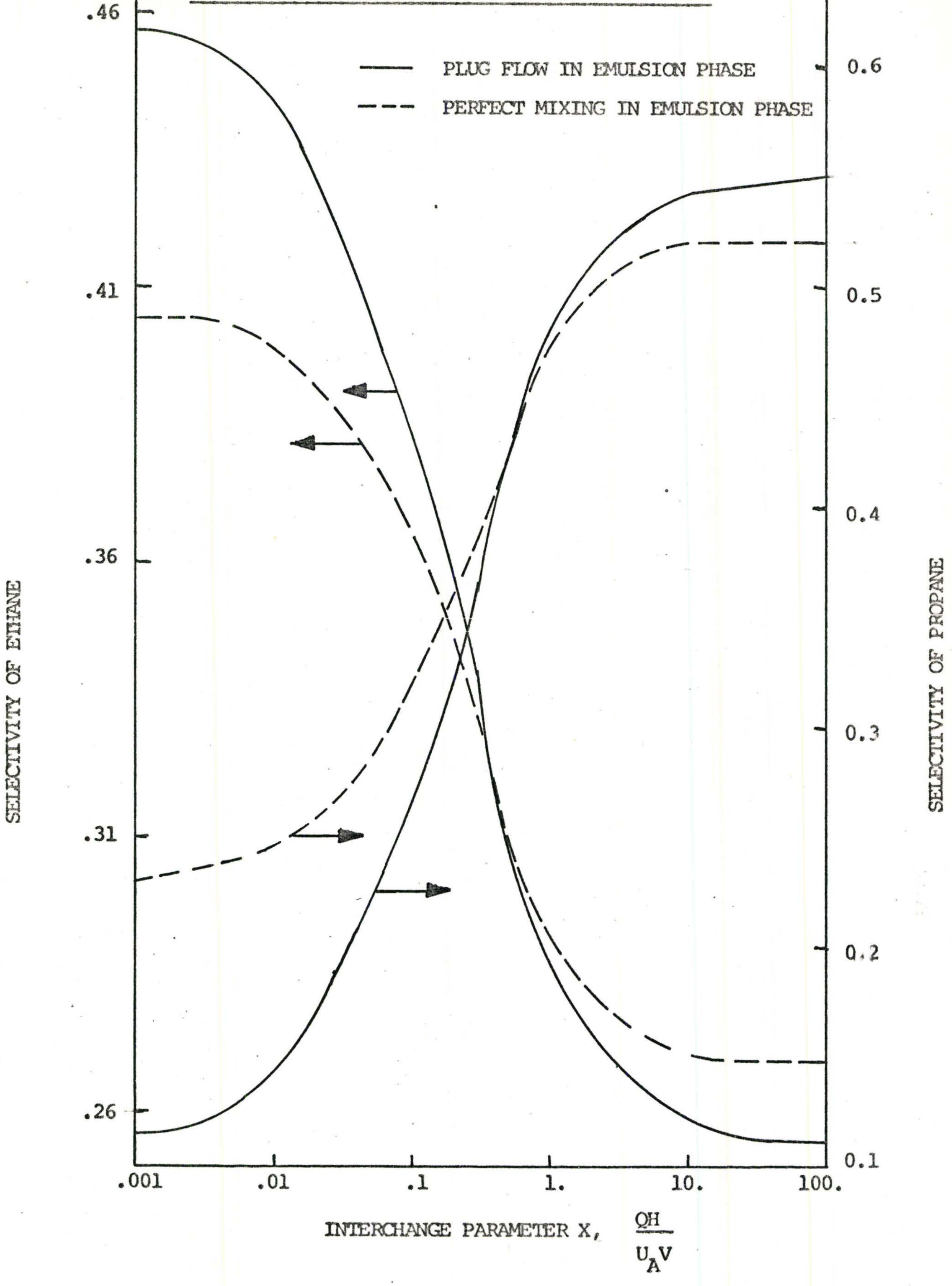


FIGURE J-4

SENSITIVITY ANALYSIS ON CATALYST ACTIVITY

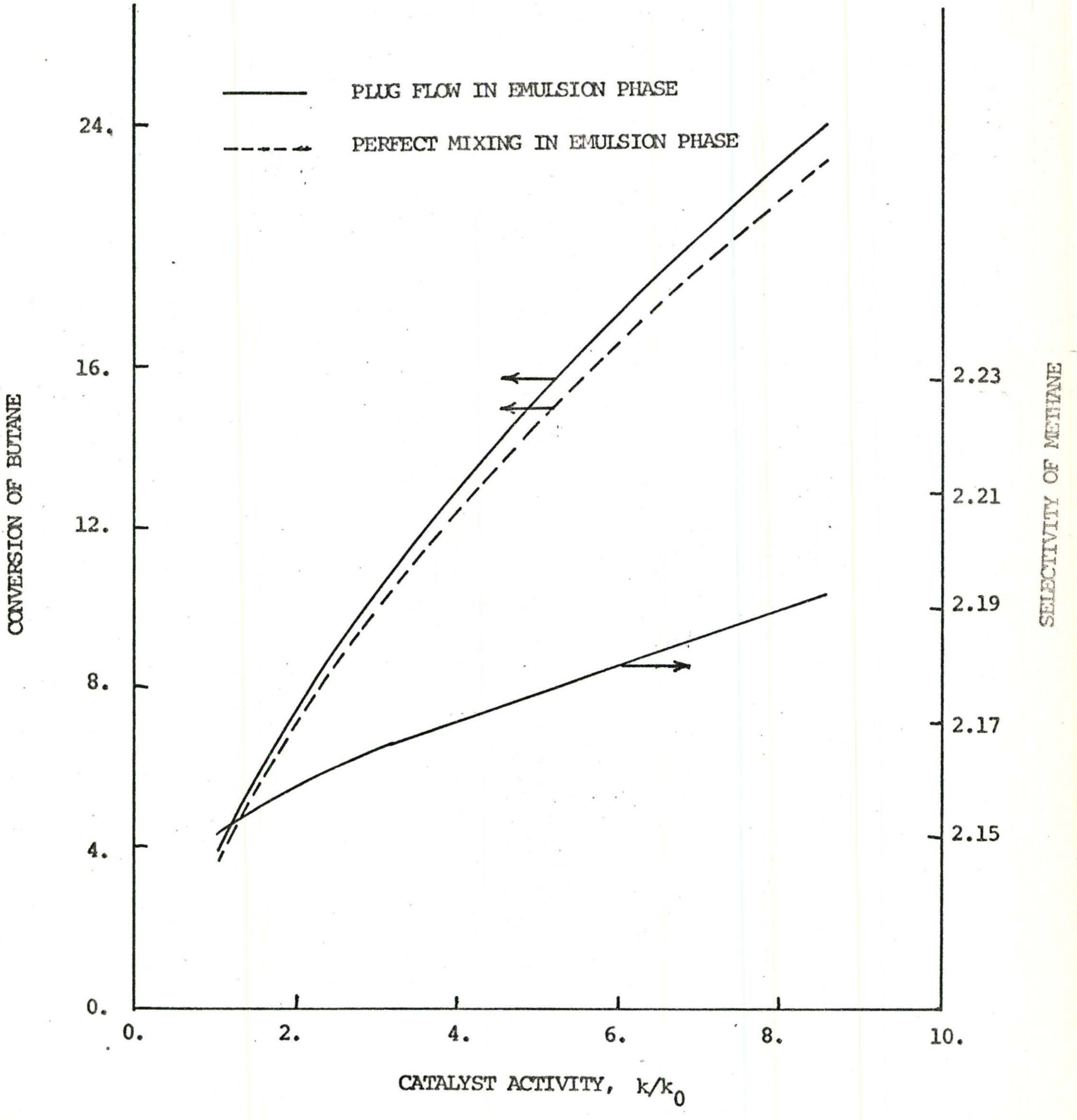
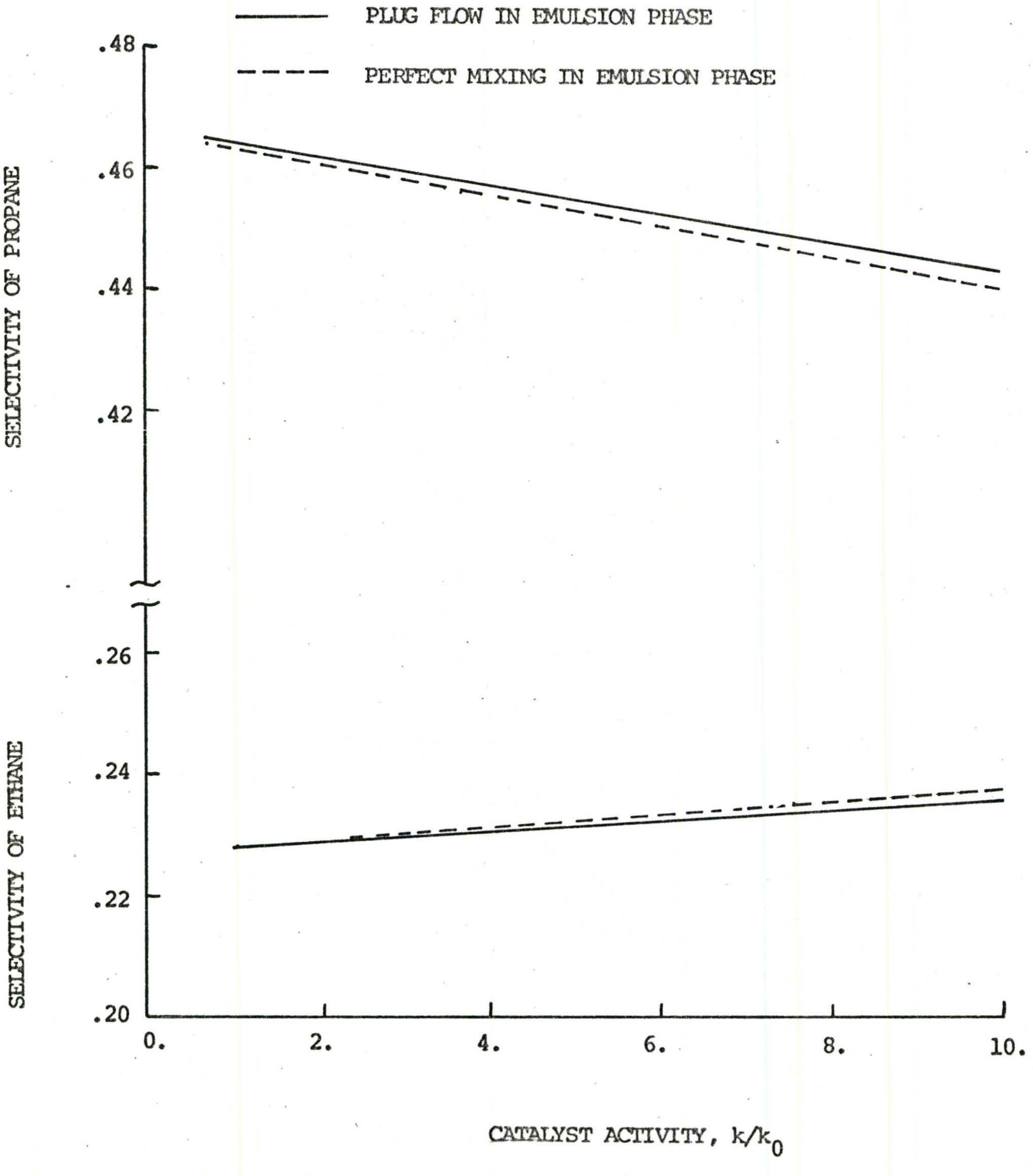


FIGURE J-5 - SENSITIVITY ANALYSIS ON CATALYST ACTIVITY



components present, ten coupled, non-linear ordinary differential equations must be solved. Since the emulsion and bubble flowrates are up the bed and since the compositions of both phases at the bottom of the reactor are known, the problem becomes an initial value one.

A fourth order Runge Kutta (L2) integration routine with error analysis was used, where the error was held between 10^{-6} and 10^{-8}. Decreasing this error to the twelfth decimal place did not change the results for wide ranges of conversion.

J.2 Sensitivity Analysis

This section presents the sensitivity of the previous two models to the dimensionless factor X and the activity of the catalyst. The response variables considered were the conversion of butane and the selectivities of methane, ethane, and propane. The operating conditions were set at reasonable values and were the same for both models. The kinetic parameters, operating conditions and fluidized bed parameters, which were held constant in the sensitivity analysis, are presented in Table J-1. The sensitivity analysis curves are shown in Figures J-2, 3, 4, and 5.

It may be seen that the conversion and selectivities have a sensitive region with respect to X. By very rough calculation the X value experienced in the actual reactor may be between 1 and 10. This is the sensitive region with respect to X and indicates that emphasis should be placed in determining the interchange factor if a reasonable simulation model is to be developed.

APPENDIX K: COMPUTER PROGRAM LISTINGS

This Appendix will give a brief explanation of, and the computer listings for, the most important programs used in the course of this study. Many other programs which were used, but which may be easily written; for example, data analysis programs, grid search routines, binary and Regula Falsi search routines, are not included in this Appendix.

The programs discussed in this Appendix are:

K.1 Packed Bed Models

- Butane Reaction Kinetics
- Propane Reaction Kinetics

K.2 Models for Catalyst Activity Change

- Model assuming constant maximum catalyst activity
- Model assuming that the maximum activity is a function of temperature

K.3 Parameter Estimation Programs

- Executives and objective subroutines for butane and propane parameter search programs
- Rosenbrock search routine
- Local Linearization program

K.4 Programs Used in Obtaining Confidence Limits on Parameters

- Program to calculate V^{-1} analytically
- Golden Section search on k_B given ΔE_B

K.5 Fluidized Bed Reactor Models of Orcutt Davidson and Pigford

- Model assuming plug flow in emulsion
- Model assuming perfect mixing in emulsion

K.1 PACKED BED MODELS

The packed bed models with butane and propane kinetics are in the form of subroutines since they were used extensively throughout the program in various search programs.

The kinetics used in these programs are given in Sections 6.1.1 and 6.1.2 of this thesis. The generally accepted fourth order Runge Kutta integration routine is described amply by Lapidus(L2).

This is a fairly comprehensive integration routine and incorporates diagnostic features which were added as the program was modified during use.

These are: the truncatin error is monitored and the step size is adjusted to maintain this error between a specified upper and lower limit, independent variables are not allowed to be negative, the program allows only a limited number of times the step size may be halved because of truncation error or negative dependent variables, a switch (NSWIT) is set if this limited number is reached.

REAC 3 is the Propane Reactor Model

REAC 4 is the Butane Reactor Model

CN - values of the dependent variables at the beginning of each step

DC - values of the derivatives X(DX)

CDX - values of the integrated variables after one step size

CN1 - values of the integrated variables after cutting a step size in half and integrating over two of these steps.

