PARAMETER SENSITIVITY STUDIES IN MODELLING OF HYDROTREATMENT KINETICS

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PREFACE

This study is concerned with an upgrading process for coal-derived liquids: hydrotreating. I have developed mathematical models for this process and have made comparisons between empirical kinetic expressions and those derived from approximations to theory.

I am especially grateful to Dr. Mayis Seapan for his consistent attentiveness. In his function as my thesis adviser he amply surpassed my expectations. Also, the work of and personal communications with Tom Pendergast were of considerable aid to me. The basic concepts and procedures which I used in this study are founded upon his M. S. Thesis at Oklahoma State University.

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a - molecular size parameter (angstroms)

a_t - total available surface area on catalyst pellet (cm^2)

a_w - wetted area of catalyst pellet (cm^2)

B - a correlation parameter referring to the adsorption equilibrium constants in LHHW rate expressions

C - component concentration (wt %)

D_{AB} - liquid diffusivity (cm_2/s)

D_{eff} - effective diffusivity (cm^2/s)

d_p - diameter of catalyst particle (cm)

E_{ads} - heat of adsorption (Btu/lbmol)

E_{act} - activation energy (Btu/lbmol)

F - molar feed rate (moles/hr)

g - gravitational acceleration (cm/s^2)

H - liquid holdup (cm^3 of liquid/cm^3 of reactor)

H_o - proportionality factor in liquid holdup correlation (cm^3/cm^3)

k - reaction rate constant (variable units)

K - adsorption equilibrium constant (1/wt %)

K_D - parameter in the correlation for liquid diffusivity

k_o - pre-exponential factor in the Arrhenius equation for the reaction rate constant

K_o - pre-exponential factor in Arrhenius' equation form of adsorption equilibrium constant (1/wt %)

k_{obs} - the observed reaction rate constant used to compute the Thiele modulus (wt %/cm^3/hr)

l - vacant L site on catalyst

L - length of catalyst bed (cm)

LHSV - liquid-hourly space velocity (hr^{-1})

m - vacant M site on catalyst; also an exponent indicating the adsorption mechanism in LHHW rate expressions

M - exponent on pressure in global model; also, the molecular weight

N - concentration order in global model

N_l - total number of molal L sites per catalyst mass

N_m - total number of molal M sites per catalyst mass

p - hydrogen pressure (psig)

P - partial pressure (psig, atm)

Ᵽ - the parachor

R - ideal gas constant (Btu/^{o}R/lbmol)

R_c - radius of catalyst particle (cm)

R_D - molar refraction (cm^{-3})

R_p - average pore radius of catalyst (angstroms)

r - rate of reaction (wt %/grams of catalyst/hr)

S_x - external surface area of sphere (cm^3)

t - time (hr)

T - absolute temperature (^{o}R, ^{o}K)

v - velocity of flowing liquid (cm/s)

V - reactor volume (cm^3)

v_{oil} - volumetric flow rate of liquid (cm^3/hr)

$\bar{V}$ - molar volume of liquid (cm^3/gmol)

W - catalyst weight (grams)

X - fractional conversion in reactor

Greek Letters

Γ - parameter used in Gunn and Yamada correlation

ϵ - catalyst internal voidage fraction

η - effectiveness factor

κ - parameter used to calculate the effectiveness factor

μ - liquid viscosity (centipoise)

ξ - parameter in viscosity correlation of Letsou and Stiel

ρ - liquid density (grams/cm^3)

σ - surface tension (dynes/cm)

ϕ - Thiele modulus

ω - accentric factor

τ - tortuosity factor

Dimensionless Groups

Fr - Froude number ($v^2/d_p g$)

Ga - Galileo number (Re^2/Fr)

Re - Reynold's number ($\rho d_p v/\mu$)

We - Weber number ($\rho v^2 d_p/\sigma$)

Superscripts

', * - denotes revised form of a quantity

s - denotes the solid surface concentration

Subscripts

A - liquid component of a reacting mixture, usually refers to dibenzothiophene

B - dissolved vapor component of a reacting mixture, usually refers to hydrogen

b - denotes property evaluated at the normal boiling point

c - value of property at the critical point

corr - refers to parameters computed from correlations

H - designates hydrogen

i - constituent of a mixture

o - reactor inlet conditions

oil - refers to the liquid feed to reactor

P - reaction products

r - reduced property, refers to ratio of property at specified conditions to the value of the property at the critical point

s - sulfur-containing compound

sc - refers to the scaling volume

CHAPTER I

INTRODUCTION

As the petroleum reserves of the world diminish, the need for alternative fuels and petroleum feedstock substitutes becomes increasingly apparent. Coal-derived liquids are one such alternative. A major reason why coal-derived liquids are not currently in widespread use is that the cost required to convert coal into distillable liquids is not favorable when compared to the processing cost for petroleum, in spite of the relative abundance of coal. If more efficient, and therefore more economical, methods for upgrading coal are to be found then the nature of coal-derived liquids (CDL's) and the way CDL's behave during processing must be better understood.

Several coal liquefaction processes have reached an advanced level of development. Some examples are Solvent-Refined Coal, H-Coal, Exxon Donor Solvent and others. The liquid product from any of these has considerably reduced concentrations of such undesirable elements as sulfur, nitrogen, oxygen, and trace metals. However, if CDL's are to be made into distillable liquids then further reduction of aromatics and the aforementioned undesirable elements must be brought about. This upgrading step is usually accomplished via hydrotreatment, a process involving the catalytic reaction of hydrogen with the CDL at high temperatures and pressures.

A survey of the literature shows some contradiction in the ways chosen by the authors to represent the kinetics of CDL hydrotreatment. Most studies reported in the literature utilize simple power-law types of correlations, containing from one to five parameters, to represent the kinetic data. These "global" models do not consider the separate effects of multiple phase mass transfer, catalytic reaction, and adsorption phenomena.

Many studies in the literature do not consider operating conditions which are relevant to industrial hydrotreatment processes. In some cases, different studies might use the same equation to correlate the respective kinetic data and consider the same range of operating conditions, but the resulting parameters in the corelations turn out to be inconsistent between the separate studies. This latter contradiction is of most importance for the purposes of this work. The simple global models used by the authors in the literature are apparently inadequate for consistent representation of the complex process of CDL hydrotreatment.

The ideal kinetic model for CDL hydrotreatment would be one that accounts for diffusion, adsorption, and reaction mass transfer steps for each of the thousands of compounds which comprise the particular CDL being processed. Such a kinetic model based upon the intrinsic reactions involved, i.e. an intrinsic model, when combined with an accurate mathematical model for the processing equipment, should provide a correlation for the kinetic data which would be valid over any range of operating conditions, given the reactor type and the type of CDL.

Since the development of an intrinsic model for an actual CDL would be extremely difficult, if not impossible, this work considers intrinsic models for a pure compound system as a first attempt. Specifically, intrinsic models are developed for the hydrodesulfurization (HDS) of dibenzothiophene, dissolved in Tetralin, in a trickle-bed reactor. The kinetic data predicted from the intrinsic models are then compared to the predictions of a four-parameter global model. By making these comparisons, the effect of changes in the intrinsic characteristics of the reacting system can then be seen in the changes of the parameters in the global model. Therefore, it is hoped that the discrepant results in the literature mentioned earlier can be explained via the intrinsic effects in the system. The results of this study should ultimately be useful in establishing the grounds for work to develop kinetic models which better describe CDL hydrotreatment.

The procedures used in this study for the evaluation of the parameters in the kinetic models are shown to be effective for models containing up to four isothermal parameters. The procedures should be equally applicable to models containing more parameters. The procedures utilized in previous studies similar in nature to this one have been found to be insufficient in evaluating kinetic models containing more than three isothermal parameters.

Variations in the parameters of the intrinsic models are demonstrated to affect the values of the global model parameters. The parameters in the global model are shown to be affected by the intrinsic reaction as well as adsorption phenomena. Hydrogen adsorption is apparently an especially important consideration.

Throughout this report, both SI and American Engineering units are utilized. Although at first this may seem confusing to the reader, the use of both systems avoids the large amount of clutter which would result from reporting the conversions from one system of units to the other.

CHAPTER II

LITERATURE REVIEW

In order to gain a better understanding of the objectives and complications involved with the upgrading of coal-derived liquids, a literature survey has been carried out. Information is included here which relates specifically to the development of the mathematical model used in this study.

Objectives of Coal Liquefaction

Coal is a complex mixture of aromatic and aliphatic hydrocarbons containing varying amounts of oxygen, nitrogen, sulfur, and metals. Several chemical structures for coal have been proposed, though in reality it is most likely that none are correct. One such example is that of Hill and Lyon (1), which exemplifies the complexity of any realistic molecular model for coal. In fact, the elemental composition of coal differs according to the location from which it is obtained, so that no one chemical structure can be considered representative of coal in general (2). In lieu of a specific chemical structure, the approximate molar formula for a typical bituminous coal is $CH_{0.8}O_{0.1}N_{0.02}S_{0.02}$ (3).

If coal is to replace petroleum as a feedstock, it must first be converted to a liquid. Furthermore, if coal is to be converted to distillable liquids then removal of mineral matter must be accomplished and reduction of sulfur and nitrogen contents must occur in order to meet emission standards. Another goal of coal liquefaction is to increase the hydrogen-to-carbon ratio to at least about 1.8. This compares to a ratio of 0.8 for solid coal. From the standpoint of liquid handling and moving during further upgrading processes, the viscosity increase caused by high asphaltene or aromatic levels is also a consideration (2).

Coal liquefaction may be accomplished via carbonization of the coal but generally involves contacting the coal with hydrogen, either directly or indirectly. In either method, temperatures and pressures above 800^{o}F and 1000 psi are to be expected as processing conditions (3). An example of a carbonization process is the COED (Char Oil Energy Development) process. Some hydrogen addition processes are SRC (Solvent-Refined Coal), H-Coal, and EDS (Exxon Donor Solvent), but several other such processes have also been developed. The liquid product from any of these processes possesses to some degree the desired reduced contents of sulfur, nitrogen and oxygen. However, further removal of the undesirable characteristics of the coal-derived liquids must be made to occur in order for the liquid to qualify for safe and economical processing.