EPSL - an estimate of the truncation errors

CRB - Butane rate constant

CRP1, CRP2 - Propane rate constants

CRE - Ethane rate constants

JCT - counter which gives the run number to be calculated

```
      SUBROUTINE REAC4
      COMMON KM,MCYC,MAXK,MKAT,NSTEP,EPS(10),ALPHA,BETA
      COMMON AKE(10),AKMAX(10),AKMIN(10),AKIN(10),SUMN
      COMMON V(10,10),D(20),BL(20,20),BLEN(20),AJ(20)
      COMMON E(20),AL(20,20),AFK(20)
      COMMON NRUNS,NOCOMP,NSWIT,JCT,HT
      COMMON VOLFL(50),TEP(50),TEMP(50),DELTP(50),RAT(50),PRESS(50)
      COMMON FRMOL(50,5),FACT(50,5),FCALC(50,5)
      COMMON C4PI(50),H2PI(50)
      COMMON RCC(50),RT(50),XACT(50),RUN(50)
      COMMON RACT(50),         CRB(50),CRP(50),CRE(50)
      COMMON CRP1(50),CRP2(50)
      COMMON SMIN
      COMMON DIF4(50)
      COMMON FIX
      DIMENSION CN(5),C(5),C1(5),DC(5),C2(5),C3(5),C4(5)
      DIMENSION CN1(5),CDX(5),EPSL(5),CIN(5)
      DIMENSION TRMAX(5),TRMIN(5)
C     **********
C     PACKED BED REACTOR MODEL
C     BUTANE REACTION KINETICS
C     SOLVED WITH FOURTH ORDER RUNGE - KUTTA INTEGRATION ROUTINE
C     WRITTEN BY AL ORLICKAS --- JAN. 1970
C     **********
C     INITIAL CALCULATIONS
C     **********
      FAX=2.0-FIX
      KNEG=0
      KFIN=0
      NK=0
      Y=0.0
      DY=0.5
      NEQ=NOCOMP
      IHALF=0
      JHALF=0
      NSWIT=0
      CN(1)=0.0
      CN(2)=0.0
      CN(3)=0.0
      CN(4)=C4PI(JCT)
      CN(5)=H2PI(JCT)
      DO3I=1,NEQ
      TRMAX(I)=1.0E-6
      TRMIN(I)=1.0E-8
 3    CONTINUE
C     **********
C     START OF RUNGE KUTTA INTEGRATION ROUTINE
C     **********
      KRET=1
 9    CONTINUE
      DO5 I=1,NEQ
 5    CIN(I)=CN(I)
 10   CONTINUE
 979  FORMAT(5E20.5)
      DO20 I=1,NEQ
 20   C(I)=CN(I)
      N=1
      GOTO400
 30   CONTINUE
      DO 40 I=1,NEQ
      C1(I)=DC(I)
```

```
40    C(I)=CN(I)+C1(I)/2.0
      N=2
      GOTO400
50    CONTINUE
      DO60 I=1,NEQ
      C2(I)=DC(I)
60    C(I)=CN(I)+C2(I)/2.0
      N=3
      GOTO400
70    CONTINUE
      DO80 I=1,NEQ
      C3(I)=DC(I)
80    C(I)=CN(I)+C3(I)
      N=4
      GOTO400
90    CONTINUE
      DO100 I=1,NEQ
      C4(I)=DC(I)
100   CN1(I)=CN(I)+(C1(I)+2.0*C2(I)+2.0*C3(I)+C4(I))/6.0
      IF(NK-1) 110,130,150
110   DY=DY/2.0
      NK=1
      DO120 I=1,NEQ
120   CDX(I)=CN1(I)
      GOTO10
130   DO140 I=1,NEQ
140   CN(I)=CN1(I)
      Y=Y+DY
      KRET=2
145   CONTINUE
      Y=Y-DY
      NK=2
      GOTO10
150   CONTINUE
      DO160 I=1,NEQ
160   CN(I)=(16.0*CN1(I)-CDX(I))/15.0
      DY=DY*2.0
      NK=0
      Y=Y+DY
      KRET=3
164   CONTINUE
      IF(KFIN)165,165,280
165   IF(Y-HT) 170,250,250
170   DO180 I=1,NEQ
180   EPSL(I)=(ABS(CDX(I)-CN1(I)))/15.0
      DO 171 I=1,NEQ
      IF(EPSL(I)-TRMIN(I))172,172,173
172   NCOUNT=NCOUNT+1
173   IF(EPSL(I)-TRMAX(I))171,171,174
174   NCOUNT=0
      GOTO209
171   CONTINUE
      IF(NCOUNT-NEQ)175,176,176
175   NCOUNT=0
      IHALF=0
      GOTO230
176   NCOUNT=0
      GOTO220
209   DO210 I=1,NEQ
210   CN(I)=CIN(I)
```

```
      Y=Y-DY
      DY=DY/2.0
      IHALF=IHALF+1
      IF(IHALF-20)310,320,320
  320 NSWIT=1
      WRITE(6,321)
  321 FORMAT(//6X,22H ADDRESS 320 IN REAC2     )
      GOTO500
  310 CONTINUE
      GOTO10
  220 DY=DY*2.0
      IHALF=0
  230 DO240 I=1,NEQ
      CIN(I)=CN(I)
  240  CONTINUE
C     **********
C     THESE VALUES OF CIN AND CN ARE THE FINAL VALUES AT THE
C     END OF A STAGE
C     **********
      IF(CN(4)-0.00001)801,801,805
  801 IF(CN(3)-0.00001)802,802,805
  802 CONTINUE
      WRITE(6,890)Y
  890 FORMAT(/6X,50H A COMPONENT HAS DECREASED BELOW SPECIFIED VALUE    ,
     1/6X,38H FINAL MOLE FRACTIONS WILL BE GIVEN        ,
     2/6X,25H HEIGHT UP THE COLUMN =    ,F20.3)
      GOTO280
  805 CONTINUE
      GOTO10
  250 IF(KFIN) 260,260,280
  260 KFIN=1
      Y=Y-DY
      KRET=4
  265 CONTINUE
      DY=HT-Y
      DO 270 I=1,NEQ
  270 CN(I)=CIN(I)
      GOTO10
  280 CONTINUE
C     **********
C     FINAL CALCULATIONS ---  PROBLEM IS SOLVED
C     FINAL VALUES ARE CN(I)
C     **********
      DO290I=1,NOCOMP
      FCALC(JCT,I)=CN(I)/PRESS(JCT)
  290 CONTINUE
      GOTO500
  400 CONTINUE
      DO430 I=1,NEQ
      IF(C(I))410,430,430
  410 CONTINUE
      WRITE(6,420)I,Y
  420 FORMAT(/6X,4H C( ,I2,27H )  HAS BECOME NEG. AT Y =   ,F20.10)
      KNEG=1
  430 CONTINUE
      IF(KNEG) 460,460,440
  440 DY=DY/2.0
      WRITE(6,450)DY
  450 FORMAT(/6X,22H DY CUT IN HALF TO      ,F20.15)
      JHALF=JHALF+1
      IF(JHALF-30)330,340,340
```

```
 340  NSWIT=1
      WRITE(6,331)
 331  FORMAT(//6X,22H ADDRESS 340 IN REAC2     )
      GOTO500
 330  CONTINUE
      KNEG=0
      GOTO10
 460  CONTINUE
      JHALF=0
C     **********
C     DIFFERENTIAL EQUATIONS
C     **********
      DD1=1.0/(C(5)**AKIN(9))
      DD5=C(4)
      DC(4)=-DY*CRB(JCT)*DD5*DD1
      DD2=C(3)/(C(5)**AKIN(10))
      DD3=DY*CRP1(JCT)*DD2
      DD4=-DC(4)
      DC(3)=CRP2(JCT)*(FIX*DD4-DD3)
      DC(2)=(FAX*DD4-DC(3))/(1.0+CRE(JCT))
      DC(1)=4.0*DD4-3.0*DC(3)-2.0*DC(2)
      DC(5)=3.0*DD4-2.0*DC(3)-DC(2)
      DC(5)=-DC(5)
      GOTO(30,50,70,90),N
 500  CONTINUE
 300  RETURN
      END

                                 CD TOT    0209
```

```
      SUBROUTINE REAC3
      COMMON KM,MCYC,MAXK,MKAT,NSTEP,EPS(10),ALPHA,BETA
      COMMON AKE(10),AKMAX(10),AKMIN(10),AKIN(10),SUMN
      COMMON V(10,10),D(20),BL(20,20),BLEN(20),AJ(20)
      COMMON E(20),AL(20,20),AFK(20)
      COMMON NRUNS,NOCOMP,NSWIT,JCT,HT
      COMMON VOLFL(50),TEP(50),TEMP(50),DELTP(50),RAT(50),PRESS(50)
      COMMON FRMOL(50,5),FACT(50,5),FCALC(50,5)
      COMMON C3PI(50),H2PI(50)
      COMMON RCC(50),RT(50),XACT(50),RUN(50)
      COMMON RACT(50),          CRB(50),CRP(50),CRE(50)
      COMMON SMIN
      DIMENSION CN(5),C(5),C1(5),DC(5),C2(5),C3(5),C4(5)
      DIMENSION CN1(5),CDX(5),EPSL(5),CIN(5)
      DIMENSION TRMAX(5),TRMIN(5)
      **********
      PACKED BED REACTOR MODEL
      PROPANE REACTION SCHEME
      WRITTEN BY AL ORLICKAS --- JAN. 1970
      **********
      INITIAL CALCULATIONS
      **********
      KNEG=0
      KFIN=0
      NK=0
      Y=0.0
      DY=0.5
      NEQ=NOCOMP
      IHALF=0
      JHALF=0
      NSWIT=0
      CN(1)=0.0
      CN(2)=0.0
      CN(3)=C3PI(JCT)
      CN(4)=H2PI(JCT)
      DO3I=1,NEQ
      TRMAX(I)=1.0E-6
      TRMIN(I)=1.0E-8
      **********
      START OF RUNGE KUTTA
      **********
      CONTINUE
      KRET=1
      CONTINUE
      DO5 I=1,NEQ
      CIN(I)=CN(I)
      CONTINUE
'9    FORMAT(5E20.5)
      DO20 I=1,NEQ
      C(I)=CN(I)
      N=1
      GOTO400
      CONTINUE
      DO 40 I=1,NEQ
      C1(I)=DC(I)
      C(I)=CN(I)+C1(I)/2.0
      N=2
      GOTO400
      CONTINUE
      DO60 I=1,NEQ
      C2(I)=DC(I)
      C(I)=CN(I)+C2(I)/2.0
```

```
      N=3
      GOTO400
70    CONTINUE
      DO80 I=1,NEQ
      C3(I)=DC(I)
80    C(I)=CN(I)+C3(I)
      N=4
      GOTO400
90    CONTINUE
      DO100 I=1,NEQ
      C4(I)=DC(I)
100   CN1(I)=CN(I)+(C1(I)+2.0*C2(I)+2.0*C3(I)+C4(I))/6.0
      IF(NK-1) 110,130,150
110   DY=DY/2.0
      NK=1
      DO120 I=1,NEQ
120   CDX(I)=CN1(I)
      GOTO10
130   DO140 I=1,NEQ
140   CN(I)=CN1(I)
      Y=Y+DY
      KRET=2
145   CONTINUE
      Y=Y-DY
      NK=2
      GOTO10
150   CONTINUE
      DO160 I=1,NEQ
160   CN(I)=(16.0*CN1(I)-CDX(I))/15.0
      DY=DY*2.0
      NK=0
      Y=Y+DY
      KRET=3
164   CONTINUE
      IF(KFIN)165,165,280
165   IF(Y-HT) 170,250,250
170   DO180 I=1,NEQ
180   EPSL(I)=(ABS(CDX(I)-CN1(I)))/15.0
      DO 171 I=1,NEQ
      IF(EPSL(I)-TRMIN(I))172,172,173
172   NCOUNT=NCOUNT+1
173   IF(EPSL(I)-TRMAX(I))171,171,174
174   NCOUNT=0
      GOTO209
171   CONTINUE
      IF(NCOUNT-NEQ)175,176,176
175   NCOUNT=0
      IHALF=0
      GOTO230
176   NCOUNT=0
      GOTO220
209   DO210 I=1,NEQ
210   CN(I)=CIN(I)
      Y=Y-DY
      DY=DY/2.0
      IHALF=IHALF+1
      IF(IHALF-20)310,320,320
320   NSWIT=1
      WRITE(6,321)
321   FORMAT(//6X,22H ADDRESS 320 IN REAC2      )
```

```
    GOTO500
310 CONTINUE
    GOTO10
220 DY=DY*2.0
    IHALF=0
230 DO240 I=1,NEQ
    CIN(I)=CN(I)
240  CONTINUE
    **********
    THESE VALUES OF CIN AND CN ARE THE FINAL VALUES AT THE
    END OF A STAGE
    **********
    GOTO10
250 IF(KFIN) 260,260,280
260 KFIN=1
    Y=Y-DY
    KRET=4
265 CONTINUE
    DY=HT-Y
    DO 270 I=1,NEQ
270 CN(I)=CIN(I)
    GOTO10
280 CONTINUE
    **********
    FINAL CALCULATIONS ---  PROBLEM IS SOLVED
    FINAL VALUES ARE CN(I)
    **********
    DO290I=1,NOCOMP
    FCALC(JCT,I)=CN(I)/PRESS(JCT)
290 CONTINUE
    GOTO500
400 CONTINUE
    DO430 I=1,NEQ
    IF(C(I))410,430,430
410 CONTINUE
420 FORMAT(/6X,4H C( ,I2,27H )  HAS BECOME NEG. AT Y =   ,F20.10)
    KNEG=1
430 CONTINUE
    IF(KNEG) 460,460,440
440 DY=DY/2.0
450 FORMAT(/6X,22H DY CUT IN HALF TO      ,F20.15)
    JHALF=JHALF+1
    IF(JHALF-30)330,340,340
340 NSWIT=1
    WRITE(6,331)
331 FORMAT(//6X,22H ADDRESS 340 IN REAC2     )
    GOTO500
330 CONTINUE
    KNEG=0
    GOTO10
460 CONTINUE
    JHALF=0
    **********
    DIFFERENTIAL EQUATIONS
    **********
    DD1=(C(3)**AKE(5))/(C(4)**AKE(6))
    DD2=CRP(JCT)*DD1
    DD2=DY*DD2
    DC(3)=-DD2
    DC(2)=DD2/(1.0+CRE(JCT))
    DC(1)=3.0*DD2-2.0*DC(2)
```

```
    DC(4)=-2.0*DD2+DC(2)
    GOTO(30,50,70,90),N
500 CONTINUE
300 RETURN
    END
```

```
                    CD TOT    0188
```

K.2 MODELS FOR CATALYST ACTIVITY CHANGE

The programs described here are used to search on the parameters in the models used to describe the increasing catalyst activity change with time.

The analytical solution of the models which must be evaluated numerically are given by equations 6.32 and 6.34. The trapezoidal rule is used to perform the integrations in these two equations.

NSEG - no. of integration segments between the calculated k values

NP - total no. of temperature data or no. of time segments involved in the total integration

CO - initial k value

DT - time interval (12 min.)