The upgrading of coal-derived liquids into feedstocks suitable for refinery processing can be accomplished through hydrotreating. Hydrotreating, as it relates to this study, consists of the reaction of hydrogen gas with the coal-derived liquid at high temperature and pressure using a catalyst. The objective is to reduce the aromaticity and the oxygen, sulfur, nitrogen and metals, in the form of heteroatoms, content. These are accomplished by saturation of double bonds and hydrogenolysis of oxygen, sulfur, and nitrogen compounds to form the byproducts water, hydrogen sulfide and ammonia, respectively (3). The resulting liquid product is richer in hydrogen and has a reduced level of undesired elements.

Hydrotreating Kinetics: Global Models

As evidenced by the available literature, several attempts have been made to characterize the kinetics of hydrotreating of coal-derived liquids (4). In very few cases, the kinetic models have accounted for the intrinsic reaction rates and external mass transfer effects. However, the kinetic models most often encountered are simple power law equations which describe only the overall observed, or global, effects in a particular system.

An exemplary study in which a global model is utilized is that of Heck and Stein (5). Heck et al. used two coal-derived liquids, an SRC product and an H-Coal product, which were hydroprocessed over two catalysts, alumina supported nickel-molybdenum and cobalt-molybdenum. The kinetic model used for heteroatom removal was second-order in heteroatom concentration and aromatic saturation was modelled using a reversible, first-order rate expression. This model for heteroatom removal is given by eq. [2.1]

$$- \frac{dC}{dt} = kp^{M}C^{2} \qquad [2.1]$$

in which C is the heteroatom concentration, p is the hydrogen pressure raised to the order M, and k is the rate constant. The rate constant is of the Arrhenius form of temperature dependence, given by eq. [2.2],

$$k = k_{o}e^{-E_{act}/RT} \qquad [2.2]$$

where k_o is a pre-exponential constant, E_{act} is the activation energy, R is the ideal gas constant and T is the absolute temperature. The value of the Heck and Stein model for heteroatom removal is that it typifies the global models seen in the literature. Actually, many other models in the literature do not account for the effect of hydrogen pressure shown in eq. [2.1], and some contain only the rate constant as the single parameter to be evaluated in the model (6).

Such kinetic expressions are capable of correlating rate data over limited ranges of operating conditions and for specific systems. The global models are unreliable, though, if scale-up or extrapolation of the data to new operating conditions is the objective. This is due to the fact that the simple power law type models do not account separately for the various mass transfer processes occurring in the system being considered. Therefore, although the kinetic data being evaluated may have been influenced by mass transfer in the bulk phase or intraparticle diffusion, for example, the said effect will be accounted for in the kinetic model only by the rate constant or some other parameters. If the model is then used for scale-up to a reactor in which the mass transfer resistances are not of the same magnitude, the predictions of the global model will most likely be in error for that reactor. Similar negative aspects of global models apply if the global model is used for operating conditions which differ from that of the original study from which the model was evaluated. These aspects show the value of a kinetic model which considers all of the important intrinsic mechanisms of the system, i.e. an intrinsic kinetic model.

Hydrotreating Kinetics: Intrinsic Models

A method commonly used for the derivation of intrinsic reaction rate expressions describing hydrotreatment processes is that described by Hougen and Watson (7), which is based upon the Langmuir-Hinshelwood theory of catalytic adsorption. Called Langmuir-Hinshelwood-Hougen-Watson, or LHHW, equations, these rate expressions are capable of describing the inhibition of the intrinsic reaction rate caused by the adsorption of particular reactants and/or products (8). The intrinsic kinetic model is made complete when the rate expression is combined with expressions for the mass transfer resistances in the system and a proper reactor model.

The studies found in the literature which utilize intrinsic models for hydrotreatment kinetics are relatively few in number. The rate equation used by Frye and Mosby (9) for the trickle-flow hydrodesulfurization of light catalytic cycle oil (petroleum) is given by eq. [2.3].

$$\frac{dC}{dt} = \frac{k\, P_S\, P_H}{(1+\sum B_i P_i)^m} \qquad [2.3]$$

In eq. [2.3], P_S and P_H are the sulfur-containing compound and hydrogen partial pressures, respectively, and $\sum B_i P_i$ represents the combination of parameters used to individually account for the non-reacting compounds which occupy the catalyst surface and cause the reaction rate to be thus inhibited. Also, k is once again the reaction rate constant and m is a parameter, theoretically having the possible values of either one or two, which indicates the type of adsorption scheme occurring on the catalyst. The integrated form of eq. [2.3] was used, without the inclusion of external mass transfer effects and for plug flow, by Frye and Mosby to provide a very good correlation of kinetic data.

Actually, eq. [2.3] is not an intrinsic kinetic model in the strictest sense because some parameters are lumped together and the rate equation is for the disappearance of a group of sulfur-containing compounds rather than being based upon the individual reaction rates.

The hydroprocessing of coal-derived liquids does not readily lend itself to the development of intrinsic models, since in such processing there are literally thousands of chemical reactions occurring simultaneously both in series and in parallel. A complete intrinsic kinetic model must contain the rate expression and corresponding expressions for the mass transfer resistances for each of these reactions. Thus, for the case of coal-derived liquids hydrotreatment, a truly abominable task is at hand if an intrinsic model is to be developed. In order to make the objective more realizeable, though, model compound systems may be studied which approximate the overall reaction characteristics of coal-derived liquids (10). A complete intrinsic model can be readily formulated for such simplified systems.

One model compound study found in the literature considers the hydrodesulfurization of dibenzothiophene (11). Dibenzothiophene is a compound thought to be representative of the sulfur heterocyclic compounds found in coal-derived liquids (10). The LHHW-type rate expression used for the rate of disapearance of dibenzothiophene (DBT) was eq. [2.4]

$$-\frac{dC_{DBT}}{dt} = \frac{k\ K_H\ K_{DBT}\ P_H\ P_{DBT}}{(1+K_{DBT}P_{DBT}+K_pP_p)\,(1+K_HP_H)} \qquad [2.4]$$

in which P_H, P_{DBT}, and P_P are the respective partial pressures of hydrogen, DBT, and products. The respective adsorption equilibrium constants are given by K_H, K_{DBT}, and K_P. The intrinsic reaction rate constant, k, is of the Arrhenius' form of temperature dependence and the adsorption equilibrium constants have the form (7) given by eq. [2.5]

$$K_i = K_{o,i}\, e^{E_{ads,i}/RT} \qquad [2.5]$$

where $E_{ads,i}$ is called the heat of adsorption of compound i and $k_{o,i}$ is a pre-exponential constant.

With eq. [2.4] integrated for a plug flow reactor and utilizing the assumption that reactants and products adsorb strongly ($K_{DBT}P_{DBT}+K_PP_P>>1$), the kinetic data are shown to correlate quite well. In this study, by Singhal et al. (10), the operating conditions considered were chosen to be relevant to industrial hydrotreating. The temperature range considered was 285 to 350^oC, and the pressure range was from 250 to 450 psia. The range of LHSV (Liquid Hourly Space Velocity, expressed in volumes of feed per volume of catalyst) was from one to fifteen reciprocal hours. A cobalt-molybdenum catalyst over alumina support was used.

In the mathematical model of Singhal et al. there was apparently no attempt to consider the mass transfer resistance offered by intraparticle diffusion or external diffusion. The lack of bulk phase mass transfer effects was validated by experiments using different fluid velocities in the reactor. However, due to the fact that particle size was shown to affect the reactant conversion, some pore diffusion effects must have existed.

Reactor Modelling

The reactor type most commonly used today for hydroprocessing is comprised of a catalyst bed over which hydrogen gas and the liquid feedstock to be reacted traverse cocurrently downward. This reactor type is referred to as a trickle-bed reactor. The gas and liquid may also flow countercurrently, but such is not the typical mode of operation (12). The advantages of the trickle-bed reactor are several when compared to other types in the service of hydroprocessing. Shah (12) summarizes the advantages and disadvantages of the trickle-bed which are listed here:

Advantages:

1. Flow is close to plug flow, allowing relatively high conversion.
2. Liquid-to-solid ratio is small, thus minimizing homogeneous side reactions.
3. Liquid flows as a film, thus offering very small mass transfer resistance.
4. Low pressure drop.
5. The liquid product may be recycled or "quenches" may be added from the side of the reactor to control temperature rise.

6. Can be operated as a partially or completely vapor-phase reactor. A trickle-bed reactor minimized the energy costs associated with reactant vaporization.

7. Lower pressure drop will allow an essentially uniform partial pressure of reactant across the length of the reactor.

8. In the commercial reactor, uniform distribution of gas and liquid are achieved. The catalyst is uniformly and effectively wetted.

Disadvantages:

1. Poor radial mixing of heat.

2. At low liquid flow rates, flow maldistribution may occur.

3. The catalyst particles cannot be very small. The intraparticle diffusion effects can be significant. The catalyst pore-mouth plugging can cause rapid deactivation.

In order to predict the conversion to be expected from a trickle-bed reactor a mathematical model is needed to simulate the effects produced by the fluid flow patterns in the system. The plug flow model is the most simple, and is apparently frequently applicable. When the plug flow model is used, the system is referred to as an ideal reactor, since the reactant conversions thus predicted are the greatest possible. Frye and Mosby (9) and others have successfully used the plug flow model to adequately predict conversions in both pilot and commercial scale reactors. The loss in what is termed "contacting effectiveness" below what can be obtained in the ideal reactor is greatest at the lowest liquid flow rates (13). In fact, the contacting effectiveness can be given by the ratio of the observed to the intrinsic reaction rate constants, due to an empirical relation developed by Bondi (14).