P(I) - time interval at which "experimental" k value is available

CEXP(I) - experimental k value

T(I) - temperature data

CMAX(I) - maximum k values

PK(I), Q(I) - as defined in equation 6.34

AKE(I), AKIN(I) - parameters searched upon by Rosenbrock direct search

```
      COMMON Y(500),RT(500),T(500)
      COMMON P(50),AINI(50),CINI(50),CC(50),CEXP(50)
      COMMON KM,MCYC,MAXK,MKAT,NSTEP
      COMMON EPS(10),AKE(10),ALPHA,BETA
      COMMON AKMAX(10),AKMIN(10),AKIN(10)
      COMMON V(10,10),D(20),BL(20,20),BLEN(20)
      COMMON AJ(20),E(20),AL(20,20),AFK(20)
      COMMON TC1(500)
C     **********
C     SEARCHING PARAMETERS FOR MODEL DESCRIBING INCRESING CATALYST
C     ACTIVITY WITH TIME
C     ASSUMING CONSTANT MAX. CAT. ACT.
C     WRITTEN BY AL ORLICKAS --- FEB. 1970
C     **********
 600  FORMAT(//6X,38H CATALYST ACTIVITY PARAMETER SEARCH     )
C     **********
C     READ IN ROSENBROCK DATA
C     **********
      READ(5,700)KM,MCYC,MAXK,MKAT,NSTEP
      READ(5,701)(EPS(I),I=1,KM)
      READ(5,701)(AKE(I),I=1,KM)
      READ(5,701)ALPHA,BETA
      READ(5,701)(AKMAX(I),I=1,KM)
      READ(5,701)(AKMIN(I),I=1,KM)
 700  FORMAT(5I5)
 701  FORMAT(3F10.5)
      DO6I=1,KM
      DO6J=1,KM
      V(I,J)=0.
 6    CONTINUE
      DO7I=1,KM
      V(I,I)=1.0
 7    CONTINUE
C     **********
C     READ IN DATA FOR MODEL
C     **********
      READ(5,500) NSEG,NP
 500  FORMAT(2I5)
      READ(5,501) CO,DT
 501  FORMAT(2F10.5)
      DO5I=1,NSEG
      READ(5,501) P(I),CEXP(I)
      WRITE(6,550)P(I),CEXP(I)
 550  FORMAT(1X,2F15.3)
 5    CONTINUE
      READ(5,502)(T(I),I=1,NP)
 502  FORMAT(8F10.5)
      DO10I=1,NP
      VM=8.0+0.05*T(I)
      TF=34.03+44.0768*VM
      TC=0.555555*(TF-32.0)
      TC1(I)=TC
      TK=TC+273.0
      RT(I)=1.99*TK
 10   CONTINUE
      WRITE(6,551)(TC1(I),I=1,NP)
 551  FORMAT(/1X,12F10.2)
C     ***********************************
      CALL SEARCH
C     ***********************************
      STOP
```

```
      END
      SUBROUTINE OBJECT
      COMMON CO,NP,DT,NSEG,SUMSQ,SUMN
      COMMON Y(500),RT(500),T(500)
      COMMON KM,MCYC,MAXK,MKAT,NSTEP
      COMMON EPS(10),AKE(10),ALPHA,BETA
      COMMON AKMAX(10),AKMIN(10),AKIN(10)
      COMMON V(10,10),D(20),BL(20,20),BLEN(20)
      COMMON AJ(20),E(20),AL(20,20),AFK(20)
      COMMON TC1(500)
C     **********
C     THIS SUBROUTINE USES THE TRAPEZOIDAL RULE TO FIND
C     CATALYST ACTIVITY AS A FUNCTION OF TIME
C     **********
 500  FORMAT(/6X,40H****************************************              )
      DO5I=1,KM
      AKIN(I)=AKE(I)
 5    CONTINUE
      DO6I=1,KM
      IF(AKE(I).GE.AKMAX(I)) AKIN(I)=AKMAX(I)
      IF(AKE(I).LE.AKMIN(I)) AKIN(I)=AKMIN(I)
 6    CONTINUE
      WRITE(6,200)(AKE(I),I=1,KM)
 200  FORMAT(1X,7H AKE =    ,3E20.7)
      AKIN(1)=10.0**AKIN(1)
      AKIN(2)=AKIN(2)*1000.
      XX=ALOG(AKIN(3)-CO)
      DO10I=1,NP
      Y(I)=AKIN(1)*EXP(-AKIN(2)/RT(I))
 10   CONTINUE
      MSEG=1
      KK=1
      XYZ=P(MSEG)
      KP=IFIX(XYZ)
 30   KL=KP-1
      KQ=KK+1
      SUM=0.0
      DO40I=KQ,KL
      SUM=SUM+Y(I)
 40   CONTINUE
      SUMS=DT*(Y(KK)/2.0+SUM+Y(KP)/2.0)
      AINT(MSEG)=SUMS
      IF(MSEG-NSEG)50,60,60
 50   MSEG=MSEG+1
      XYW=P(MSEG)
      XYP=P(MSEG-1)
      KP=IFIX(XYW)
      KK=IFIX(XYP)
      GOTO30
 60   DO70I=1,NSEG
      CINT(I)=0.
      DO80J=1,I
      CINT(I)=CINT(I)+AINT(J)
 80   CONTINUE
 70   CONTINUE
 550  FORMAT(1X,5E20.5)
      DO90I=1,NSEG
      XY=EXP(XX-CINT(I))
      CC(I)=AKIN(3)-XY
 90   CONTINUE
```

```
      WRITE(6,300)(CC(I),I=1,NSEG)
  300 FORMAT(/6X,10F10.2)
      SUMSQ=0.
      DO110I=1,NSEG
      W=ABS(CC(I)-CEXP(I))
      SUMSQ=SUMSQ+W*W
  110 CONTINUE
      SUMN=SUMSQ
      WRITE(6,501) AKIN(1),AKIN(2),AKIN(3),SUMN
  501 FORMAT(1X,8H AKIN =      ,E15.5,2F15.5,5X,9HSUMSQ =      ,F30.4)
      WRITE(6,502) (CC(I),I=1,NSEG)
  502 FORMAT(1X,19F6.1)
      RETURN
      END

                             CD TOT    0136
```

```
      COMMON CO,NP,DT,NSEG,SUMSQ,SUMN
      COMMON Y(500),RT(500),T(500)
      COMMON P(50),AINT(50),CINT(50),CC(50),CEXP(50)
      COMMON KM,MCYC,MAXK,MKAT,NSTEP
      COMMON EPS(10),AKE(10),ALPHA,BETA
      COMMON AKMAX(10),AKMIN(10),AKIN(10)
      COMMON V(10,10),D(20),BL(20,20),BLEN(20)
      COMMON AJ(20),E(20),AL(20,20),AFK(20)
      COMMON TK(500),PK(500),Q(500),A(500)
      COMMON CMAX(500),CK(500)
      **********
      SEARCH PARAMETERS FOR MODEL DESCRIBING CATALYST ACTIVITY CHANGE
      ASSUMING MAX. CAT. ACT. IS A FUNCTION OF REDUCING TEMPERATURE
      WRITTEN BY AL ORLICKAS ---   FEB.1970
      **********
      WRITE(6,600)
600   FORMAT(//6X,38H CATALYST ACTIVITY PARAMETER SEARCH     )
      **********
      READ IN ROSENBROCK DATA
      **********
      READ(5,700)KM,MCYC,MAXK,MKAT,NSTEP
      READ(5,701)(EPS(I),I=1,KM)
      READ(5,701)(AKE(I),I=1,KM)
      READ(5,701)ALPHA,BETA
      READ(5,701)(AKMAX(I),I=1,KM)
      READ(5,701)(AKMIN(I),I=1,KM)
700   FORMAT(5I5)
701   FORMAT(4F10.5)
      DO6I=1,KM
      DO6J=1,KM
      V(I,J)=0.
6     CONTINUE
      DO7I=1,KM
      V(I,I)=1.0
7     CONTINUE
      **********
      READ IN DATA FOR MODEL
      **********
      READ(5,500) NSEG,NP
500   FORMAT(2I5)
      READ(5,501) CO,DT
501   FORMAT(2F10.5)
      DO5I=1,NSEG
      READ(5,501) P(I),CEXP(I)
5     CONTINUE
      READ(5,502)(T(I),I=1,NP)
502   FORMAT(8F10.5)
      DO10I=1,NP
      VM=8.0+0.05*T(I)
      TF=34.03+44.0768*VM
      TC=0.555555*(TF-32.0)
      TK(I)=TC+273.
      RT(I)=1.99*TK
10    CONTINUE
      *********************************
      CALL SEARCH
      *********************************
      STOP
      END
      SUBROUTINE OBJECT
      COMMON CO,NP,DT,NSEG,SUMSQ,SUMN
      COMMON Y(500),RT(500),T(500)
```

```
      COMMON P(50),AINT(50),CINT(50),CC(50),CEXP(50)
      COMMON KM,MCYC,MAXK,MKAT,NSTEP
      COMMON EPS(10),AKE(10),ALPHA,BETA
      COMMON AKMAX(10),AKMIN(10),AKIN(10)
      COMMON V(10,10),D(20),BL(20,20),BLEN(20)
      COMMON AJ(20),E(20),AL(20,20),AFK(20)
      COMMON TK(500),PK(500),Q(500),A(500)
      COMMON CMAX(500),CK(500)
      **********
      THIS SUBROUTINE USES THE TRAPEZOIDAL RULE TO FIND
      CATALYST ACTIVITY AS A FUNCTION OF TIME
      **********
500   FORMAT(/6X,40H***************************************        )
      DO5I=1,KM
      AKIN(I)=AKE(I)
5     CONTINUE
      CHECK CONSTRAINTS
      DO6I=1,KM
      IF(AKE(I).GE.AKMAX(I)) AKIN(I)=AKMAX(I)
      IF(AKE(I).LE.AKMIN(I)) AKIN(I)=AKMIN(I)
6     CONTINUE
      WRITE(6,200)(AKE(I),I=1,KM)
200   FORMAT(1X,7HAKE =     ,4E20.7)
      AKIN(1)=10.0**AKIN(1)
      AKIN(4)=AKIN(4)*1.0E+3
      DO10I=1,NP
      PK(I)=AKIN(1)*EXP(-AKIN(4)/RT(I))
      Q(I)=AKIN(2)*PK(I)*(TK(I)-AKIN(3))
      CMAX(I)=AKIN(2)*(TK(I)-AKIN(3))
10    CONTINUE
      A(1)=0.
      DO15I=2,NP
      A(I)=((PK(I-1)+PK(I))/2.0)*DT
15    CONTINUE
      S=0.0
      KS=0
      COP=CO
      CK(1)=COP
      AO=A(1)
      DO20I=2,NP
      IF(KS)40,40,41
41    IF(CMAX(I-1)-CK(I-1))30,30,45
45    KS=0
      COP=CK(I-1)
      AO=0.
      A(I-1)=0.
      S=0.
40    AO=AO+A(I-1)
      IF(AO-640.0)50,50,55
50    IF(AO+A(I)-640.)51,51,55
55    SUMN=1.0E100
      GOTO111
51    C1=Q(I-1)*EXP(AO)
      C2=Q(I)*EXP(AO+A(I))
      S=S+DT*((C1+C2)/2.0)
      CK(I)=(COP+S)/EXP(AO+A(I))
      IF(CK(I)-CK(I-1))30,19,19
30    CK(I)=CK(I-1)
      KS=1
19    CONTINUE
20    CONTINUE
```

```
      DO90I=1,NSEG
      XW=P(I)
      IMP=IFIX(XW)
      CC(I)=CK(IMP)
 90   CONTINUE
      WRITE(6,300)
 300  FORMAT(/6X,13HCONVERSIONS     )
      WRITE(6,301)(CK(I),I=1,NP)
 301  FORMAT(/1X,10F12.3)
      SUMSQ=0.
      DO110I=1,NSEG
      W=ABS(CC(I)-CEXP(I))
      SUMSQ=SUMSQ+W*W
 110  CONTINUE
      SUMN=SUMSQ
      WRITE(6,501)AKIN(1),AKIN(2),AKIN(3),AKIN(4),SUMN
 501  FORMAT(1X,8H AKIN =   ,E15.5,3F15.5,5X,9H SUMSQ =   ,F30.4)
      WRITE(6,502) (CC(I),I=1,NSEG)
 502  FORMAT(1X,19F6.1)
 111  CONTINUE
      RETURN
      END

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```

K.3 PARAMETER ESTIMATION PROGRAMS

The program used to search on the butane and propane parameters consisted of four parts; the executive which read in the data and performed preliminary calculations, the SEARCH subroutine which directed the multivariable search, the OBJECT subroutine which evaluated the weighted sum of squares, the REAC 3 or REAC 4 subroutine which performed the reactor calculations. The SEARCH subroutine was a Rosenbrock search written by H. Pang, a former Ph.D. student at McMaster University.

In the butane parameter searching, the variables searched upon were:

AKE (1) = $\Delta E_B/1000.0$
AKE (2) = $\Delta E_{P1}/1000.0$
AKE (3) = $\Delta E_{P2}/1000.0$
AKE (4) = $\Delta E_E/1000.0$
AKE (5) = $\log_{10.}\ k_B$
AKE (6) = $\log_{10.}\ K_{P1}$
AKE (7) = $\log_{10.}\ K_{P2}$
AKE (8) = $\log_{10.}\ k_E$
AKE (9) = exponent of hydrogen in butane rate expression
AKE (10) = exponent of hydrogen in propane rate expression

In the propane parameter searching, the variables searched upon were:

AKE (1) = $\Delta E_P/1000.0$
AKE (2) = $\Delta E_E/1000.0$
AKE (3) = $\log_{10.}\ k_P$

AKE (4) = $\log_{10.} k_E$

AKE (5) = exponent of propane partial pressure

AKE (6) = exponent of hydrogen partial pressure

RUN - Run number

VOLFL - Volumetric flowrate through reactor (ml./sec.)

TEP - Average Reactor Temperature (°C.)

DELTP - Pressure Drop across reactor (atm.)

RAT - Feed hydrogen to butane molar ratio

XACT - k value for run number RUN

BASAC - reference k value, i.e k_o

HT - length of catalyst bed (25 cm.)

PRESS - Average pressure in reactor (atm.)

C4PI - Initial partial pressure of butane (atm.)

C3PI - Initial partial pressure of propane (atm.)

H2PI - Initial partial pressure of hydrogen (atm.)

RACT - Catalyst activity

FACT - Weighting factors in equal-weighting matrix

S(1) - Sum of absolute value of differences of mole fractions

SS(1) - Sum of squares of differences of mole fractions

SUMSQ - weighted sum of squares

FRMOL - experimental mole fractions

The theory for the local linearization iteration technique is given in Section 6.2.1 of this thesis.

AKE - parameter values

DELT - maximum change allowed in parameter per iteration

T - maximum percent change in parameter per iteration

AKMIN, AKMAX, - minimum and maximum allowable parameter values

```
      COMMON KM,MCYC,MAXK,MKAT,NSTEP,EPS(10),ALPHA,BETA
      COMMON AKE(10),AKMAX(10),AKMIN(10),AKIN(10),SUMN
      COMMON V(10,10),D(20),BL(20,20),BLEN(20),AJ(20)
      COMMON E(20),AL(20,20),AFK(20)
      COMMON NRUNS,NOCOMP,NSWIT,JCT,HT
      COMMON VOLFL(50),TEP(50),TEMP(50),DELTP(50),RAT(50),PRESS(50)
      COMMON FRMOL(50,5),FACT(50,5),FCALC(50,5)
      COMMON C4PI(50),H2PI(50)
      COMMON RCC(50),RT(50),XACT(50),RUN(50)
      COMMON RACT(50),          CRB(50),CRP(50),CRE(50)
      COMMON CRP1(50),CRP2(50)
      COMMON SMIN
      COMMON DIF4(50)
      COMMON FIX
C     **********
C     SEARCHING BUTANE PARAMETERS BY ROSENBROCK SEARCH
C     WRITTEN BY AL ORLICKAS ---  JAN.1970
C     **********
C     READ IN ROSENBROCK DATA
C     **********
      FIX=0.9
      READ(5,500) KM,MCYC,MAXK,MKAT,NSTEP
      READ(5,501)(EPS(I),I=1,KM)
      READ(5,501)(AKE(I),I=1,KM)
      READ(5,501) ALPHA,BETA
      READ(5,501)(AKMAX(I),I=1,KM)
      READ(5,501)(AKMIN(I),I=1,KM)
      SMIN=1.0E10
      WRITE(6,200)
 200  FORMAT(//6X,48H SEARCHING KINETIC PARAMETERS - BUTANE CRACKING    )
      DO5I=1,KM
      DO5J=1,KM
      V(I,J)=0.0
 5    CONTINUE
      DO10I=1,KM
      V(I,I)=1.0
 10   CONTINUE
 500  FORMAT(5I5)
 501  FORMAT(10F8.1)
C     **********
C     READ IN REACTOR DATA
C     **********
      READ(5,502)NRUNS,NOCOMP
      READ(5,505) AREA,HT,BASAC
      WRITE(6,551)BASAC
 551  FORMAT(/6X,9HBASAC =    ,F10.3)
 505  FORMAT(3F10.5)
 502  FORMAT(2I5)
      DO20I=1,NRUNS
      READ(5,503)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I),XACT(I)
      WRITE(6,550)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I),XACT(I)
 550  FORMAT(6X,6F15.3)
 20   CONTINUE
 503  FORMAT(6F10.5)
      DO30I=1,NRUNS
      READ(5,504)(FRMOL(I,J),J=1,NOCOMP)
 30   CONTINUE
 504  FORMAT(5F10.5)
      GC=82.06
      DO40I=1,NRUNS
      PRESS(I)=(29.92+DELTP(I)/2.0)/29.92
      C4PI(I)=PRESS(I)/(1.0+RAT(I))
```

```
      H2PI(I)=PRESS(I)-C4PI(I)
      TEMP(I)=TEP(I)+273.0
      RCC(I)=(GC*TEMP(I)*AREA)/VOLFL(I)
      RT(I)=1.99*TEMP(I)
      RACT(I)=XACT(I)/BASAC
 40   CONTINUE
C     **********
C     CALCULATE WEIGHTING FACTORS IN EQUAL WEIGHTING MATRIX
C     **********
      DO100I=1,NRUNS
      DO90J=1,NOCOMP
      IF(FRMOL(I,J)-0.01)50,60,60
 50   FACT(I,J)=1000.0
      GOTO90
 60   IF(FRMOL(I,J)-0.1)70,80,80
 70   FACT(I,J)=100.0
      GOTO90
 80   FACT(I,J)=10.0
 90   CONTINUE
 100  CONTINUE
      NSWIT=0
C     **********
C     INITIATE MULTIVARIABLE SEARCH
C     **********************************************
      CALL SEARCH
C     **********************************************
      STOP
      END
      SUBROUTINE OBJECT
      COMMON KM,MCYC,MAXK,MKAT,NSTEP,EPS(10),ALPHA,BETA
      COMMON AKE(10),AKMAX(10),AKMIN(10),AKIN(10),SUMN
      COMMON V(10,10),D(20),BL(20,20),BLEN(20),AJ(20)
      COMMON E(20),AL(20,20),AFK(20)
      COMMON NRUNS,NOCOMP,NSWIT,JCT,HT
      COMMON VOLFL(50),TEP(50),TEMP(50),DELTP(50),RAT(50),PRESS(50)
      COMMON FRMOL(50,5),FACT(50,5),FCALC(50,5)
      COMMON C4PI(50),H2PI(50)
      COMMON RCC(50),RT(50),XACT(50),RUN(50)
      COMMON RACT(50),          CRB(50),CRP(50),CRE(50)
      COMMON CRP1(50),CRP2(50)
      COMMON SMIN
      COMMON DIF4(50)
      COMMON FIX
C     **********
C     THIS SUBROUTINE CALCULATES WRIGHTED SUM OF SQUARES
C     OBJECTIVE FUNCTION
C     **********
      DO5I=1,8
      AKIN(I)=AKE(I)
 5    CONTINUE
      AKIN(9)=1.59
      AKIN(10)=2.47
C     CHECK CONSTRAINTS
      DO10I=1,KM
      IF(AKE(I).GE.AKMAX(I))  AKIN(I)=AKMAX(I)
      IF(AKE(I).LE.AKMIN(I))  AKIN(I)=AKMIN(I)
 10   CONTINUE
      WRITE(6,60)
 60   FORMAT(/6X,40H****************************************     )
      WRITE(6,201)(AKIN(I),I=1,10)
 201  FORMAT(1X,8H AKIN =     ,8F15.7)
```

```
      AKIN(1)=AKIN(1)*1.0E+3
      AKIN(2)=AKIN(2)*1.0E+3
      AKIN(3)=AKIN(3)*1.0E+3
      AKIN(4)=AKIN(4)*1.0E+3
      AKIN(5)=10.0**AKIN(5)
      AKIN(6)=10.**AKIN(6)
      AKIN(7)=10.**AKIN(7)
      AKIN(8)=10.0**AKIN(8)
      SUMSQ=0.0
      S1=0.
      S2=0.
      S3=0.
      S4=0.
      S5=0.
      SS1=0.
      SS2=0.
      SS3=0.
      SS4=0.
      SS5=0.
      JCT=0
C     CALCULATE REACTION RATE CONSTANTS
      DO20I=1,NRUNS
      CRB(I)=RCC(I)*RACT(I)*AKIN(5)*EXP(-AKIN(1)/RT(I))
      CRE(I)=AKIN(8)*EXP(-AKIN(4)/RT(I))
      CRP1(I)=AKIN(6)*RACT(I)*EXP(-AKIN(2)/RT(I))
      CRP1(I)=CRP1(I)*RCC(I)
      CRP2(I)=AKIN(7)*EXP(-AKIN(3)/RT(I))
      CRP2(I)=1.0/(1.0+CRP2(I))
 20   CONTINUE
 30   JCT=JCT+1
C     ***************************************************
      CALL REAC4
C     ***************************************************
      IF(NSWIT)35,35,36
 36   DO37I=1,NOCOMP
      FCALC(JCT,I)=10.
 37   CONTINUE
 35   DO40I=1,NOCOMP
      ZZK=FACT(JCT,I)*ABS(FRMOL(JCT,I)-FCALC(JCT,I))
      SUMSQ=SUMSQ+ZZK*ZZK
 40   CONTINUE
      ZZ1=FACT(JCT,1)*ABS(FRMOL(JCT,1)-FCALC(JCT,1))
      ZZ2=FACT(JCT,2)*ABS(FRMOL(JCT,2)-FCALC(JCT,2))
      ZZ3=FACT(JCT,3)*ABS(FRMOL(JCT,3)-FCALC(JCT,3))
      ZZ4=FACT(JCT,4)*ABS(FRMOL(JCT,4)-FCALC(JCT,4))
      ZZ5=FACT(JCT,5)*ABS(FRMOL(JCT,5)-FCALC(JCT,5))
      S1=S1+ZZ1
      S2=S2+ZZ2
      S3=S3+ZZ3
      S4=S4+ZZ4
      S5=S5+ZZ5
      SS1=SS1+ZZ1*ZZ1
      SS2=SS2+ZZ2*ZZ2
      SS3=SS3+ZZ3*ZZ3
      SS4=SS4+ZZ4*ZZ4
      SS5=SS5+ZZ5*ZZ5
      IF(JCT-NRUNS)30,50,50
 50   CONTINUE
      DO65I=1,NRUNS
      DIF4(I)=FCALC(I,4)-FRMOL(I,4)
 65   CONTINUE
```

```
      WRITE(6,300)S1,S2,S3,S4,S5,SUMSQ
C     **********
C     SUMSQ IS THE WEIGHTED SUM OF SQUARES
C     *********
      SUMSQ=SS1+SS2+SS3+SS4
      WRITE(6,300)SS1,SS2,SS3,SS4,SS5,SUMSQ
 300  FORMAT(6X,6F15.7)
      IF(SUMSQ-SMIN)70,71,71
 70   DO75I=1,NRUNS
      WRITE(6,76)FRMOL(I,1),FCALC(I,1),FRMOL(I,2),FCALC(I,2),
     1FRMOL(I,3),FCALC(I,3),FRMOL(I,4),FCALC(I,4),
     2FRMOL(I,5),FCALC(I,5),DIF4(I)
 75   CONTINUE
 76   FORMAT(1X,2F8.5,5X,2F8.5,5X,2F8.5,5X,2F8.5,5X,2F8.5,5X,F8.5)
      SMIN=SUMSQ
 71   SUMN=SUMSQ
      RETURN
      END

                              CD TOT   0202
```

```
      COMMON KM,MCYC,MAXK,MKAT,NSTEP,EPS(10),ALPHA,BETA
      COMMON AKE(10),AKMAX(10),AKMIN(10),AKIN(10),SUMN
      COMMON V(10,10),D(20),BL(20,20),BLEN(20),AJ(20)
      COMMON E(20),AL(20,20),AFK(20)
      COMMON NRUNS,NOCOMP,NSWIT,JCT,HT
      COMMON VOLFL(50),TEP(50),TEMP(50),DELTP(50),RAT(50),PRESS(50)
      COMMON FRMOL(50,5),FACT(50,5),FCALC(50,5)
      COMMON C3PI(50),H2PI(50)
      COMMON RCC(50),RT(50),XACT(50),RUN(50)
      COMMON RACT(50),          CRB(50),CRP(50),CRE(50)
C     **********
C     SEARCHING PARAMETERS FOR PROPANE MODEL
C     USING ROSENBROCK DIRECT SEARCH
C     WRITTEN BY AL ORLICKAS ---  JAN. 1970
C     **********
C     READ IN ROSENBROCK DATA
C     **********
      READ(5,501)(EPS(I),I=1,KM)
      READ(5,501)(AKE(I),I=1,KM)
      READ(5,501) ALPHA,BETA
      READ(5,501)(AKMAX(I),I=1,KM)
      READ(5,501)(AKMIN(I),I=1,KM)
      SMIN=1.0E10
      WRITE(6,200)
 200  FORMAT(//2X,30HSEARCHING PROPANE PARAMETERS       )
      DO5I=1,KM
      V(I,J)=0.0
 5    CONTINUE
      DO10I=1,KM
      V(I,I)=1.0
 10   CONTINUE
 500  FORMAT(5I5)
 501  FORMAT(8F10.5)
C     **********
C     READ IN REACTOR DATA
C     **********
      READ(5,502)NRUNS,NOCOMP
      READ(5,505) AREA,HT
 505  FORMAT(3F10.5)
 502  FORMAT(2I5)
      DO20I=1,NRUNS
      READ(5,503)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I)
 20   CONTINUE
 503  FORMAT(6F10.5)
      DO30I=1,NRUNS
      READ(5,504)(FRMOL(I,J),J=1,NOCOMP)
 30   CONTINUE
 504  FORMAT(5F10.5)
C     **********
C     INITIAL CALCULATIONS
C     **********
      GC=82.06
      DO40I=1,NRUNS
      PRESS(I)=(29.92+DELTP(I)/2.0)/29.92
      C3PI(I)=PRESS(I)/(1.0+RAT(I))
      H2PI(I)=PRESS(I)-C3PI(I)
      TEMP(I)=TEP(I)+273.0
      RCC(I)=(GC*TEMP(I)*AREA)/VOLFL(I)
      RT(I)=1.99*TEMP(I)
 40   CONTINUE
C     **********
C     CALCULATE WEIGHTING FACTORS FOR EQUAL WEIGHTING MARIX
```

```
C     **********
      DO100I=1,NRUNS
      DO90J=1,NOCOMP
      IF(FRMOL(I,J)-0.01)50,60,60
 50   FACT(I,J)=1000.0
      GOTO90
 60   IF(FRMOL(I,J)-0.1)70,80,80
 70   FACT(I,J)=100.0
      GOTO90
 80   FACT(I,J)=10.0
 90   CONTINUE
 100  CONTINUE
      NSWIT=0
C     **********
C     INITIATE MULTIVARIABLE SEARCH
C     ***********************************************
      CALL SEARCH
C     ***********************************************
      STOP
      END
      SUBROUTINE OBJECT
      COMMON KM,MCYC,MAXK,MKAT,NSTEP,EPS(10),ALPHA,BETA
      COMMON AKE(10),AKMAX(10),AKMIN(10),AKIN(10),SUMN
      COMMON V(10,10),D(20),BL(20,20),BLEN(20),AJ(20)
      COMMON E(20),AL(20,20),AFK(20)
      COMMON NRUNS,NOCOMP,NSWIT,JCT,HT
      COMMON VOLFL(50),TEP(50),TEMP(50),DELTP(50),RAT(50),PRESS(50)
      COMMON FRMOL(50,5),FACT(50,5),FCALC(50,5)
      COMMON C3PI(50),H2PI(50)
      COMMON RCC(50),RT(50),XACT(50),RUN(50)
      COMMON RACT(50),          CRB(50),CRP(50),CRE(50)
      COMMON SMIN
C     **********
C     THIS SUBROUTINE CALCULATES WEIGHTED SUM OF SQUARES
C     OBJECTIVE FUNCTION
C     **********
      AKIN(1)=49.183
      AKIN(2)=18.791
      AKIN(3)=14.023
      AKIN(4)=7.719
      AKE(5)=0.94
      AKE(6)=2.498
C     CHECK CONSTRAINTS
      DO10I=1,KM
      IF(AKE(I).GE.AKMAX(I))  AKIN(I)=AKMAX(I)
      IF(AKE(I).LE.AKMIN(I))  AKIN(I)=AKMIN(I)
 10   CONTINUE
      WRITE(6,60)
 60   FORMAT(/6X,40H****************************************      )
      WRITE(6,200)(AKE(I),I=1,KM)
 200  FORMAT(1X,7H AKE =    ,8E15.4)
      WRITE(6,201)(AKIN(I),I=1,KM)
 201  FORMAT(1X,8H AKIN =    ,8F15.3)
      AKIN(1)=AKIN(1)*1.0E+3
      AKIN(2)=AKIN(2)*1.0E+3
      AKIN(3)=10.0**AKIN(3)
      AKIN(4)=10.0**AKIN(4)
      SUMSQ=0.0
      S1=0.
      S2=0.
      S3=0.
```