If deviations from plug flow exist in the reactor then the axial dispersion model may be able to characterize the system. This nonideal model has one parameter, the dispersion coefficient, or the reciprocal of the Peclet number. The dispersion coefficient characterizes the degree of backmixing in the liquid phase of the reactor. Gas phase dispersion is generally neglected in trickle-bed reactors (13). The model reduces to plug flow at a dispersion coefficient of zero and predicts completely mixed flow when the dispersion coefficient is infinitely large. The axial dispersion model is best suited for reactors which exhibit only small deviations from plug flow.

The axial dispersion model was applied by Mears (15) to give a satisfactory fit to experimental data from a trickle-bed reactor. The use of this model is also demonstrated in the study by Furzer and Mitchell (16), although they suggest the calculation of the Peclet number from a least-squares fit of experimental data. Further credence of the model in application to trickle-beds is given by Schwartz and Roberts (17), who in fact suggest that plug flow is practically achieved in many commercial scale reactors.

On the other hand, cases have been cited in which the axial dispersion model was inadequate, especially when "tailing" was found in the residence time distribution (RTD) curves. For example, Hoogendorn and Lips (18) noticed strong tailing in their RTD data and proposed a model of their own to account for the observed behavior.

For trickle-bed reactors operating at relatively low liquid flow rates, such as in pilot scale systems, the reactant conversions have been thought to be related to the liquid holdup (19). According to Henry and Gilbert the liquid holdup is a measure of the contacting effectiveness between the flowing liquid and the solid catalyst. Commonly expressed as a fractional reactor volume (volume of liquid per volume of empty reactor), the holdup is comprised of the liquid held in the catalyst pores and of that outside the catalyst particles, which is called the external holdup. The latter can be further subdivided into the free-draining, or dynamic, holdup and the static holdup (20). It is the dynamic holdup which Henry and Gilbert use in their correlation.

The model of Henry and Gilbert utilizes a liquid holdup correlation developed by Satterfield et al. for a string of glass beads (21). The correlation is given by eq. [2.6],

$$H = H_o\ (Re)^{1/3}(Ga)^{-1/3} \qquad [2.6]$$

in which H is the liquid holdup and H_o is a proportionality constant. The group Re is the Reynold's number $(d_p v / \rho)$, and Ga is known as the Galileo number. The Galileo number is made up of the ratio fo the Reynold's number squared and the Froude number $(Fr=v^2/d_p g)$. The range over which eq. [2.6] is valid is for Reynold's numbers between 10 and 600 (21).

The basis of the model of Henry and Gilbert is their assumption that the reaction rate is proportional to the volume of fluid flowing rather than the bulk volume of catalyst. The success of this analysis is supposed to be due to the ability of the model to account for the number of active sites present and being utilized by the fluid. Therefore, the material balance for a component A reacting at a rate of $-r_A$ moles per liquid volume per time in a differential element of catalyst volume, dV, in a plug flow reactor is

$$\text{input} = \text{output} + \text{disappearance by reaction} \qquad [2.7]$$

$$F_A = (F_A + dF_A) + (-r_A)HdV \qquad [2.8]$$

where F_A is the flow rate of A in moles per time. If X_A is the fractional conversion of A, then

$$dF_A = -F_{Ao}dX_A \qquad [2.9]$$

Eq. [2.8] can be rearranged and integrated to give

$$HV/F_{Ao} = \int_{X_{Ao}}^{X_A} dX_A/(-r_A) \qquad [2.10]$$

Where X_{Ao} is the inlet conversion of A in the reactor. From the definition of LHSV, eq. [2.11] is applicable

$$VC_{Ao}/F_{Ao} = 1/LHSV \qquad [2.11]$$

In which C_{Ao} is the inlet concentration of A expressed in moles per volume of liquid. Combination of equations [2.10] and [2.11] gives the Henry and Gilbert model for general kinetics. This combination is given by eq. [2.12]

$$H/LHSV = C_{Ao} \int_{X_{Ao}}^{X_A} dX_A/(-r_A) \qquad [2.12]$$

where the quantity H/LHSV is referred to as the space time for the reaction. Using a first-order rate expression to replace $-r_A$ and then inserting eq. [2.6], Henry and Gilbert finally arrived at

$$\log\,(C_{Ao}/C_A) \propto (L)^{1/3}(LHSV)^{-2/3}(d_p)^{-2/3}(\ /\ )^{1/3} \qquad [2.13]$$

where C_A is the concentration at length L in the reactor.

Henry and Gilbert (19) use eq. [2.13] to yield linear plots for data which were unable to be correlated by simple first or second-order kinetic models. One of several examples given by Henry and Gilbert is for the hydrocracking of

West Texas heavy vacuum gas oil (HVGO), for which the model is used to account for simultaneous changes in both catalyst bed length and liquid space velocity (19). A table of physical properties of the West Texas HVGO and the relevant figures, condensed from Henry et al. (19), are given in Table I and Figure 1, respectively.

The main criticism of the Henry and Gilbert model is that there is no theoretical justification for assuming the reaction rate to be proportional to the liquid holdup (13). Also, as Mears (22) points out, the correlation of Satterfield, that is eq. [2.6], should not be used too generally, as the correlation was set up for a string of glass beads. Finally, the suggestion has been made that the first-order kinetics used by Henry and Gilbert are questionable when applied to complex systems in which multiple reactions occur simultaneously (13).

Mears questioned the role of liquid holdup as given by Henry and Gilbert and proceeded to develop a trickle-bed model of his own (22). The model of Mears is based upon the assumption that the conversion is proportional to the effective wetted area in the reactor. According to Mears, the empirical dependence of the Henry and Gilbert model on the one-third power of velocity does not agree with the exponent of three-fourths suggested in the literature. It is, however, consistent with the velocity dependence of the effectively wetted area. Thus, the ratio of the wetted area to the total area, aw/a_t, may be estimated by the relation

TABLE I

PROPERTIES OF WEST TEXAS HVGO (19)

Density, °API	21.9
Sulfur, wt %	1.9
Total nitrogen, ppm	1800
Viscosity at 210°F, cSt	23.57
Gc distillation, °F	
5 %	837
50 %	977
95 %	1103

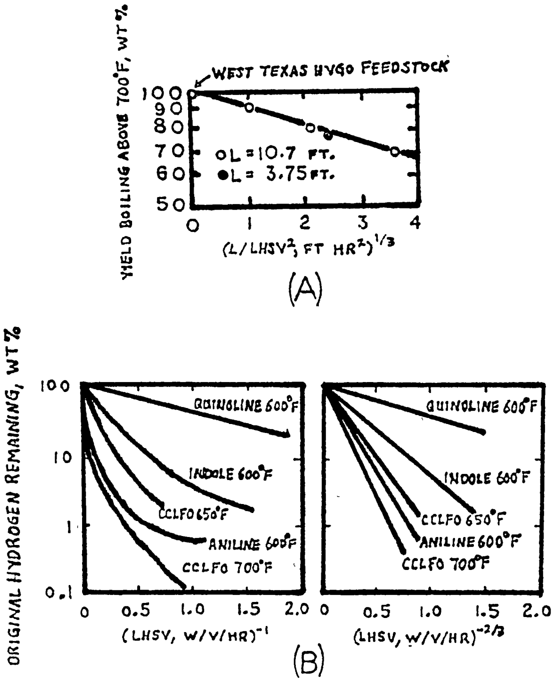


Figure 1. Application of Henry and Gilbert Model Showing (A) Bed Length Effects and (B) HDN of Catalytically Cracked Light Furnace Oil (19)

$$aw/a_t = Re^{0.047} We^{0.135} (\sigma_c/\sigma)^{0.206}$$

where We = Webber number, $\rho v^2 d_p/\sigma$

σ = surface tension of liquid

σ_c = critical value of surface tension

[2.14]

The reactor model must also account for the mass transfer resistances in the system. Briefly, external mass transfer effects are typically ignored for hydrotreating in trickle-bed reactors, since the liquid film on the catalyst is very thin (13). Pore diffusion in the catalyst is usually not negligible and is compensated for with the effectiveness factor. Effectiveness factors are considered in detail in the next section, so suffice it to say that values of the effectiveness factor are usually found to be slightly less than unity for many of the feeds and catalysts of interest to this work (23).

Finally, the heat transfer effects must be considered. Trickle-bed reactors are usually designed assuming adiabatic operation, although for several cases in the literature near-isothermal conditions have also been considered (13).

To summarize, the plug flow reactor model has been found to be generally valid in application to trickle-bed reactors. Also, mass-transfer resistances may be neglected, with the exception of pore diffusion, for this reactor type. These factors were used in the development of the mathematical model in this study. The assumption of isothermal conditions in the reactor was also used.

CHAPTER III

DEVELOPMENT OF MATHEMATICAL MODEL AND PROCEDURE

Objectives

The major objective of this project was to develop a mathematical model to describe trickle-bed hydrodesulfurization kinetics for a coal derived liquid model compound system. The model compound chosen for this study is dibenzothiophene, dissolved in Tetralin. The model is based upon the intrinsic reaction rate and compensates for the resistance to mass transfer caused by pore diffusion in the catalyst. All other mass transfer resistances are considered to be negligible.

The intended value of the mathematical model is threefold:

1. The intrinsic kinetic model can be used to provide a correlation to experimental data. Therefore, different reaction rate expressions may be evaluated for their ability to describe kinetic data.

2. Once the values of the parameters are provided, the operating conditions may be varied to any values, within the range of applicability of of the model, to provide a set of simulated reactor data. A global kinetic model, such as the

type commonly utilized in the literature, can then be fit to this pseudo-experimental data. By changing the operating conditions and/or the values of the intrinsic model parameters, the effect upon the global model parameters can be seen. The values of the global model parameters can then be compared with those found in the literature in order to evaluate the intrinsic reaction effects which produce given values of the global model parameters.

3. The procedures utilized in this study for the development of the mathematical model should be useful in the development of similar models describing systems which better approximate the characteristics of coal-derived liquids.