```
      S4=0.
      SP1=0.0
      SP2=0.0
      SP3=0.0
      SP4=0.0
      JCT=0
C     CALCULATE REACTION RATE CONSTANTS
      DO20I=1,NRUNS
      CRP(I)=RCC(I)*AKIN(3)*EXP(-AKIN(1)/RT(I))
      CRE(I)=AKIN(4)*EXP(-AKIN(2)/RT(I))
   20 CONTINUE
   30 JCT=JCT+1
C     ***********************************************************
      CALL REAC3
C     ***********************************************************
      IF(NSWIT)35,35,36
   36 DO37I=1,NOCOMP
      FCALC(JCT,I)=100.0
   37 CONTINUE
   35 DO40I=1,NOCOMP
      ZZK=FACT(JCT,I)*ABS(FRMOL(JCT,I)-FCALC(JCT,I))
      SUMSQ=SUMSQ+ZZK*ZZK
   40 CONTINUE
      SP1=FACT(JCT,1)*ABS(FRMOL(JCT,1)-FCALC(JCT,1))
      S1=S1+SP1*SP1
      SP2=FACT(JCT,2)*ABS(FRMOL(JCT,2)-FCALC(JCT,2))
      S2=S2+SP2*SP2
      SP3=FACT(JCT,3)*ABS(FRMOL(JCT,3)-FCALC(JCT,3))
      S3=S3+SP3*SP3
      SP4=FACT(JCT,4)*ABS(FRMOL(JCT,4)-FCALC(JCT,4))
      S4=S4+SP4*SP4
      IF(JCT-NRUNS)30,50,50
   50 CONTINUE
      WRITE(6,300)S1,S2,S3,S4,SUMSQ
  300 FORMAT(6X,6F15.2)
C     **********
C     SUMSQ IS THE WEIGHTED SUM OF SQUARES
C     **********
      SUMSQ=S2+2.0*S3
      IF(SUMSQ-SMIN)70,70,71
   70 DO75I=1,NRUNS
      WRITE(6,76)(FRMOL(I,J),J=1,NOCOMP)
      WRITE(6,76)(FCALC(I,J),J=1,NOCOMP)
   76 FORMAT(6X,5F20.5)
   75 CONTINUE
      SMIN=SUMSQ
   71 SUMN=SUMSQ
      RETURN
      END

                                   CD TOT   0172
```

```
      SUBROUTINE SEARCH
C     *********
C     OPTIMIZATION BY ROSENBROCK METHOD
C     THIS PROGRAM WAS WRITTRN BY H. PANG
C     AT MCMASTER UNIVERSITY   1969
C     THIS IS THE ROSENBROCK DIRECT SEARCH ROUTINE
C     *********
C   AJ= INDICATORS
C   AFK= OPTIMIZED VALUES FOR VARIABLES
C   AKE = VARIBLES
C   ALPHA =SCALE FACTOR FOR STEP SIZE  WHEN STEP IS SUCCESSFUL
C   BETA =SCALE FACTOR FOR STEP SIZE WHEN STEP IS UNSUCCESSFUL
C   E = TEMPORARY STORAGE FOR STEP SIZE
C   EPS =STEP SIZE
C   KAT = NO OF TIMES OBJECT BEING CALLED
C   KK1  =NO OF STAGES
C   KM = NO OF VARIBLES
C   MCYC = NO OF SUCCESSIVE FAILURES ENCOUNTERED IN ALL DIRECTIONS
C   NSTEP =1, USE INITIAL STEP SIZE FOR EVERY NEW STAGE
C   NSTEP =2, USE STEP SIZE OF KTH STAGE FOR (K+1)TH STAGE
C   OBJECT = SUBROUTINE FOR OBJECTIVE FUNCTION SUMN
C   SUMO = STORAGE FOR MINIMUM SUMN
C   V =ORTHOGONAL UNIT VECTORS
C   V IS A UNIT MATRIX INITIALLY
C   THE PROGRAMME TERMINATES AFTER  MAXK STAGES
C           OR AFTER  OBJECT BEING CALLED MKAT TIMES
C           OR AFTER MCYC SUCCESSIVE FAILURES BEINNG ENCOUNTERED
C    BEFORE TERMINATION
C   MAX NUMBER OF VARIBLES =20  ( LIMITED BY DIMENSION)
C
C
      COMMON KM,MCYC,MAXK,MKAT,NSTEP,EPS(10),ALPHA,BETA
      COMMON AKE(10),AKMAX(10),AKMIN(10),AKIN(10),SUMN
      COMMON V(10,10),D(20),BL(20,20),BLEN(20),AJ(20)
      COMMON E(20),AL(20,20),AFK(20)
      COMMON NRUNS,NOCOMP,NSWIT,JCT,HT
      COMMON VOLFL(50),TEP(50),TEMP(50),DELTP(50),RAT(50),PRESS(50)
      COMMON FRMOL(50,5),FACT(50,5),FCALC(50,5)
      COMMON C3PI(50),H2PI(50)
      COMMON RCC(50),RT(50),XACT(50),RUN(50)
      COMMON RACT(50),        CRB(50),CRP(50),CRE(50)
      COMMON SMIN
      WRITE(6,751)
 751  FORMAT(//6X,11H IN SEARCH     )
C
      KAT =1
      CALL OBJECT
      SUMO =SUMN
      DO 812 K=1,KM
      AFK(K) =AKE(K)
  812 CONTINUE
      KK1=1
      IF (NSTEP .EQ.1) GO TO 1000
      DO 350 I=1,KM
      E(I)  =EPS(I)
  350 CONTINUE
 1000 DO 250 I=1,KM
      AJ(I) =2.0
      IF (NSTEP .NE.1) GO TO 250
      E(I) =EPS(I)
  250 D(I) =0.0
      III=0
```

```
  397 III=III+1
  258 I=1
  259 DO 251 J=1,KM
  251 AKE(J) =AKE(J) +E(I) *V(I,J)
      CALL OBJECT
C   ************************************************************************
C    PRINT HERE IF DESIRED NO OF TIMES OBJECTIVE FUNCTION BEING CALLED
C     (KAT), OBJECTIVE FUNCTION(SUMN), VARIBLES(AKE(I))
C   ************************************************************************
      KAT =KAT +1
      IF (KAT .EQ. MKAT ) GO TO 1002
      IF(SUMN.LT.SUMO) GOTO253
      DO 254 J=1,KM
  254 AKE(J) =AKE(J) -E(I) *V(I,J)
      E(I) =-BETA*E(I)
      IF (AJ(I) .LT. 1.5) AJ(I) =0.0
      GO TO 255
  253 D(I) =D(I) +E(I)
      E(I) =ALPHA *E(I)
      SUMO =SUMN
      DO 813 K=1,KM
  813  AFK(K) =AKE(K)
      IF (AJ(I) .GT. 1.5) AJ(I) =1.0

  255 DO 256 J=1,KM
      IF (AJ(J) .GT. 0.5) GO TO 299
  256 CONTINUE
      GO TO 257
  299 IF (I.EQ. KM) GO TO 399
      I=I+1
      GO TO 259
  399 DO 398 J=1,KM
      IF (AJ(J) . LT.2. ) GO TO 258
  398 CONTINUE
      IF (III.LT. MCYC ) GO TO 397
      GO TO 1001
  257 CONTINUE
      DO 290 I=1,KM
      DO 290 J=1,KM
  290 AL(I,J) =0.0
C
C    ORTHOGONALIZATION
C
      WRITE (6,280 ) KK1
      WRITE (6,281) SUMO,(AKE(I) ,I=1,KM)
      DO 260 I=1,KM
      KL=I
      DO 260 J=1,KM
      DO 261 K=KL,KM
  261 AL(I,J) =D(K) *V(K,J) +AL(I,J)
  260 BL (1,J)= AL(1,J)
      BLEN(1)=0.0
      DO 351 K=1,KM
      BLEN(1)= BLEN(1) +BL(1,K)*BL(1,K)
  351 CONTINUE
      BLEN(1) =SQRT(BLEN(1))
      DO 352 J=1,KM
      V(1,J) =BL(1,J) /BLEN(1)
  352 CONTINUE
      DO 263 I=2,KM
      II=I-1
      DO 263 J=1,KM.
```

```
      SUMAV =0.0
      DO 262 K=1,KM
  262 SUMAV=SUMAV + AL(I,K)*V(KK,K)
  264 SUMAVV =SUMAV*V(KK,J) +SUMAVV
  263 BL(I,J) =AL(I,J) -SUMAVV
      DO 266 I=2, KM
      BLEN(I) =0.0
      DO 267 K=1,KM
  267 BLEN(I) =BLEN(I) +BL(I,K) *BL(I,K)
      BLEN(I) = SQRT(BLEN(I) )
      DO 266 J=1, KM
  266 V(I,J) =BL(I,J) / BLEN(I)
      KK1 =KK1+1
      IF (KK1.EQ.MAXK ) GO TO 1001
      GO TO 1000
 1002 WRITE (6,910 ) KAT
 1001 WRITE (6, 1003) KK1, KAT ,III
      WRITE (6, 1004) SUMO
      WRITE (6, 1006) (AFK(I),I=1, KM)
      WRITE (6, 294)
      WRITE(6,815) (( V (I,J) ,J=1,KM),I=1,KM)
  150 FORMAT (8F10.5)
  152 FORMAT (10I5)
  280 FORMAT(//3X, 12HNO OF STAGE=, 3X, I5/)
  281 FORMAT (10X,  18HSUMO AND VARIABLES,3X, 6E12.4/)
  294 FORMAT(/3X, 23HORTHOGONAL UNIT VECTORS/)
  815 FORMAT (3X,9E12.4/)
  905 FORMAT ( 8F10.5)
  910 FORMAT(//3X,25HPROGRAM HAS CALLED OBJECT,2X,I5, 2X,
     1 25HTIMES WITHOUT CONVERGANCE/)
 1003 FORMAT(/3X, 13HNO OF STAGES=,I5, 3X, 23HAND OBJECT BEING CALLED,
     1 I5, 3X, 5HTIMES,3X,26HNO OF SUCCESSIVE FAILURES=,I5/)
 1004 FORMAT(/3X, 7HOBJECT=, E15.5/)
 1006 FORMAT(/3X, 16HTHE VARIBLES ARE, 6E12.5/)
      RETURN
      END

                               CD TOT    0036
```

```
C     ************************************
C     NON LINEAR PARAMETER ESTIMATION
C     GAUSS JORDAN ITERATION METHOD
C     LOCAL LINEARIZATION -----      PROPANE RUNS
C     WRITTEN BY AL ORLICKAS ---   FEB. 1970
C     ***************************************
      COMMON NPAR,NRUN
      COMMON AKE(10),T(10),DELT(10),AKMIN(10),AKMAX(10)
      COMMON AKIN(10)
      COMMON AREA,HT,JCT
      COMMON NSWIT
      COMMON RUN(50),VOLFL(50),TEP(50),DELTP(50),RAT(50),XACT(50)
      COMMON FRMOL(50,5),FCALC(50,5)
      COMMON PRESS(50),C3PI(50),H2PI(50),TEMP(50),RCC(50),RT(50)
      COMMON RACT(50)
      COMMON FACT(50,5)
      COMMON FCLO(50,5),FCLP(50,5,8),JCOMP
      COMMON SB(5)
      COMMON THETA(10)
      COMMON Y(90),XP(10,90),X(90,10),XTOT(90,10),YTOT(90)
      COMMON YOBS(50),YCLC(50), COEF(10),AKEO(10),XPX(10,10),XC(10)
      COMMON CRB(50),CRE(50),CRP1(50),CRP2(50)
      COMMON CRP(50)
      COMMON NCMP
      DIMENSION AA(100)
      READ(5,875) NPAR,NRUN
 875  FORMAT(2I5)
      DO5I=1,NPAR
      READ(5,501) AKE(I),T(I),DELT(I)
 5    CONTINUE
      READ(5,505)(AKMIN(I),I=1,NPAR)
      READ(5,505)(AKMAX(I),I=1,NPAR)
 505  FORMAT(6F10.5)
 501  FORMAT(3F10.5)
C     READ IN REACTOR DATA
      READ(5,502) AREA,HT
 502  FORMAT(2F10.5)
      DO10I=1,NRUN
      READ(5,503)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I)
 10   CONTINUE
 503  FORMAT(5F10.5)
      DO20I=1,NRUN
      READ(5,504)(FRMOL(I,J),J=1,4)
 20   CONTINUE
      NCMP=4
 504  FORMAT(4F10.5)
      WRITE(6,901)
 901  FORMAT(/6X,29H EXPERIMENTAL MOLE FRACTIONS      )
      DO902I=1,NRUN
      WRITE(6,903)(FRMOL(I,J),J=1,NCMP)
 902  CONTINUE
 903  FORMAT(6X,4F20.5)
C     PRELIMINARY CALCULATIONS
      GC=82.06
      DO41I=1,NRUN
      PRESS(I)=(29.92+DELTP(I)/2.0)/29.92
      C3PI(I)=PRESS(I)/(1.0+RAT(I))
      H2PI(I)=PRESS(I)-C3PI(I)
      TEMP(I)=TEP(I)+273.
      RCC(I)=(GC*TEMP(I)*AREA)/VOLFL(I)
      RT(I)=1.99*TEMP(I)
 41   CONTINUE
```

```
      LOOPS=0
      LOOPM=300.
C     WEIGHTS OF MOLE FRACTIONS
      DO29I=1,NRUN
      DO28J=1,NCMP
      IF(FRMOL(I,J)-0.01)21,22,22
 21   FACT(I,J)=1000.
      GOTO28
 22   IF(FRMOL(I,J)-0.1)23,24,24
 23   FACT(I,J)=100.0
      GOTO28
 24   FACT(I,J)=10.0
 28   CONTINUE
 29   CONTINUE
C     **********************************
 100  CONTINUE
C     CALCULATE RESPONSE AT BEST PARAMETERS AVAILABLE
      CALL OBJECT
      DO55I=1,NRUN
      DO55J=1,NCMP
      FCLO(I,J)=FCALC(I,J)
 55   CONTINUE
      WRITE(6,810)
 810  FORMAT(/6X,12H AKE VALUES    )
      WRITE(6,811)(AKE(I),I=1,NPAR)
 811  FORMAT(8F15.3)
      DO815I=1,NRUN
      WRITE(6,802)FRMOL(I,1),FCALC(I,1),
     1FRMOL(I,2),FCALC(I,2),FRMOL(I,3),FCALC(I,3),
     2FRMOL(I,4),FCALC(I,4)
 815  CONTINUE
 802  FORMAT(1X,2F10.5,5X,2F10.5,5X,2F10.5,5X,2F10.5)
C     CALCULATE RESPONSES AT INCREMENTS OF PARAMETERS TO EVALUATE
C     NUMERICAL PARTIAL DERIVATIVES
      DO65II=1,NPAR
      AKE(II)=AKE(II)+DELT(II)
      CALL OBJECT
      AKE(II)=AKE(II)-DELT(II)
      DO70J=1,NRUN
      DO70K=1,NCMP
      FCLP(J,K,II)=FCALC(J,K)
 70   CONTINUE
 65   CONTINUE
      JCOMP=0
      NLOW=1
      NHI=NRUN
      NKP=1
C     **********************************
C     SET UP VECTOR OF OBSERVATIONS
 200  CONTINUE
      JCOMP=JCOMP+1
      SB(JCOMP)=0.0
      DO80I=1,NRUN
      YOBS(I)=FRMOL(I,JCOMP)
      YCLC(I)=FCLO(I,JCOMP)
      Y(I)=YOBS(I)-YCLC(I)
      SB(JCOMP)=SB(JCOMP)+FACT(I,JCOMP) *ABS(Y(I))
 80   CONTINUE
C     SET UP MATRIX OF CONSTANTS
      DO90JJ=1,NRUN
      DO90KK=1,NPAR
```