Intrinsic Model: Reaction Rate Expressions

The basis of the intrinsic kinetic model is the rate expression for the intrinsic reactions on the catalyst. In the case of the models developed in this study, LHHW rate expressions are used. The form of the rate expression differs according to the mechanism for catalytic adsorption of the participating components of the system.

The details of the derivation method for the LHHW rate expressions used in this work are given in Appendix A. The derivation of a rate equation is straightforward after the following have been defined: the reaction mechanism; the adsorption mechanism; and the rate-controlling mechanism (e.g. the surface reaction rate or the adsorption/desorption of a particular component).

The final intrinsic kinetic model is obtained by integrating the rate expression for the mathematical model chosen to represent the reactor. For the purposes of this work, the plug flow reactor model was assumed to be adequate. The method by which the rate expression is integrated to yield the final intrinsic kinetic model is illustrated in Appendix A. With the intrinsic kinetic model thus obtained, the parameters in the model, the reaction rate constant and the adsorption equilibrium constants, may be evaluated from measurable quantities. That is, the only experimental data required to evaluate the intrinsic model parameters are the operating conditions and the reactant conversion data.

Intrinsic Model: Physical Properties

This study considers a model compound system involving dibenzothiophene (DBT), dissolved in Tetralin, which is reacting with dissolved hydrogen. The mathematical model for the hydrodesulfurization of this system requires some relevant physical data for the components involved, or some method for the estimation of these data. The latter has been chosen in lieu of the actual physical data, so that the model might apply to other hydrotreating model compound studies by replacing a minimal amount of information.

The critical temperature, pressure, and volume of DBT and Tetralin are estimated from correlations given by Meissner (24). Meissner's correlations are based upon the parachor ($\bar{P}$) and the molar refraction (R_D), which are calculated via group contribution methods. With the parachor and the molar refraction thus computed the critical temperature (T_c), pressure (P_c), and volume ($\bar{V}_c$) are estimated from the three equations that follow:

$$T_c=20.2(T_b)^{0.6}-143-1.2[\bar{P}]+10.4[R_D]+A \qquad [3.1]$$

$$P_c=60.3(T_c)/(1.5[\bar{P}]+9-4.34[R_D])^{1.226} \qquad [3.2]$$

$$\bar{V}_c=0.55(1.5[\bar{P}]+9-4.34[R_d])^{1.155} \qquad [3.3]$$

In eq. [3.1], T_b is the normal boiling temperature (degrees Kelvin) and A is a correlating parameter which has a value of zero for Tetralin and ten for DBT. The equations give the critical temperature, pressure, and volume in units of degrees Kelvin, atmospheres, and cc/gmol, respectively. The correlation of Letsou and Stiel as modified by Reid, Prausnitz, and Sherwood is used to determine the liquid viscosities (25). The viscosity correlation is based upon corresponding-states relations and employs the accentric factor, ω. The correlation of Letsou and Stiel is given by eq. [3.4].

$$\mu\xi = (\mu\xi)^{(o)} + (\mu\xi)^{(1)}$$

$$\text{where } \xi = \frac{T_c^{1/6}}{M^{1/2}\ P_c^{2/3}} \qquad [3.4]$$

In eq. [3.4], μ is the liquid viscosity in centipoise and M is the molecular weight. Due to the small concentrations of DBT used in this study (the DBT conversion data used in this study are taken from Singhal et al., reference 10), the liquid viscosity is taken to be that of Tetralin alone. Over the range of reduced temperature, or T_r, of $0.76 \leq T_r \leq 0.98$, the two parameters appearing in eq. [3.4] can be represented by equations [3.5a] and [3.5b].

$$\mu\xi^{(o)} = 0.01574 - 0.02135(T_r) + 0.0075(T_r)^2 \qquad [3.5a]$$

$$\mu\xi^{(1)} = 0.042552 - 0.07674(T_r) + 0.0340(T_r)^2 \qquad [3.5b]$$

The accentric factor can be estimated from the following relation (26):

$$\omega = \frac{3}{7}\left[\frac{\log P_c}{(T_c/T_b) - 1}\right] - 1 \qquad [3.6]$$

Using the above relations, the liquid viscosity is then computed from eq. [3.7].

$$\mu = (\mu\xi)/\xi \qquad [3.7]$$

As will be shown later, it is necessary to determine molar volumes of the reacting liquid species, DBT, and the solvent in order to arrive at effectiveness factors for the system. Liquid molar volumes are computed using the method of Gunn and Yamada (25), which is given by eq. [3.8].

$$\bar{V}/\bar{V}_{sc} = V_r^{(o)}(1-\omega\Gamma) \qquad [3.8]$$

In eq. [3.8], $\bar{V}$ is the molar volume in cc/gmol and $\bar{V}_{sc}$ and $\bar{V}_r^{(o)}$ are the "scaling volume" in cc/gmol and a dimensionless corresponding-states related parameter, respectively. For the range $0.2 \leq T_r \leq 0.8$,

$$\bar{V}_r^{(o)} = 0.33593 - 0.33953(T_r) + 1.51941(T_r)^2 - 2.02512(T_r)^3 + 1.11422(T_r)^4 \qquad [3.9]$$

and for $0.8 < T_r < 1.0$,

$$\bar{V}_r^{(o)} = 1.0 + 1.3(1-T_r)^{1/2}\log(1-T_r) - 0.50879(1-T_r) - 0.91534(T_r)^2 \qquad [3.10]$$

The quantity Γ in eq. [3.8] can be given, in the range $0.2 \leq T_r \leq 1.0$, as

$$\Gamma = 0.29607 - 0.09045(T_r) - 0.04842(T_r)^2 \qquad [3.11]$$

For lack of emperical data, the quantity V_{sc} in eq. [3.8] is approximated by the relation

$$\bar{V}_{sc} = \frac{RT_c}{P_c}(0.2920 - 0.0967(\omega)) \qquad [3.12]$$

Now that a means has been provided to determine viscosities and molar volumes, the liquid diffusivities may be estimated. The estimation of diffusivities is taken care of by using Scheibel's correlation (25). For the system of DBT in Tetralin, the liquid diffusivity, D_{AB}, is computed from eq. [3.13],

$$D_{AB} = \frac{K_D T}{\mu \bar{V}_A^{1/3}} \tag{3.13}$$

where V_A is the liquid reactant molar volume and μ is the solvent viscosity. The value of K_D in eq. [3.13] depends upon the ratio of the solvent and liquid reactant molar volumes. For $V_A < V_B$, $K_D = 25.2 \times 10^{-8}$; for $V_A < V_B \times 2.5$, $K_D = 17.5 \times 10^{-8}$; otherwise, K_D is computed from [3.14].

$$K_D = (8.2 \times 10^{-8}) \left[1 + \left(\frac{3\bar{V}_B}{\bar{V}_A}\right)^{2/3}\right] \tag{3.14}$$

In eq. [3.13] the units of D_{AB} are cm^2/sec. In [3.14], $\bar{V}_B$ is the molar volume of the solvent. A summary of the physical constants computed for DBT and Tetralin are given in Table II.

The correlation used to predict hydrogen solubility is given by eq. [3.15].

TABLE II

PHYSICAL CONSTANTS FOR TETRALIN AND DIBENZOTHIOPHENE

	DBT	Tetralin
Molecular Weight, M	184.27	132.21
Normal Boiling Point, T_b	606°K	480.7°K
Parachor, $\mathcal{P}$	400.4	335.4
Molar Refraction, R_D	56.184	42.579
Critical Temperature, T_c	915°K	719°K
Critical Pressure, P_c	39.7 atm	35.8 atm
Critical Molar Volume, $\bar{V}_c$	502 cc/gmol	441.7 cc/gmol
Molecular Size, a	21 Å	18 Å
Other Quantities:		
Internal Voidage Fraction, ϵ	0.5	
Tortuosity Factor, τ	3.5	
Pore Radius, R_p	150 Å	
Catalyst Particle Radius, R_c	0.01 cm*	

* This value was used due to its application in a similar mathematical model (see reference 32).

$$C_H = P\left[e^{-(12.23+716.01T)}\right]100 \qquad [3.15]$$

This equation was developed for SRC recycle solvent for a range of temperatures between 100 and 400°C and pressures between 400 and 3000 psia (27).

Intrinsic Model: Effectiveness Factors

In reaction processes involving a catalyst the reactants must first diffuse to the catalyst surface, where reaction then occurs. For the porous catalysts currently in use for industrial hydroprocessing, the surface area available for reaction is almost completely located on the inner walls of the catalyst pores. Thus, the reactants must diffuse into these pores in order to react. If the mass transfer resistance caused by this inner pore diffusion is not negligible then a decrease in reactant concentration will occur along the length of the pore. Due to the loss in reactant concentration, a corresponding decline in reaction rate will occur, as compared to a reaction which occurs on an equal amount of area in which the surface is completely exposed to the reactants. The loss in reaction rate due to inner pore diffusion resistance is accounted for in the intrinsic rate expression by using the effectiveness factor, η.

The intrinsic kinetic model utilizes LHHW reaction rate expressions. Effectiveness factors have been derived for these types of rate equations by Roberts and Satterfield (28). However, the equations required to solve for the effectiveness factor are quite complex so as to inhibit their usefulness. In fact, since several different rate expressions are considered in this work, and since the effectiveness factor would have to be derived again for each specific LHHW rate equation, it is felt by this author that these types of effectiveness factors are not practical for use in this work. Anyway, the accuracy provided by these types of effectiveness factors is most likely not much improved over the type to be suggested below. This is especialy true when consideration is given to the error involved with the physical properties, estimated via correlations, used to compute the effectiveness factors.

By definition, the effectiveness factor is the ratio of the reaction rate with pore diffusion effects included to the rate which would exist if there were no pore diffusion resistance (7, 28, 29). Although the basic definition of η is almost universally accepted as stated above, the application of effectiveness factors is apparently not in such general agreement. Differences in the application of effectiveness factors are discussed in Appendix C.

The type of effectiveness factor given by eq. [3.16] is suggested by the literature (20, 30).

$$\eta = \tanh\Phi/\Phi \qquad [3.16]$$

where Φ, called the Thiele modulus, is given by

$$\Phi = \frac{R_c}{3}(k/D_{eff})^{1/2} \qquad [3.17]$$

In eq. [3.17] the effectiveness diffusivity, D_{eff}, can be computed as follows (20)

$$D_{eff} = \frac{\epsilon D_{AB}}{\tau}(1-\frac{a}{R_p})^4 \qquad [3.18]$$

in which ϵ is the internal voidage fraction, τ is the tortuosity factor, a is a molecular size parameter and R_p is the average radius of the catalyst pores. The values of the parameters used in this work are given in Table II.

The effectiveness factor given by eq. [3.16] was actually developed for slab geometry using a mass balance on an incremental area inside of a single cylindrical pore. However, for the high values of η considered in this work (e.g. 0.99998) geometry effects are negligible (see Appendix C).

The intrinsic model considers a model compound system in which the hydrodesulfurization of DBT is carried out. The hydrogen is assumed to saturate the liquid, in accordance with most of the hydrodesulfurization studies found in the literature (for example, see Frye et al. (9)). Thus, the liquid phase hydrogen concentration is essentially constant throughout the reactor. Therefore, the reaction becomes pseudo first-order and the use of a first-order Thiele modulus, as implied by the use of eq. [3.16], is justified.

Global Model

The global kinetic model used in this work is intended to provide a comprehensive representation of those found in the literature. The kinetic model chosen to represent the sulfur heteroatom removal is an expanded version of that used by Heck and Stein (5), which is discussed in the last chapter (see eq. [2.1]). The global kinetic expression used in this work is given by eq. [3.19]

$$-\frac{dC}{dt} = kp^{M}C^{N} \qquad [3.19]$$

where the order on heteroatom concentration is N, rather than two as in the Heck and Stein model.

In order to compensate for nonideal catalyst utilization, the liquid holdup model of Henry and Gilbert has been incorporated with the global model (see eq. [2.13]). Thus, the integration of [3.20] begins with eq. [2.12]

$$H/LHSV = C_{Ao} \int_{X_{Ao}}^{X_A} dX_A/(-r_A) \qquad [2.12]$$

Integration of [2.12] for an isothermal plug flow reactor and using eq. [3.19] to replace $-r_A$ and representing H with the Satterfield correlation (eq. [2.6]) gives the following results.

$$\frac{C_o^{1-N}-C^{1-N}}{(1-N)p^M k} = \frac{H_o(Re)^{1/3}(Ga)^{-1/3}}{LHSV}, \quad N \neq 1 \qquad [3.20]$$

$$\frac{\ln {}^{Co}/C}{p^M k} = \frac{H_o(Re)^{1/3}(G_a)^{-1/3}}{LHSV}, \quad N = 1 \qquad [3.21]$$

Where C_o and C are the inlet and outlet heteroatom concentrations, respectively, of the reactor. In fact, simplification of the equations leads to the following results

$$\frac{C_o^{1-N}-C^{1-N}}{(1-N)p^M} = H_o(L)^{1/3}(LHSV)^{-2/3}(d_p)^{-2/3} (\mu/\rho)^{1/3}, \quad N \neq 1 \qquad [3.22]$$

$$\frac{\ln {}^{Co}/C}{p^M} = H_o(L)^{1/3}(LHSV)^{-2/3}(d_p)^{-2/3} (\mu/\rho)^{1/3}, \quad N = 1 \qquad [3.23]$$

where H_o is a constant which absorbs both the reaction rate constant and H_o. When the bed length and the particle diameter remain constant and the changes in the ratio of viscosity and density are negligible, eqs. [3.22] and [3.23] may be condensed to give

$$\frac{C_o^{1-N} - C^{1-N}}{(1-N)P^M} = H_o e^{-E_{act}/RT} (LHSV)^{-2/3}, \quad N \neq 1 \tag{3.24}$$

$$\frac{\ln^{Co}/C}{P^M} = H_o e^{-E_{act}/RT} (LHSV)^{-2/3}, \quad N = 1 \tag{3.25}$$

For the purpose of comparison, the global model may be developed for the case in which the liquid holdup is not taken into account. In fact, the only difference between this approach and that of Henry and Gilbert is that the liquid holdup, H, does not appear in the material balance. Following the same procedure used to arrive at eq. [2.12], the design equation for general-order kinetics for this case is

$$1/LHSV = C_{Ao} \int_{X_{Ao}}^{X_A} dX_A/-r_A) \tag{3.26}$$

Notice that, for the case in which the liquid holdup is not taken into account, the space time is given by 1/LHSV rather than H/LHSV. Now the integral in [3.26] may be evaluated, using the rate equation given by eq. [3.19] to get

$$\frac{C_o^{1-N} - C^{1-N}}{(1-N)P^M} = k_o e^{-E_{act}/RT} / (LHSV), \quad N \neq 1 \tag{3.27}$$

$$\frac{\ln{}^{Co}/C}{p^{M}} = k_o\ {}^{-E_{act}/RT}/(\mathrm{LHSV}),\quad N = 1 \tag{3.28}$$

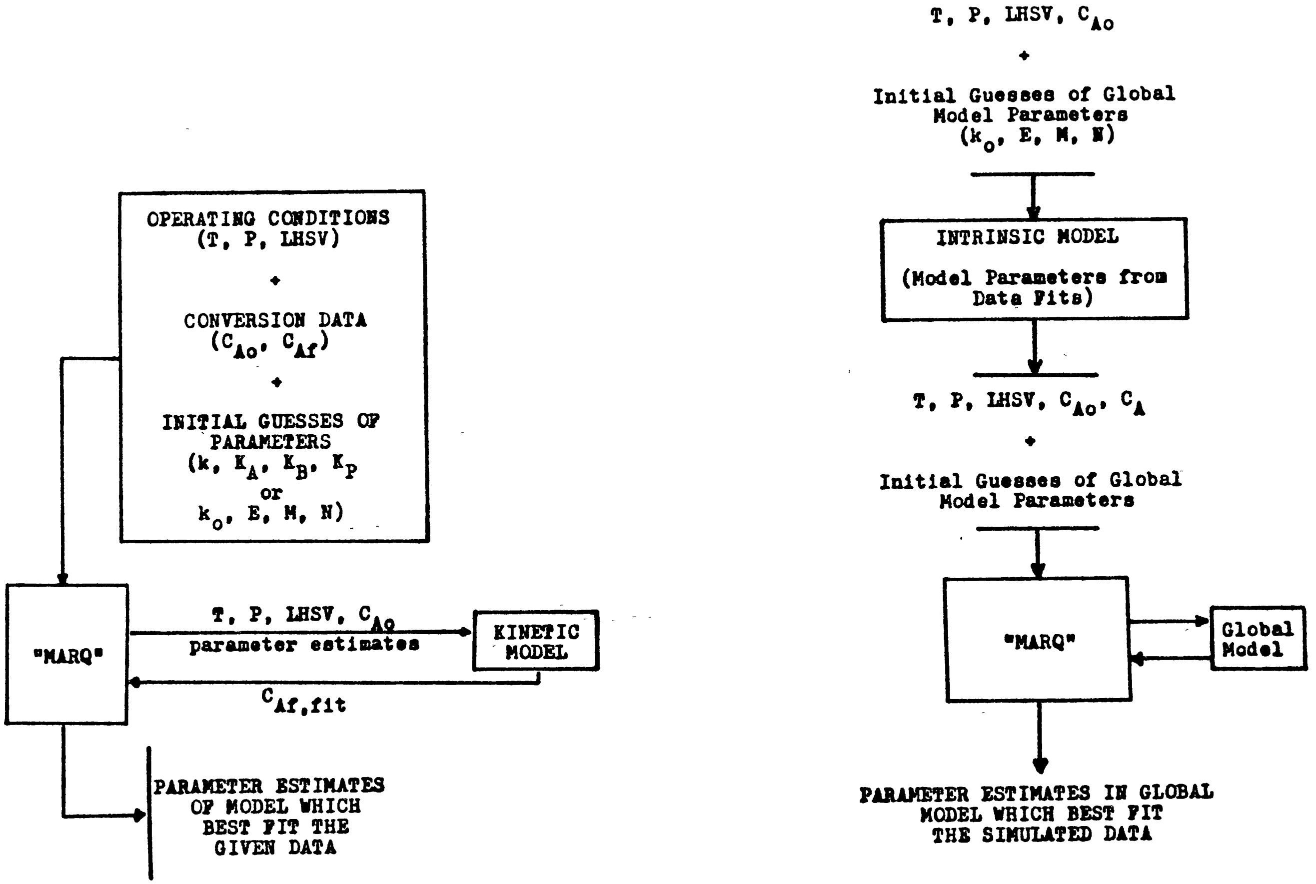
which are the desired comparisons for eqs. [3.24] and [3.25].

Procedure for Parameter Evaluation

Once the kinetic model, whether the intrinsic or the global, has been established as a computer program, the use of experimental data to evaluate the parameters in the model is accomplished via non-linear regression techniques. The method of regression used was a computer program called MARQ to carry out Marquardt's method. This regression routine was provided by the Oklahoma State University Computer Center. A listing of MARQ and associated computer programs is given in Appendix D.

Thus, the kinetic model parameter values are determined by supplying the experimental data and the kinetic model to MARQ, which then generates the parameter values of best fit. These parameters are generated from MARQ by minimizing the error between the outlet reactant conversion data and the outlet conversions predicted by the model. This parameter evaluation (i.e. data fit) process is shown schematically in Figure 2 (schematic A).