```
      X(JJ,KK)=(FCLP(JJ,JCOMP,KK)-FCLO(JJ,JCOMP))
   90 CONTINUE
      KC=0
      DO300I=NLOW,NHI
      KC=KC+1
      DO300J=1,NPAR
      XTOT(I,J)=X(KC,J)
      YTOT(I)=Y(KC)
  300 CONTINUE
      IF(JCOMP-NCMP)301,220,220
C     USE LINEAR LEAST SQUARES TO FIND NEW PARAMETERS
  301 NLOW=NHI+1
      NKP=NKP+1
      NHI=NKP*NRUN
      GOTO200
  220 CONTINUE
      DO302I=1,NHI
      DO302J=1,NPAR
      X(I,J)=XTOT(I,J)
      Y(I)=YTOT(I)
  302 CONTINUE
      DO35I=1,NHI
      DO35J=1,NHI
      XC(I)=0.0
      COEF(I)=0.0
   35 CONTINUE
      DO30I=1,NHI
      DO30 J=1,NPAR
      XP(J,I)=X(I,J)
   30 CONTINUE
      DO40 I=1,NPAR
      DO40 K=1,NPAR
      XPX(I,K)=0.
      DO40J=1,NHI
      XPX(I,K) = XPX(I,K)+XP(I,J)*X(J,K)
   40 CONTINUE
C     ***************************************
C     INVERT XPX MATRIX
      L=0
      DO 45 I=1,NPAR
      DO 45 J=1,I
      L=L+1
      AA(L)=XPX(I,J)
   45 CONTINUE
      CALL INVSYM (AA,NPAR,IERR)
      IF(IERR.NE.0)  GOTO170
      L=0
      DO47 I=1,NPAR
      DO47 J=1,I
      L=L+1
   47 XPX(I,J)=AA(L)
      DO48 I=1,NPAR
      DO48 J=1,NPAR
   48 XPX(I,J)=XPX(J,I)
C     ***************************************
      DO50 I=1,NPAR
      DO50J=1,NHI
      XC(I)=XC(I)+XP(I,J)*Y(J)
   50 CONTINUE
      DO60 I=1,NPAR
      DO60 J=1,NPAR
```

```
      COEF(I)=COEF(I)+XPX(I,J)*XC(J)
60    CONTINUE
      DO210I=1,NPAR
      THETA(I)=AKE(I)+COEF(I)*DELT(I)
210   CONTINUE
      WRITE(6,821)(THETA(I),I=1,NPAR)
821   FORMAT(8E15.6)
      WRITE(6,506)
506   FORMAT(/6X,40H**************************************      )
      WRITE(6,507)(SB(I),I=1,NCMP)
507   FORMAT(1X,36H SUM OF ABS VALUE OF DIFFERENCES =     ,5X,4F20.4)
      DO240I=1,NPAR
      AKEO(I)=AKE(I)
240   CONTINUE
      DO251I=1,NPAR
      AKE(I)=THETA(I)
251   CONTINUE
      DO260I=1,NPAR
      DD=(AKE(I)-AKEO(I))/AKEO(I)
      DDD=ABS(DD)
      IF(DDD-T(I))260,260,262
262   IF(DD)263,264,264
263   AKE(I)=AKEO(I)-T(I)*AKEO(I)
      GOTO260
264   AKE(I)=AKEO(I)+T(I)*AKEO(I)
260   CONTINUE
      IF(LOOPS-LOOPM)250,590,590
250   LOOPS=LOOPS+1
      GOTO100
590   WRITE(6,591)
591   FORMAT(//6X,43H MAXIMUM NUMBER OF SPECIFIED LOOPS REACHED       )
      GOTO592
500   CONTINUE
170   WRITE(6,171)
171   FORMAT(//6X,24H MATRIX DID NOT INVERSE     )
592   CONTINUE
      STOP
      END
      SUBROUTINE OBJECT
      COMMON NPAR,NRUN
      COMMON AKE(10),T(10),DELT(10),AKMIN(10),AKMAX(10)
      COMMON AKIN(10)
      COMMON AREA,HT,JCT
      COMMON NSWIT
      COMMON RUN(50),VOLFL(50),TEP(50),DELTP(50),RAT(50),XACT(50)
      COMMON FRMOL(50,5),FCALC(50,5)
      COMMON PRESS(50),C3PI(50),H2PI(50),TEMP(50),RCC(50),RT(50)
      COMMON RACT(50)
      COMMON FACT(50,5)
      COMMON FCLO(50,5),FCLP(50,5,8),JCOMP
      COMMON SB(5)
      COMMON THETA(10)
      COMMON Y(90),XP(10,90),X(90,10),XTOT(90,10),YTOT(90)
      COMMON YOBS(50),YCLC(50), COEF(10),AKEO(10),XPX(10,10),XC(10)
      COMMON CRB(50),CRE(50),CRP1(50),CRP2(50)
      COMMON CRP(50)
      COMMON NCMP
C     **********
C     THIS SUBROUTINE SETS UP CALCULATION OF REACTOR MODEL
C     TO OBTAIN MOLE FRACTION RESPONSES
```

```
C     **********
C     CHECK CONSTRAINTS
      DO10I=1,NPAR
      IF(AKE(I).GT.AKMAX(I)) AKE(I)=AKMAX(I)-DELT(I)
      IF(AKE(I).LT.AKMIN(I)) AKE(I)=AKMIN(I)
 10   CONTINUE
      AKIN(1)=AKE(1)*1.0E+3
      AKIN(2)=AKE(2)*1.0E+3
      AKIN(3)=10.0**AKE(3)
      AKIN(4)=10.0**AKE(4)
      JCT=0
C     CALCULATE REACTION RAT CONSTANTS
      DO20I=1,NRUN
      CRP(I)=RCC(I)*AKIN(3)*EXP(-AKIN(1)/RT(I))
      CRE(I)=AKIN(4)*EXP(-AKIN(2)/RT(I))
 20   CONTINUE
 30   JCT=JCT+1
C     **********************************
      CALL REAC3
C     **********************************
      IF(NSWIT)35,35,36
 36   DO37I=1,NCMP
      FCALC(JCT,I)=10.
 37   CONTINUE
 35   CONTINUE
      IF(JCT-NRUN)30,50,50
 50   CONTINUE
      RETURN
      END

                           CD TOT   0273
```

K.4 PROGRAMS USED TO OBTAIN CONFIDENCE LIMITS ON PARAMETERS

The theory for the analytically determined covariance matrix is described in Appendix H.1. The nomenclature used in this Appendix is also followed quite closely in the program.

The Golden Section searching technique is described fully by Wilde(W4), and is used here to find the pre-exponential factor for the butane rate expression given a butane activation energy and evaluated at the best estimate values of the remaining parameters.

VINV - inverse of covariance matrix for all of the experimental runs

RLMAX - minimum weighted sum of squares of difference between mole fraction of reactor effluent

ROTLI - likelihood ratio

BBR, BBL - upper and lower limits of variable being searched

BIR, BIL - experimental search points inside BBR and BBL

RRR, RRL - value of likelihood ratio at BBR and BBL

NLOOP - number of pairs of searching experiments

FCLP - storage matrix for mole fractions of components after perturbations, in calculating partial derivatives

Y - vector of observations for linear regression

X - matrix of constants for linear regression

THETA - new parameter value (unconstrained)

AKE - new parameter value (constrained by maximum percent change per iteration)

```
      COMMON NRUNS,NCMP,JJ,NSWIT
      COMMON AREA,HT,BASAC
      COMMON RUN(30),VOLFL(30),TEP(30),DELTP(30),RAT(30),XACT(30)
      COMMON A1(30),AT(30),A3(30),A4(30),A5(30)
      COMMON TDIF(30)
      COMMON G1,G2,G3,G4,G5
      COMMON AK1,AK2,AK3,AK4,AK5,AK6,AK7,AK8,AK9,AK10
      COMMON RACT(30)
      COMMON V(4),VA(5,5),R(6,6),S(6,5)
      COMMON ACALC(5),ANOM(5)
      COMMON RP(6,6),SP(6,5)
      COMMON SSS(6,5),SSP(5,6),SSQ(6,5),SSR(6,6)
      COMMON C4IN,H2IN
      COMMON CRB,CRE,CRP1,CRP2
      COMMON PRESS(30)
      COMMON SSZ(10,10),SSY(10,10)
      COMMON XKM(6)
      COMMON VS(6,6)
      COMMON VRV(6,6),N1(24)
      DIMENSION AA(100)
C     **********
C     PROGRAM TO CALCULATE INVERSE OF ANALYTICAL COVARIANCE MATRIX
C     WRITTEN BY AL ORLICKAS --- MAY 1970
C     **********
C     READ IN DATA
C     **********
      DO1I=2,6
      XKM(I)=0.0
 1    CONTINUE
      XKM(1)=1.
      READ(5,500)NRUNS,NCMP
      READ(5,501)AREA,HT,BASAC
      WRITE(6,502)BASAC
 502  FORMAT(/6X,9HBASAC =     ,F10.3)
 500  FORMAT(2I5)
 501. FORMAT(3F10.5)
      DO10I=1,NRUNS
      READ(5,503)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I),XACT(I)
      WRITE(6,504)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I),XACT(I)
      READ(5,505)A1(I),AT(I),A3(I),A4(I),A5(I)
      WRITE(6,506)A1(I),AT(I),A3(I),A4(I),A5(I)
      READ(5,507)TDIF(I)
      WRITE(6,508)TDIF(I)
 10   CONTINUE
 503  FORMAT(6F10.5)
 504  FORMAT(/6X,6F15.3)
 505  FORMAT(5F10.5)
 506  FORMAT(16X,5F15.3)
 507  FORMAT(F10.5)
 508  FORMAT(16X,F10.2)
C     **********
C     CHROMATOGRAPH CALIBRATION FACTORS
C     **********
      G1=0.1532
      G2=0.1032
      G3=0.07895
      G4=0.0692
      G5=4.464
      G1P=G1-G2
      G5P=G5-G2
      AK1=56454.
      AK2=54397.
```

```
      AK3=37514.
      AK4=16751.
      AK5=10.0**17.507
      AK6=10.0**16.097
      AK7=10.0**15.043
      AK8=10.0**6.984
      AK9=1.7
      AK10=2.45
      DO20I=1,NRUNS
      PRESS(I)=(29.92+DELTP(I)/2.0)/29.92
      RACT(I)=XACT(I)/BASAC
 20   CONTINUE
      DT=1.0
      DF=0.01
      DR=0.06
      V(1)=0.0025
      V(3)=0.0009
      V(4)=0.0009
C     **********
C     FOR EACH RUN - JJ - FIND INVERSE OF COVARIANCE MATRIX
C     **********
      JJ=0
C     **********
C     FIND - R- MATRIX OF DERIVATIVES OF MOLE FRACTIONS
C     WITH RESPECT TO AREAS
C     USE ONLY 4 INDEPENDENT AREAS AND FIRST THREE
C     INDEPENDENT COMPONENTS
C     **********
 100  JJ=JJ+1
      Z1=G1*A1(JJ)
      Z2=G2*AT(JJ)
      Z3=G3*A3(JJ)
      Z4=G4*A4(JJ)
      Z5=G5*A5(JJ)
      Z5P=G5P*A5(JJ)
      Z1P=G1P*A1(JJ)
      R(1,1)=G1*(Z2+Z3+Z4+Z5P)
      R(1,2)=-Z1*G2
      R(1,3)=-Z1*G3
      R(1,4)=-Z1*G4
      R(1,5)=-Z1*G5P
      R(2,1)=G2*(-Z3-Z4-Z5-G1*AT(JJ))
      R(2,2)=G2*(Z1+Z3+Z4+Z5)
      R(2,3)=G2*G3*(A1(JJ)-AT(JJ)+A5(JJ))
      R(2,4)=G2*G4*(A1(JJ)-AT(JJ)+A5(JJ))
      R(2,5)=G2*(A1*(G5-G1)-Z3-Z4-G5*AT(JJ))
      R(3,1)=-Z3*G1P
      R(3,2)=-Z3*G2
      R(3,3)=G3*(Z1P+G2*AT(JJ)+Z4+Z5P)
      R(3,4)=-Z3*G4
      R(3,5)=-Z3*G5P
C     **********
C     LEAVE OUT R(5,I) --
C     LEAVE OUT R(4,I) - TAKE C4 AND H2 AS THE DEPENDENT VARIABLES
C     **********
      R(4,1)=-Z4*G1P
      R(4,2)=-Z4*G2
      R(4,3)=-Z4*G3
      R(4,4)=G4*(Z1P+G2*AT(JJ)+Z3+Z5P)
      R(4,5)=-Z4*G5P
      R(5,1)=-Z5*G1P
```

```
      R(5,2)=-Z5*G2
      R(5,3)=-Z5*G3
      R(5,4)=-Z5*G4
      R(5,5)=G5*(Z1P+G2*AT(JJ)+Z3+Z4)
      DEE=Z1+Z3+Z4+Z5
      DEE=DEE+G2*(AT(JJ)-A1(JJ)-A5(JJ))
      DEE=DEE*DEE
      DO21I=1,4
      DO21J=1,4
      R(I,J)=R(I,J)/DEE
 21   CONTINUE
      WRITE(6,510)
 510  FORMAT(/5X,25H R MATRIX OF DERIVATIVES      )
      M=3
      DO30I=1,M
      WRITE(6,511)(R(I,J),J=1,4)
 511  FORMAT(2X,5E20.5)
 30   CONTINUE
      V(2)=(0.25*TDIF(JJ))*(0.25*TDIF(JJ))
C     **********
C     FIND - S - MATRIX OF DERIVATIVES OF AREAS WITH RESPECT TO PEN
C     ERROR,TEMPERATURE,FEED FLOWRATE, AND FEED RATIO
C     **********
      CALL OBJECT
      DO50I=1,5
      ANOM(I)=ACALC(I)
 50   CONTINUE
      WRITE(6,512)(ANOM(I),I=1,5)
 512  FORMAT(/6X,17HNOMINAL AREAS =     ,5X,5F15.2)
      TEP(JJ)=TEP(JJ)+DT
      CALL OBJECT
      TEP(JJ)=TEP(JJ)-DT
      DO60I=1,5
      S(I,2)=(ACALC(I)-ANOM(I))/DT
 60   CONTINUE
      RSQ=RAT(JJ)/2.0
      RAT(JJ)=RAT(JJ)+DR
      CALL OBJECT
      RAT(JJ)=RAT(JJ)-DR
      DO70I=1,5
      S(I,4)=(ACALC(I)-ANOM(I))/DR
      S(I,4)=S(I,4)*RSQ
 70   CONTINUE
      FSQ=VOLFL(JJ)/2.0
      VOLFL(JJ)=VOLFL(JJ)+DF
      CALL OBJECT
      VOLFL(JJ)=VOLFL(JJ)-DF
      DO80I=1,5
      S(I,3)=(ACALC(I)-ANOM(I))/DF
      S(I,3)=S(I,3)*FSQ
 80   CONTINUE
      S(1,1)=A1(JJ)/2.0
      S(2,1)=AT(JJ)/2.0
      S(3,1)=A3(JJ)/2.0
      S(4,1)=A4(JJ)/2.0
      S(5,1)=A5(JJ)/2.0
      WRITE(6,515)
 515  FORMAT(/6X,25HS MATRIX OF DERIVATIVES    )
      DO90I=1,4
      WRITE(6,516)(S(I,J),J=1,M)
 90   CONTINUE
```