Owing to the complexity of the reaction rate expressions, numerical solution of the intrinsic kinetic model was necessitated. Either the secant method or interval-halving (i.e. bisection) method were used to solve for the outlet



(A) Data Fit Procedure

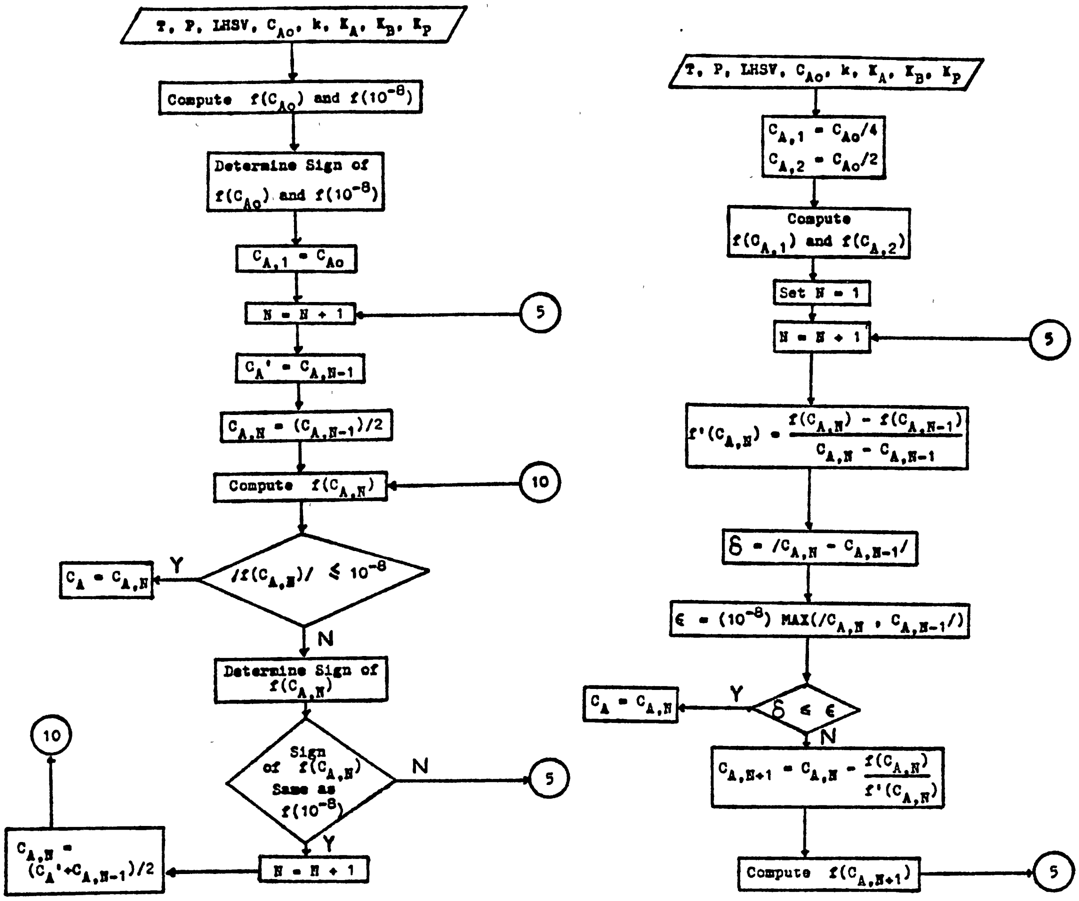
(B) Method for Parameter Sensitivity Study

Figure 2. Flow Charts for Parameter Evaluation Methods

reactant conversions of the intrinsic kinetic model. Flow dia grams for both root-finding methods are given in Figure 3.

Procedure for Parameter Sensitivity Study

With the parameters evaluated in the intrinsic model, the intrinsic model can be used to provide simulated kinetic data to which the global model may be fit. With the computer program containing the mathematical models set up in this form, and the intrinsic model providing the data to which the global model is to be fit, the sensitivity of the global model parameters may be tested. That is, the effect that would be produced by, say, increases in the amount adsorbed of a particular component could be measured with the corresponding effects upon the fitted global model parameters. Hopefully, the information provided by this parameter sensitivity study will be useful in drawing some conclusions about the values of the global model parameters published in the literature. The flow chart illustrating the procedure used in the parameter sensitivity study is shown in Figure 2 (schematic B).



(A) Bisecting Method (B) Secant Method

Figure 3. Numerical Root-Finding Flow Charts

CHAPTER IV

RESULTS AND DISCUSSION

Selected kinetic models were fit to literature data in order to establish estimates of the kinetic model parameters to be expected for the HDS of coal-derived liquids. The global models were fit to HDS conversion data for an actual coal-derived liquid and the intrinsic models were fit to conversion data for the HDS of a pure compound.

The global models used consisted of the second-order Heck and Stein model (see Chapter II) and the general-order model, based upon the liquid holdup model, which is developed in Chapter III. These models were fit to the HDS conversion data of Heck and Stein (5) for an H-Coal distillate. The Heck and Stein model was used in order to compare the data fit techniques of this study to those techniques utilized by Heck and Stein. The general-order model was fit to this data in order to provide parameter estimates in the model corresponding to an actual coal-derived liquid.

Three intrinsic models were developed for use in this work, corresponding to different adsorption mechanisms. The literature data to which these models were fit was that of Singhal et al. (11) for the HDS of dibenzothiophene. The main purpose of the intrinsic model data fits was to provide parameter estimates which would equip the model to produce realistic simulated data for use in the parameter sensitivity study.

In the parameter sensitivity study, an intrinsic model was used to produce simulated conversion data. The general-order global model was then fit to the simulated data. By inducing variations in the intrinsic model parameters, the sensitivity of the global model parameters to these intrinsic effects was then observed. Similarly, the effect of variations in operating conditions upon the global model parameters could be investigated.

Although variations in the operating conditions were not actually investigated in this work, the intrinsic model was equipped to do so. This was accomplished by correlating the effect of temperature on the intrinsic model parameters, as opposed to simply reading in the intrinsic parameters at each temperature used in the data fits.

Initially, attempts were made to correlate temperature dependency of the intrinsic parameters with an Arrhenius type equation. Since this method proved to be unsatisfactory, a simple third-degree polynomial in temperature was used. Thus, interpolation capability was provided for the intrinsic model parameters.

The variation of the intrinsic parameters was facilitated through the use of "variation constants", or VARK's. These were used as efficiency aids in the computer programs. The VARK's acted as multipliers corresponding to each of the intrinsic model parameters. Thus, variations in the intrinsic parameters could be made to occur by setting the values of the VARK's at one location in the computer program. This was an improvement upon the alternative necessity of changing the values of the actual intrinsic parameters in the computer program. The use of the VARK's also made the plotting of the results much less complex.

Only one of the intrinsic models developed for use in the data fits was used to provide simulated data in the parameter sensitivity study. This model was developed by postulating a dual-site adsorption mechanism involving the adsorption of the two reactants and the products. Three variations of this model were also considered in order to decide which of the intrinsic parameters most strongly affected the sensitivity of the global model parameters. Each of the intrinsic model variations corresponded to a different reactant or product component not being adsorbed.

Global Model Data Fits

Heck and Stein Model

The kinetic model of Heck and Stein, eq. [2.1], was fit, in integrated form, to the HDS data by the same authors. The integrated form of eq. [2.1] is

$$\frac{C_o}{C}-1 = \frac{C_o k_{oe}^{-Eact/RT}}{(LHSV)} \qquad [4.1]$$

where the space time for the reaction is given by 1/LHSV. Using the method prescribed in Chapter III, this equation was fit to the HDS data for H-Coal distillate using the American Cyanamide HDS-1441A catalyst. The computer program listing for the data fits is given in Appendix E.

In this project, two different criteria for obtaining the parameters of best fit were used. In one case, the criterea was used that the difference between the quantities $C_o/C - 1$, evaluated from conversion data and model-predicted conversions, be minimized. This criterea can be stated as given by eq. [4.2].

$$\mathrm{DEV} = \sum \left| \left(\frac{C_o}{C_{\mathrm{data},i}}-1\right) - \left(\frac{C_o}{C_{\mathrm{model},i}}-1\right) \right| \qquad [4.2]$$

This basis of error minimization gave the resulting parameters shown in eq. [4.3],

$$\frac{C_o}{C}-1 = C_o(7.18E2)e^{-9095/RT}p^{0.194}/(LHSV) \qquad [4.3]$$

where k_o has the units psig^{-N}/wt %/hr and E is in Btu/lbmol, which provided a mean deviation (based upon outlet stream concentrations) between data and model predictions of

0.0113 wt. percent. The other criterea for parameter evaluation involved the direct comparison of outlet stream concentrations to model-predicted concentrations. This criterea is given by eq. [4.4].

$$\mathrm{DEV'} = \sum \left|(C_{data,i} - C_{model,i})\right| \qquad [4.4]$$

This latter method produced the results

$$\frac{C_o}{C} - 1 = C_o(2.45_E5)\,e^{-31580/RT\ 0.794}/(\mathrm{LHSV}) \qquad [4.5]$$

where the mean deviation in conversions (difference between data model predictions) was 0.0052 wt. percent. These results compare to eq. [4.6],

$$\frac{C_o}{C} - 1 = C_o(8.52_E7)\,e^{-45360/RT\ 0.84}/(\mathrm{LHSV}) \qquad [4.6]$$

which are the results published by Heck and Stein using a Marquardt data fit technique similar to the one used in this work. The mean deviation obtained by Heck and Stein for the model fit to this particular set of data was 0.008 wt. percent.

Immediately, the question arose as to why discrepant results were obtained for the two criterea used to arrive at eqs. [4.3] and [4.5]. After all, which of the two sets of results is actually more correct? Might not even more sets of parameter values be obtained if the form of the criterion used to evaluate the parameters were changed? This curve-fitting hazard, which was apparently a typical inherent weakness in the curve-fitting technique and in the programming was not fully invested. Rather, the criterion for comparison of data to model predictions was kept the same for all further data fits. In this case, the criterion which provided the best fit was that used to arrive at the parameter values given in eq. [4.5], which was the criterion chosen for all remaining runs. Actually, this criterea was put in a form to yield the average percent error (APE) of the data and the model-predicted concentrations, as given by eq. [4.7].

$$\mathrm{APE} = \sum \left| \left(\frac{C_{data,i} - C_{fit,i}}{C_{data,i}} \right) x100 \right| \qquad [4.7]$$

The variance between the parameter values in eq. [4.5] and those obtained by Heck and Stein are presumably due to the different accuracies of parameter estimation techniques. Although the values in both equations were arrived at via Marquardt's method, the computer programs used to carry out the regression scheme are surely different in some respects.

General Global Model

The global model given by eq. [3.24] and [3.25] was fit to the same data as the Heck and Stein model. This model contains four parameters: the reaction rate constant (contains the pre-exponential constant and the activation energy), the order of hydrogen pressure, and the heteroatom concentration order. The liquid holdup model of Henry and Gilbert, discussed in Chapter 3, is included in this global model. For this model, it was necessary to specify the value of one of the parameters in order to generate the data fit with the three remaining parameters. Thus, the data fit results for this model are given in Table III as a function of the concentration order, N, which was the parameter held fixed during the data fit. As the table shows, the results for N equals 3.5 provides the best overall fit to the data, based upon the mean deviation of the outlet stream concentrations.

Actually, this method of parameter evaluation is equivalent to that of Heck and Stein, where the concentration order was specified at two. It is possible that the parameter values providing the best fit to the data would have been different if all of the parameters were allowed to vary during the data-fitting process. The fact that specification of one parameter was necessary could have been due to a lack of precision in the data to which the model was fit. The data given by Heck and Stein contains many instances in which the same outlet stream conversion is reported for different sets of operating conditions. Most probably, though, a data fit could have been obtained without fixing one of the parameters

TABLE III

RESULTS FOR GLOBAL MODEL DATA FIT

N	k_o*	E (Btu/lbmol)	M	Mean Deviation (wt %)
0.8**	- - -	- - -	- - -	- - -
1.0***	6.72 E3	2.146 E4	0.2824	0.00938
1.2	1.15 E4	2.330 E4	0.3959	0.00866
1.4	1.76 E4	2.495 E4	0.5132	0.00780
1.6	3.16 E4	2.673 E4	0.6196	0.00688
1.8	7.57 E4	2.890 E4	0.7121	0.00600
2.0	2.45 E5	3.160 E4	0.7940	0.00521
2.2	1.03 E6	3.470 E4	0.8691	0.00457
2.4	5.44 E6	3.830 E4	0.9403	0.00410
2.7	9.40 E7	4.430 E4	1.0433	0.00356
3.0	2.29 E9	5.100 E4	1.1442	0.00324
3.5	8.13 E11	6.340 E4	1.3114	0.00320
4.0	4.55 E14	7.680 E4	1.4787	0.00341

* The units for k_o are:

$(\text{wt }\%)^{1-N}/(\text{psig})^{M}/(\text{hr})$.

** No parameter estimates were obtained for values of M less than unity.

***These results were generated using eq. [3.26] .

if the regression routine had been supplied with proper initial guesses for the parameters.

In many cases throughout the course of this work it was necessary to initialize the data fitting process by providing MARQ, the computer program to carry out Marquardt's method, with extremely good estimates of what the final, fitted parameter values would be. Arriving at these parameter estimates was largely a matter of trial-and-error or else luck. This hindrance to obtaining good data fit results existed when either the global or the intrinsic models were applied.

Intrinsic Model Data Fits

Data Fit for Model I-1

The intrinsic kinetic models and corresponding LHHW rate expressions considered in this work are given in Table IV. The kinetic models are listed in the form according to which they were solved numerically. The data to which these models were fit was obtained via back calculation of graphical information given by Singhal et al (11). These data were for the HDS of dibenzothiophene (DBT), as discussed in Chapter 2.

Model I-1 in Table IV was derived from the rate equation said to be superior in describing the HDS kinetics of DBT (10). The model incorporates the effectiveness factor, , in order to account for the loss in reaction rate due to inner pore diffusion in the catalyst. No other reactor nonidentities, including catalyst deactivation, have been included.

TABLE IV

INTRINSIC MODELS USED IN DATA FITS

Model No.	Rate Expression	Kinetic Model
I-1	$-r_A = \frac{kK_AK_Bc_Ac_B\eta}{(1+K_Ac_A+K_Pc_P)(1+K_Bc_B)}$	$f(c_A) = 0 = (1+K_Pc_{Po}+K_Pc_{Ao}M_P/M_A)\ln(c_{Ao}/c_A)$ $+(K_A-K_PM_P/M_A)(c_{Ao}-c_A)$ $-\frac{kK_AK_Bc_B\eta}{(1+K_Bc_B)}\left(\frac{wM_A}{\rho_{oil}V(LHSV)}\right)$
I-2	$-r_A = \frac{kK_AK_Bc_Ac_B\eta}{(1+K_Ac_A+K_Bc_B)^2}$	$f(c_A) = 0 = (1+K_Bc_B)^2\ln(c_{Ao}/c_A)$ $+ 2K_A(1+K_Bc_B)(c_{Ao}-c_A)$ $+ 0.5K_A^2(c_{Ao}^2-c_A^2)$ $- kK_AK_Bc_B\eta\left(\frac{wM_A}{\rho_{oil}V(LHSV)}\right)$
I-3	$-r_A = \frac{kK_Bc_Ac_B\eta}{(1+K_Bc_B+K_Pc_P)}$	$f(c_A) = 0 = (1+K_Bc_B+K_Pc_{Po}+K_Pc_{Ao}M_P/M_A)\ln(c_{Ao}/c_A)$ $- K_PM_P/M_A\ (c_{Ao}-c_A)$ $- kK_Bc_B\eta\left(\frac{wM_A}{\rho_{oil}V(LHSV)}\right)$

The computer program used to accomplish the data fit for model I-1 is listed in Appendix F.

For lack of better information, the ratio of the catalyst weight (W) to catalyst volume (V) is set equal to unity (i.e. catalyst bed density equals one gram per cubic centimeter). The ratio of product molecular weight (M_p) to that of DBT (M_A) used was 0.85 based upon the average molecular weights of the products formed in the study of Singhal et al. (10). These results are to be used for parameter sensitivity study rather than comparison to other reported data.

The effectiveness factor is computed from eq. [3.16]. The quantities used in this equation are the reaction rate constant (k_{obs}), catalyst radius (R_c), and effective diffusivity (D_{eff}). This equation was based on a derivation where no consideration is given to the adsorption of the reacting components on the catalyst. Therefore, the assumption was made that the following combination of terms could be used to represent the reaction rate constant in the computation of the Thiele modulus,

$$k_{obs} = kK_AK_BC_BM_A \qquad [4.8]$$

This results in a modified Thiele modulus similar to the one suggested in the literature to correct for adsorption effects in catalytic reactions involving gasses (34). The quantity C_B is included to account for pseudo-first order reaction. The terms on the right-hand side of eq. [4.7] are taken from the intrinsic kinetic model and have the combined units of reciprocal seconds. The reaction rate constant, k_{obs}, is the quantity meant to be replaced in eq. [3.16]. The results of the data fits show that the values of η are consistently very close to unity (e.g. 0.99998). The calculations for η assume that R_c equals 0.0105 cm., since this is one of the catalyst sizes used by Singhal et al. (11) and has been used in a similar work by Pendergast (32).

The problem having to do with providing the initial guesses of the parameters to MARQ was apparent in fitting model I-1 to the kinetic data. Without good initial guesses for the parameters, MARQ could not converge to final values for the model parameters. However, for the case of this particular model, another problem having to do with the initial guesses for the parameters was encountered. The values of parameters which were supposed to provide the best fit to the data were different when the initial guesses for those parameters were changed. Thus, in some cases if five sets of initial guesses for the parameters were tried then five different sets of fitted parameters resulted. The matter was confounded even more due to the fact that, in many cases, each set of fitted parameters provided about the same accuracy with respect to predicting the kinetic data. The reaction rate constant was the parameter most especially sensitive to the initial guesses.

Actually, the modified method for computing the Thiele modulus as given by eq. [4.8] might have played a major role in affecting the sensitivity of the needed parameters to the initial guesses. In computer runs with the effectiveness factor set equal to one, data fits with smaller average percent errors resulted, too.

Since the intrinsic model contains the adsorption equilibrium constants as well as the reaction rate constant, the inclusion of the respective heats of adsorption and the activation energy in the model would have been necessary in order to fit the model to non-isothermal data. In order to eliminate the aded complexity of including the heat effects of the parameters in the model, the data was broken down into five separate isothermal data sets. The intrinsic model was then fit to these isothermal data sets in five different computer programs.

The isothermally fit model parameters are given in Table V. Neither the isothermal adsorption equilibrium constants nor the intrinsic reaction rate constant could be well-correlated using Arrhenius-type temperature dependencies. However, if this type of temperature dependence is to be used to represent the results, the following are the best representations (see Figures 4-7) based upon eye-ball-estimated trend lines:

$$k = (10^{21}) e^{-96000/RT} \qquad [4.9]$$

$$K_A = K_{DBT} = (100) e^{-16700/RT} \qquad [4.10]$$

TABLE V

ISOTHERMALLY-FIT PARAMETERS FOR MODEL I-1

Temperature (^{o}F)	k	K_A	K_P	K_B	APE*
545	0.88977	0.008934	79.819	1572.7	0.32
572	4.3489	0.016874	0.20494	143.16	3.62
590**	1.2546	0.012255	7.978E6	23.742	17.65
617	59.408	0.019367	0.5741E-8	31.387	4.66
662	90.778	0.027268	0.00	28.903	12.49

*APE is the average percent error, defined as

$$\sum\left(\frac{C_{data} - C_{fit}}{C_{data}}\right) \times 100$$

**The results of the data fit at 590^{o}F were discarded due to excessive APE and lack of desired trend when compared to the other isothermal data fits. These results are given here for the purpose of documentation.