```
  516 FORMAT(6X,4E20.5)
C     **********
C     MATRIX MANIPULATIONS TO ARRIVE AT INVERSE COVARIANCE MATRIX
C     **********
      DO110I=1,4
      DO110J=1,M
      RP(I,J)=R(J,I)
  110 CONTINUE
      WRITE(6,570)
  570 FORMAT(/6X,11HRP MATRIX    )
      DO571I=1,4
      WRITE(6,572)(RP(I,J),J=1,M)
  571 CONTINUE
  572 FORMAT(6X,4E20.6)
      DO120I=1,4
      DO120J=1,4
      SP(J,I)=S(I,J)
  120 CONTINUE
      WRITE(6,573)
  573 FORMAT(/6X,11HSP MATRIX      )
      DO579I=1,4
      WRITE(6,575)(SP(I,J),J=1,4)
  579 CONTINUE
  575 FORMAT(6X,5E20.6)
      DO130I=1,M
      DO130J=1,4
      SSS(I,J)=0.0
      DO130K=1,4
      SSS(I,J)=SSS(I,J)+R(I,K)*S(K,J)
  130 CONTINUE
      WRITE(6,580)
  580 FORMAT(/6X,12HSSS MATRIX     )
      DO581I=1,M
      WRITE(6,582)(SSS(I,J),J=1,4)
  582 FORMAT(6X,4E20.6)
  581 CONTINUE
      DO140I=1,4
      DO140J=1,M
      SSP(I,J)=0.0
      DO140K=1,4
      SSP(I,J)=SSP(I,J)+SP(I,K)*RP(K,J)
  140 CONTINUE
      WRITE(6,585)
  585 FORMAT(/6X,12HSSP MATRIX     )
      DO586I=1,4
      WRITE(6,587)(SSP(I,J),J=1,M)
  587 FORMAT(6X,5E20.6)
  586 CONTINUE
      DO145I=1,4
      DO145J=1,4
      VA(I,J)=0.0
  145 CONTINUE
      DO146I=1,4
      VA(I,I)=V(I)
  146 CONTINUE
      DO150I=1,M
      DO150J=1,4
      SSQ(I,J)=0.0
      DO150K=1,4
      SSQ(I,J)=SSQ(I,J)+SSS(I,K)*VA(K,J)
  150 CONTINUE
```

```
      WRITE(6,590)
  590 FORMAT(/6X,12HSSQ MATRIX      )
      DO591I=1,M
      WRITE(6,592)(SSQ(I,J),J=1,4)
  592 FORMAT(6X,4E20.6)
  591 CONTINUE
C     **********
C     SSR IS THE COVARIANCE MATRIX
C     **********
      DO160I=1,M
      DO160J=1,M
      SSR(I,J)=0.0
      DO160K=1,4
      SSR(I,J)=SSR(I,J)+SSQ(I,K)*SSP(K,J)
  160 CONTINUE
      WRITE(6,595)
  595 FORMAT(/6X,19HCOVARIANCE MATRIX     )
      DO596I=1,M
      WRITE(6,597)(SSR(I,J),J=1,M)
  597 FORMAT(6X,5E20.6)
  596 CONTINUE
C     **********
C     INVERT THE COVARIANCE MATRIX
C     **********
      DO2I=1,M
      DO2J=1,M
      SSR(I,J)=SSR(I,J)*1.0E+8
      VS(I,J)=SSR(I,J)
      VRV(I,J)=SSR(I,J)
 2    CONTINUE
C     **********
C     FIND DETERMINANT TO CHECK FOR SINGULARITY
C     **********
      CALL SOLVE(VS,XKM,ID,3,6)
      BB=FLOAT(ID)
      DETT=2.0**BB
      WRITE(6,3)DETT
 3    FORMAT(/6X,18HDETT IS APPEOX =      ,E20.7)
      ZERO=1.0E-8
C     **********
C     INVERT MATRIX BY -- INVMAT --
C     **********
      CALL INVMAT(VRV,6,3,ZERO,IERR,N1)
      WRITE(6,210)
  210 FORMAT(//6X,22HINVERSE BY INVMAT IS     )
      DO211I=1,M
      DO211J=1,M
      WRITE(6,212)(VRV(I,J),J=1,M)
  211 CONTINUE
  212 FORMAT(1X,4E15.5)
      L=0
      DO45I=1,M
      DO45J=1,I
      L=L+1
      AA(L)=SSR(I,J)
  45  CONTINUE
C     **********
C     INVERT MATRIX BY -- INVSYM --
C     **********
      CALL INVSYM(AA,M,IERR)
      IF(IERR.NE.0)GOTO170
```

```
      L=0
      DO47I=1,M
      DO47J=1,I
      L=L+1
 47   SSZ(I,J)=AA(L)
      DO48I=1,M
      DO48J=1,M
      SSZ(I,J)=SSZ(J,I)
 48   CONTINUE
      DO49I=1,M
      DO49J=1,M
      SSZ(I,J)=SSZ(I,J)*1.0E-8
 49   CONTINUE
      GOTO172
 170  WRITE(6,171)
 171  FORMAT(//6X,24HMATRIX DID NOT INVERSE     )
      GOTO200
 172  CONTINUE
      WRITE(6,173)
 173  FORMAT(/6X,23HINVERSE OF VAR MATRIX     )
      DO174I=1,M
      WRITE(6,175)(SSZ(I,J),J=1,M)
      WRITE(7,176)(SSZ(I,J),J=1,M)
 174  CONTINUE
 175  FORMAT(6X,5E20.5)
 176  FORMAT(4E15.7)
      WRITE(6,180)
 180  FORMAT(/6X,21HX-1X UNITY MATRIX ,     )
C     **********
C     MULTIPLY MATRIX BY INVERSE TO GET DIAGONAL UNITY MATRIX
C     **********
      DO181I=1,M
      DO181J=1,M
      SSY(I,J)=0.0
      DO181K=1,M
      SSY(I,J)=SSY(I,J)+SSZ(I,K)*SSR(K,J)
 181  CONTINUE
      DO182I=1,M
      WRITE(6,183)(SSY(I,J),J=1,M)
 182  CONTINUE
 183  FORMAT(2X,5F20.10)
      WRITE(6,185)
      WRITE(6,185)
 185  FORMAT(2X,40H************************************                    )
C     **********
C     CONTINUE FINDING MATRICES FOR REST OF RUNS
C     **********
      IF(JJ-NRUNS)100,200,200
 200  CONTINUE
      STOP
      END
      SUBROUTINE OBJECT
      COMMON NRUNS,NCMP,JJ,NSWIT
      COMMON AREA,HT,BASAC
      COMMON RUN(30),VOLFL(30),TEP(30),DELTP(30),RAT(30),XACT(30)
      COMMON A1(30),AT(30),A3(30),A4(30),A5(30)
      COMMON TDIF(30)
      COMMON G1,G2,G3,G4,G5
      COMMON AK1,AK2,AK3,AK4,AK5,AK6,AK7,AK8,AK9,AK10
      COMMON RACT(30)
      COMMON V(4),VA(5,5),R(6,6),S(6,5)
```

```
      COMMON ACALC(5),ANOM(5)
      COMMON RP(6,6),SP(6,5)
      COMMON SSS(6,5),SSP(5,6),SSQ(6,5),SSR(6,6)
      COMMON C4IN,H2IN
      COMMON CRB,CRE,CRP1,CRP2
      COMMON PRESS(30)
      COMMON SSZ(10,10),SSY(10,10)
      COMMON XKM(6)
      COMMON VS(6,6)
      COMMON VRV(6,6),N1(24)
C     **********
C     THIS SUBROUTINE SETS UP REACTION CALCULATIONS
C     IN EVALUATION OF NUMERICAL PARTIAL DERIVATIVES
C     **********
      TEMP=TEP(JJ)+273.
      C4IN=PRESS(JJ)/(1.0+RAT(JJ))
      H2IN=PRESS(JJ)-C4IN
      RCC=(82.06*TEMP*AREA)/VOLFL(JJ)
      RT=1.99*TEMP
      CRB=RCC*RACT(JJ)*AK5*EXP(-AK1/RT)
      CRE=AK8*EXP(-AK4/RT)
      CRP1=AK6*RACT(JJ)*EXP(-AK2/RT)
      CRP1=CRP1*RCC
      CRP2=AK7*EXP(-AK3/RT)
      CRP2=1.0/(1.0+CRP2)
C     **********
      CALL REAC4
C     **********
      RETURN
      END

                                         CD TOT   0397
```

```
      COMMON NRUNS,NCMP,JCT,NSWIT
      COMMON AREA,HT,BASAC
      COMMON RUN(30),VOLFL(30),TEP(30),DELTP(30),RAT(30),XACT(30)
      COMMON FRMOL(30,5),FCALC(30,5)
      COMMON PRESS(30),C4PI(30),H2PI(30),TEMP(30),RCC(30),RT(30)
      COMMON RACT(30)
      COMMON AKE(11),ANOM(11),DA(11),AKIN(11)
      COMMON NP1,NP2
      COMMON VINV(30,6,6)
      COMMON SUMSQ
      COMMON ACIT(15),ACNT(15)
      COMMON RATLIK(11,11)
      COMMON CRB(30),CRE(30),CRP1(30),CRP2(30)
      COMMON YDIF(6),VV(6),VVV(30)
      COMMON FIX,FAX
      COMMON VA1(40,10)
      COMMON VA2(50,6)
C     **********
C     PROGRAM TO FIND BUTANE PRE-EXPONENTIAL FACTOR
C     GIVEN BUTANE ACTIVATION ENERGY
C     GOLDEN SECTION SEARCH USED
C     WRITTEN BY AL ORLICKAS ----    JUNE 1970
C     **********
C     READ IN REACTOR DATA
      FIX=0.9
      READ(5,500)NRUNS,NCMP
 500  FORMAT(2I5)
      READ(5,501)AREA,HT,BASAC
 501  FORMAT(3F10.5)
      WRITE(6,502)BASAC
 502  FORMAT(/6X,9HBASAC =     ,F10.3)
      DO20I=1,NRUNS
      READ(5,503)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I),XACT(I)
      WRITE(6,550)RUN(I),VOLFL(I),TEP(I),DELTP(I),RAT(I),XACT(I)
 550  FORMAT(6X,6F15.3)
 20   CONTINUE
 503  FORMAT(6F10.5)
      DO30I=1,NRUNS
      READ(5,504)(FRMOL(I,J),J=1,NCMP)
      WRITE(6,504)(FRMOL(I,J),J=1,NCMP)
 30   CONTINUE
 504  FORMAT(5F10.5)
      GC=82.06
      DO40I=1,NRUNS
      PRESS(I)=(29.92+DELTP(I)/2.0)/29.92
      C4PI(I)=PRESS(I)/(1.0+RAT(I))
      H2PI(I)=PRESS(I)-C4PI(I)
      TEMP(I)=TEP(I)+273.0
      RCC(I)=(GC*TEMP(I)*AREA)/VOLFL(I)
      RT(I)=1.99*TEMP(I)
      RACT(I)=XACT(I)/BASAC
 40   CONTINUE
C     READ IN PARAMETER DATA
      DO50I=1,11
      READ(5,505) AKE(I),ANOM(I),DA(I)
      WRITE(6,530)AKE(I),ANOM(I),DA(I)
 530  FORMAT(2X,3F20.4)
 505  FORMAT(3F10.5)
 50   CONTINUE
      READ(5,507) NP1,NP2
 507  FORMAT(2I5)
C     SET UP WEIGHTING MATRIX --- VINV
```

```
      DO29I=1,NRUNS
      DO28J=1,5
      IF(FRMOL(I,J)-0.01)21,22,22
 21   VA1(I,J)=0.0001
      GOTO28
 22   IF(FRMOL(I,J)-0.1)23,24,24
 23   VA1(I,J)=0.001
      GOTO28
 24   VA1(I,J)=0.01
 28   CONTINUE
 29   CONTINUE
      DO308I=1,NRUNS
      DO308J=1,5
      VA2(I,J)=VA1(I,J)*VA1(I,J)
 308  CONTINUE
      DO306I=1,NRUNS
      WRITE(6,307)(VA2(I,J),J=1,5)
 306  CONTINUE
 307  FORMAT(1X,5E20.6)
      DO302I=1,NRUNS
      DO302J=1,5
      VA1(I,J)=1.0/(VA1(I,J)*VA1(I,J))
 302  CONTINUE
      DO303I=1,NRUNS
      DO303J=1,5
      DO303K=1,5
      VINV(I,J,K)=0.0
 303  CONTINUE
      DO304I=1,NRUNS
      DO304J=1,5
      VINV(I,J,J)=VA1(I,J)
 304  CONTINUE
      DO51I=1,NRUNS
      DO51J=1,5
      WRITE(6,531)(VINV(I,J,K),K=1,5)
 531  FORMAT(5X,5E15.7)
 51   CONTINUE
 52   FORMAT(5E15.7)
C     CALC. SUM OF SQUARES ABOUT BEST PARAMETERS
C     **********
      CALL SSQ
C     **********
      RLMAX=SUMSQ
C     START GOLDEN SECTION SEARCH
      AKE(1)=57.20
      NLOOP=0
      NMAX=15
      BBL=17.823
      BBR=17.832
      AKE(5)=BBL
      CALL SSQ
C     CALCULATE LIKELIHOOD RATIOS
      ROTLI=EXP(-0.5*(RLMAX-SUMSQ))
      RRL=ROTLI
      AKE(5)=BBR
      CALL SSQ
      ROTLI=EXP(-0.5*(RLMAX-SUMSQ))
      RRR=ROTLI
      WRITE(6,83)BBL,BBR,RRL,RRR
 83   FORMAT(/6X,2F20.6,2E30.4)
      TAU=1.618
```

```
 81    BB=(TAU*BBR+BBL)/(TAU+1.)
       NNI=1
       GOTO65
 60    BIR=BB
       RIR=ROTLI
       BB=(TAU*BBL+BBR)/(1.0+TAU)
       NNI=2
       GOTO65
 61    BIL=BB
       RIL=ROTLI
       GOTO67
 65    CONTINUE
       AKE(5)=BB
       CALL SSQ
       ROTLI=EXP(-0.5*(RLMAX-SUMSQ))
       WRITE(6,68)BB,ROTLI
 68    FORMAT(/6X,6HBB =      ,F20.7,9HROTLI =    ,E20.5)
       GOTO(60,61),NNI
 67    NLOOP=NLOOP+1
       IF(NLOOP-NMAX)73,73,74
 73    IF(RIL-RIR)69,71,71
 71    RRL=RIL
       BBL=BIL
       GOTO81
 69    BBR=BIR
       RRR=RIR
       GOTO81
 74    STOP
       END
       SUBROUTINE SSQ
       COMMON NRUNS,NCMP,JCT,NSWIT
       COMMON AREA,HT,BASAC
       COMMON RUN(30),VOLFL(30),TEP(30),DELTP(30),RAT(30),XACT(30)
       COMMON FRMOL(30,5),FCALC(30,5)
       COMMON PRESS(30),C4PI(30),H2PI(30),TEMP(30),RCC(30),RT(30)
       COMMON RACT(30)
       COMMON AKE(11),ANOM(11),DA(11),AKIN(11)
       COMMON NP1,NP2
       COMMON VINV(30,6,6)
       COMMON SUMSQ
       COMMON ACIT(15),ACNT(15)
       COMMON RATLIK(11,11)
       COMMON CRB(30),CRE(30),CRP1(30),CRP2(30)
       COMMON YDIF(6),VV(6),VVV(30)
       COMMON FIX,FAX
       COMMON VA1(40,10)
       COMMON VA2(50,6)
C      **********
C      THIS SUBROUTINE CALCULATES THE WEIGHTED SUM OF SQUARES FOR THE
C      PARAMETER VALUES --- AKIN(I)
C      **********
       AKIN(1)=AKE(1)*1.0E+3
       AKIN(2)=AKE(2)*1.0E+3
       AKIN(3)=AKE(3)*1.0E+3
       AKIN(4)=AKE(4)*1.0E+3
       AKIN(5)=10.0**AKE(5)
       AKIN(6)=10.0**AKE(6)
       AKIN(7)=10.0**AKE(7)
       AKIN(8)=10.0**AKE(8)
       AKIN(9)=AKE(9)
       AKIN(10)=AKE(10)
```

```
      AKIN(11)=AKE(11)
      JCT=0
C     CALCULATE REACTION RATE CONSTANTS
      DO20I=1,NRUNS
      CRB(I)=RCC(I)*RACT(I)*AKIN(5)*EXP(-AKIN(1)/RT(I))
      CRE(I)=AKIN(8)*EXP(-AKIN(4)/RT(I))
      CRP1(I)=AKIN(6)*RACT(I)*EXP(-AKIN(2)/RT(I))
      CRP1(I)=CRP1(I)*RCC(I)
      CRP2(I)=AKIN(7)*EXP(-AKIN(3)/RT(I))
      CRP2(I)=1.0/(1.0+CRP2(I))
 20   CONTINUE
 30   JCT=JCT+1
C     ***********************************************************
      CALL REAC4
C     ***********************************************************
      IF(NSWIT)35,35,36
 36   DO37I=1,NCMP
      FCALC(JCT,I)=10.
 37   CONTINUE
 35   CONTINUE
      IF(JCT-NRUNS)30,50,50
 50   CONTINUE
      JCT=0
 60   JCT=JCT+1
C     CALCULATE WEIGHTED SUM OF SQUARES
      DO70I=1,5
      YDIF(I)=FRMOL(JCT,I)-FCALC(JCT,I)
 70   CONTINUE
      DO80I=1,4
      VV(I)=0.0
      DO80J=1,4
      VV(I)=VV(I)+YDIF(J)*VINV(JCT,J,I)
 80   CONTINUE
 591  FORMAT(6X,9HVV(I) =    ,5E20.6)
      VVV(JCT)=0.0
      DO90I=1,4
      VVV(JCT)=VVV(JCT)+VV(I)*YDIF(I)
 90   CONTINUE
      IF(JCT-NRUNS)60,100,100
 100  CONTINUE
 592  FORMAT(6X,5E20.6)
      SUMSQ=0.0
      DO110I=1,NRUNS
      SUMSQ=SUMSQ+VVV(I)
 110  CONTINUE
      WRITE(6,593) SUMSQ
 593  FORMAT(/6X,9HSUMSQ =    ,E20.5)
      RETURN
      END

                        CD TOT   0233
```

K.5 FLUIDIZED BED REACTOR MODELS OF ORCUTT, DAVIDSON AND PIGFORD

The theoretical developement of these models and a description of the mathematical methods used to solve the resulting equations are given in Appendix J.

For the model assuming plug flow in the emulsion phase the Runge Kutta part of the program is deleted from the print-out. This part of the program may be seen in K.1. Here the preliminary calculations, the differential equations and the final calculations will be shown.

```
      DIMENSION CN(15),C(15),C1(15),DC(15),C2(15),C3(15),C4(15)
      DIMENSION CN1(15),CDX(15),EPSL(15),CIN(15)
      DIMENSION TRMAX(15),TRMIN(15)
      DIMENSION A(15)
C     *********
C     FLUIDIZED BED REACTOR MODEL OF ORCUTT DAVIDSON AND PIGFORD
C     PLUG FLOW IN EMULSION PHASE
C     WRITTEN BY AL ORLICKAS -----  MARCH 1970
C     *********
C     PRELIMINARY CALCULATIONS
C     *********
      NEQ=10
      UO=0.88
      HO=90.0
      HT=100.
      U=8.8
      T=270.0
      NU=0
      TEMP=T+273.
      RT=1.99*TEMP
      RTT=RT
      A(1)=56454.
      A(2)=54397.
      A(3)=37514.
      A(4)=16751.
      A(5)=10.0**17.507
      A(6)=10.0**16.097
      A(7)=10.0**15.043
      A(8)=10.0**6.984
      A(9)=1.7
      A(10)=2.45
      RAT=7.0
      CACT=0.5
  622 CACT=CACT+0.5
      RKB=CACT*A(5)*EXP(-A(1)/RTT)
      RKE=A(8)*EXP(-A(4)/RTT)
      RKP1=CACT*A(6)*EXP(-A(2)/RTT)
      RKP2=A(7)*EXP(-A(3)/RTT)
  626 CONTINUE
      C40=1.0/(RAT+1.)
      H2O=1.0-C40
      X=1.0
      WRITE(6,612)
  612 FORMAT(/1X,40H.......................................          )
      BETA=1.0-UO/U
      Z1=(HO*1.99*TEMP)/(U*HT*(1.0-BETA))
      Z2=(BETA*X)/(HT*(1.0-BETA))
      Z3=X/HT
      CN(1)=0.
      CN(2)=0.
      CN(3)=0.
      CN(4)=C40
      CN(5)=H2O
      CN(6)=0.
      CN(7)=0.
      CN(8)=0.
      CN(9)=C40
      CN(10)=H2O
      KNEG=0
      KFIN=0
      NK=0
      Y=0.0
```

```
      DY=0.5
      IHALF=0
      IHAMAX=40
      JHALF=0
      NSWIT=0
      DO3I=1,NEQ
      TRMAX(I)=1.0E-6
      TRMIN(I)=1.0E-8
C     **********
C     FINAL CALCULATIONS ---  PROBLEM IS SOLVED
C     FINAL VALUES ARE CN(I)
C     **********
      WRITE(6,613)X,RAT,U
 613  FORMAT(6X,12HX VALUE IS    ,F30.8,
     1/6X,15HFEED RATIO IS   ,F20.4,
     2/6X,30HFEED SUPERFICIAL VELOCITY IS    ,F20.3)
      WRITE(6,925) T
 925  FORMAT(/6X,13HTEMPERATURE     ,F20.2)
      WRITE(6,710)CACT
 710  FORMAT(/6X,8H CACT =    ,F10.2)
      WRITE(6,614)(CN(I),I=1,10)
 614  FORMAT(/6X,35HEMULSION AND BUBBLE PRESSURES ARE      ,
     1/6X,5F20.8,
     2/6X,5F20.8)
      DO610I=1,5
      CN(I)=(U0*CN(I)+(U-U0)*CN(I+5))/U
 610  CONTINUE
      DDDD=C40-CN(4)
      CONV=(DDDD/C40)*100.
      S1=CN(1)/DDDD
      S2=CN(2)/DDDD
      S3=CN(3)/DDDD
      WRITE(6,611)CN(1),CN(2),CN(3),CN(4),CN(5),CONV,S1,S2,S3
 611  FORMAT(1X,25HPRODUCT DISTRIBUTION IS    ,5F10.5,
     1/1X,25HCONVERSION OF BUTANE IS       ,F20.5,
     2/1X,19HSELECTIVITIES ARE     ,3F20.10)
C     **********
C     DIFFERENTIAL EQUATIONS
C     **********
      RB=0.725*RKB*C(4)*(C(5)**A(9))
      DD1=0.725*RKP1*C(3)*(C(5)**A(10))
      RP=(0.9*RB-DD1)/(1.0+RKP2)
      RE=-(1.1*RB-RP)/(1.0+RKE)
      RP=-RP
      RM=-4.0*RB-3.0*RP-2.0*RE
      RH=3.0*RB+2.0*RP+RE
      W1=C(1)-C(6)
      W2=C(2)-C(7)
      W3=C(3)-C(8)
      W4=C(4)-C(9)
      W5=C(5)-C(10)
      Z4=-DY*Z1
      Z5=-DY*Z2
      DC(1)=Z4*RM+Z5*W1
      DC(2)=Z4*RE+Z5*W2
      DC(3)=Z4*RP+Z5*W3
      DC(4)=Z4*RB+Z5*W4
      DC(5)=Z4*RH+Z5*W5
      WW6=Z3*DY
      DC(6)=WW6*W1
      DC(7)=WW6*W2
```

```
      DC(8)=WW6*W3
      DC(9)=WW6*W4
      DC(10)=WW6*W5
      GOTO(30,50,70,90),N
  500 CONTINUE
  300 CONTINUE

                            CD TOT   0129
```

```
      DIMENSION A(15)
```

```
C     *********
C     FLUIDIZED BED REACTOR MODEL OF ORCUTT DAVIDSON AND PIGFORD
C     PERFECT MIXING IN EMULSION PHASE
C     WRITTEN BY AL ORLICKAS  ----   MARCH 1970
C     *********
C     SET VARIABLES AND INITIAL CALCULATIONS
      NU=0
      T=270.0
      TEMP=T+273.
      RTT=1.99*TEMP
      A(1)=56454.
      A(2)=54397.
      A(3)=37514.
      A(4)=16751.
      A(5)=10.0**17.507
      A(6)=10.0**16.097
      A(7)=10.0**15.043
      A(8)=10.0**6.984
      A(9)=1.7
      A(10)=2.45
      RAT=7.0
      U=8.8
      CACT=0.5
  622 CACT=CACT+0.5
      RKB=CACT*A(5)*EXP(-A(1)/RTT)
      RKE=A(8)*EXP(-A(4)/RTT)
      RKP1=CACT*A(6)*EXP(-A(2)/RTT)
      RKP2=A(7)*EXP(-A(3)/RTT)
      UO=0.88
      HO=90.
      HT=100.
      U=8.8
  626 CONTINUE
      C40=1.0/(RAT+1.)
      H2O=1.0-C40
      BETA=1.0-UO/U
      FAC=.725
      X=1.0
      WRITE(6,925) CACT,X
  925 FORMAT(1X,8HCACT =    ,F10.2,5HX =    ,F20.7)
      X1=BETA/EXP(X)
      X2=1.-X1
      GAM=(U*X2)/(RTT*HO)
      TOL=0.000001
      NSW=1
C     INITIAL GUESSES FOR PARTIAL PRESSURE OF HYDROGEN
      P5=H2O
C     STARTING POINT FOR EACH ITERATION
  800 CONTINUE
      Y1=GAM+FAC*RKB*(P5**A(9))
C     CALCULATE EMULSION PHASE PARTIAL PRESSURES
      P4=(C40*GAM)/Y1
      RB=FAC*RKB*P4*(P5**A(9))
      Z1=0.9*RB
      Z2=GAM*(1.0+RKP2)
      Z3=RKP1*FAC*(P5**A(10))
      P32=Z1/(Z3+Z2)
      RP2=(Z1-Z3*P32)/(1.0+RKP2)
      RE2=(1.1*RB-RP2)/(1.0+RKE)
      Z10=H2O*GAM-3.0*RB
      P52=(Z10+2.0*RP2+RE2)/GAM
```

```
      P12=(4.0*RB-3.0*RP2-2.0*RE2)/GAM
      P22=(1.1*RB-RP2)/(GAM*(1.0+RKE))
      ZZ1=1.0/EXP(X)
C     BUBBLE PHASE PARTIAL PRESSURES
      PB4=P4+ZZ1*(C40-P4)
      PB12=P12-P12*ZZ1
      PB22=P22-P22*ZZ1
      PB32=P32-P32*ZZ1
      PB52=P52+ZZ1*(H20-P52)
      PDIF=P5-P52
  730 FORMAT(1X,6HP5 =    ,F20.10,10X,8HPDIF =     ,F30.15)
C     BINARY SEARCH DECISIONS AND CALCULATIONS
      GOTO(702,703),NSW
  702 CONTINUE
      IF(PDIF)700,700,701
  701 PRT=P5
      P5=P5-0.01
      DIFR=PDIF
      GOTO800
  700 PLT=P5
      DIFL=PDIF
      NSW=2
      P5=(PLT+PRT)/2.
      GOTO800
  703 CONTINUE
      IF(ABS(PDIF)-TOL)704,704,705
  705 IF(PDIF)706,706,707
  706 PLT=P5
      DIFL=PDIF
      P5=(PLT+PRT)/2.
      GOTO800
  707 PRT=P5
      DIFR=PDIF
      P5=(PLT+PRT)/2.
      GOTO800
  704 CONTINUE
C     FINAL CALCULATIONS AND PRINTOUT
      WRITE(6,710)
  710 FORMAT(//6X,40H........................................          )
      WRITE(6,711)X,RAT,U
  711 FORMAT(/6X,12HX VALUE IS   ,F30.8,
     1/6X,15HFEDD RATIO IS   ,F20.3,
     2/6X,18HFEED VELOCITY IS    ,F20.2)
      WRITE(6,600)P12,P22,P32,P4,P52
  600 FORMAT(/6X,24HEMULSION PRESSURES ARE    ,
     1/6X,5F20.8)
      WRITE(6,601)PB12,PB22,PB32,PB4,PB52
  601 FORMAT(/6X,22HBUBBLE PRESSURES ARE    ,
     1/6X,5F20.8)
      F1=U0/U
      F2=(U-U0)/U
      POUT1=F1*P12+PB12*F2
      POUT2=F1*P22+PB22*F2
      POUT3=F1*P32+PB32*F2
      POUT5=F1*P52+PB52*F2
      POUT4=F1*P4+F2*PB4
      DDDD=C40-POUT4
      CONV=(DDDD/C40)*100.
      S1=POUT1/DDDD
      S2=POUT2/DDDD
      S3=POUT3/DDDD
```