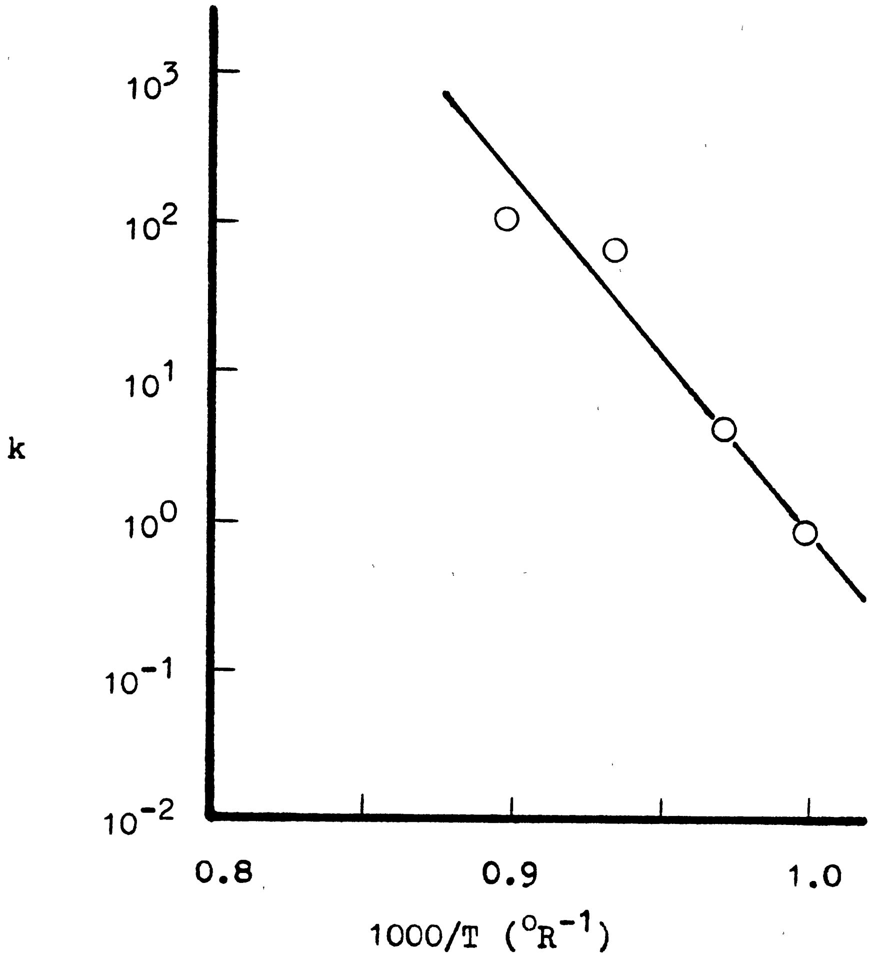


Figure 4. Arrhenius Plot for the Intrinsic Reaction Rate Constant

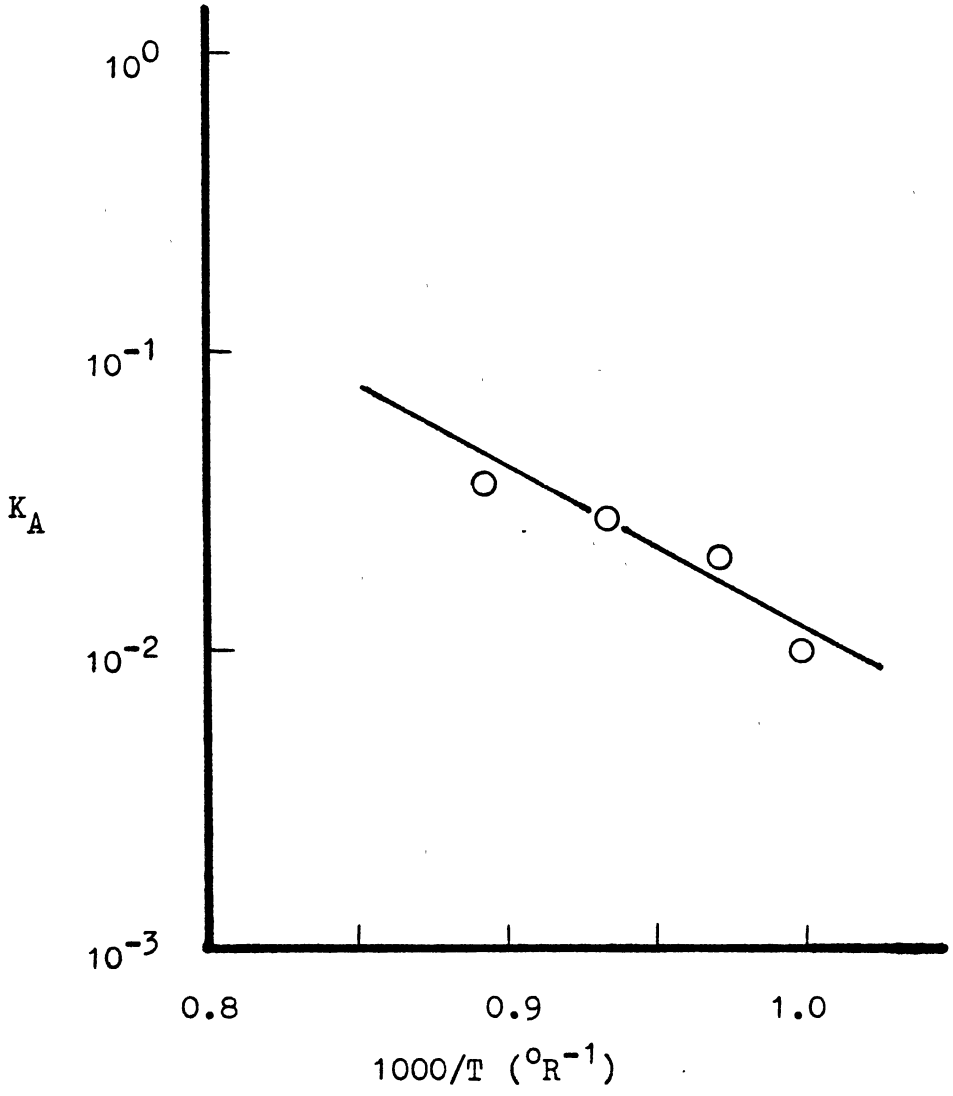


Figure 5. Plot of the DBT Adsorption Equilibrium Constant Against Reciprocal Temperature

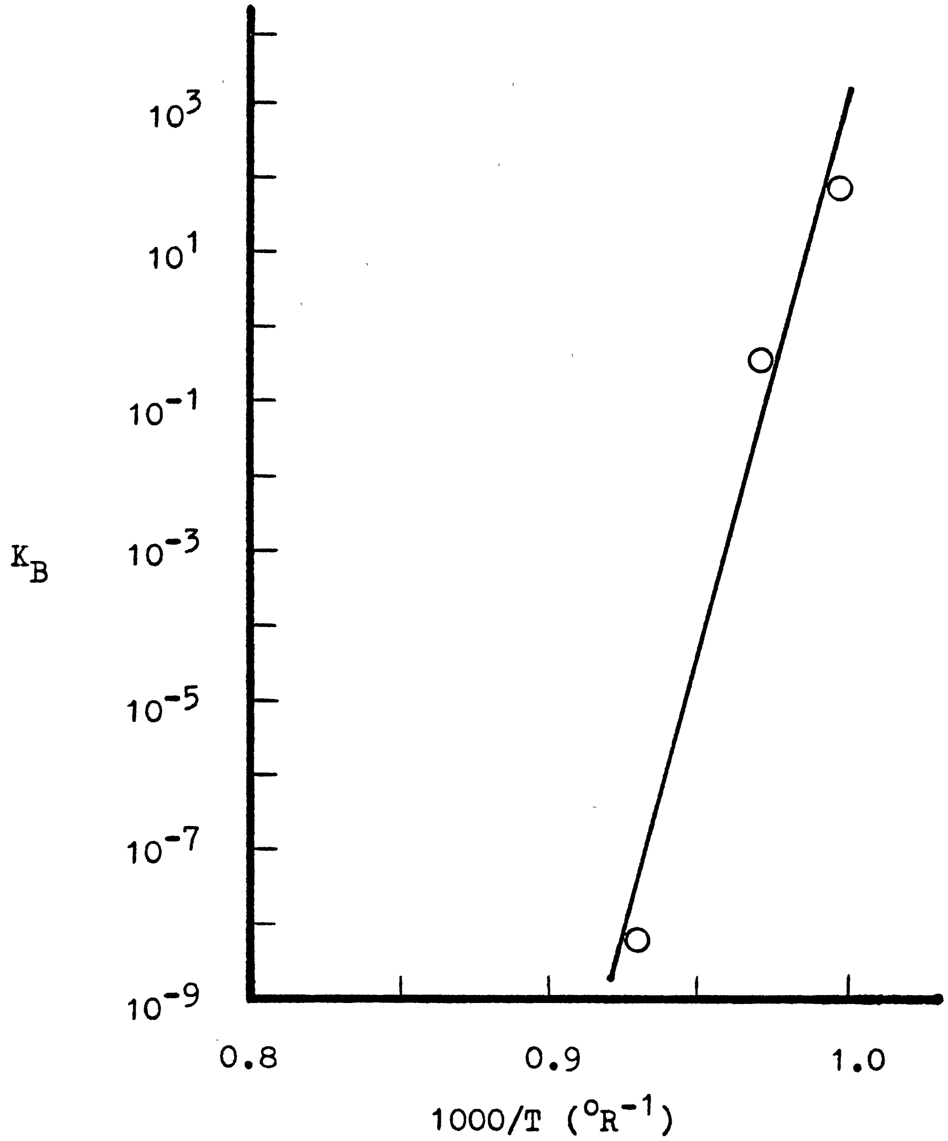


Figure 6. Plot of the Adsorption Equilibrium Constant of Hydrogen Against Reciprocal Temperature

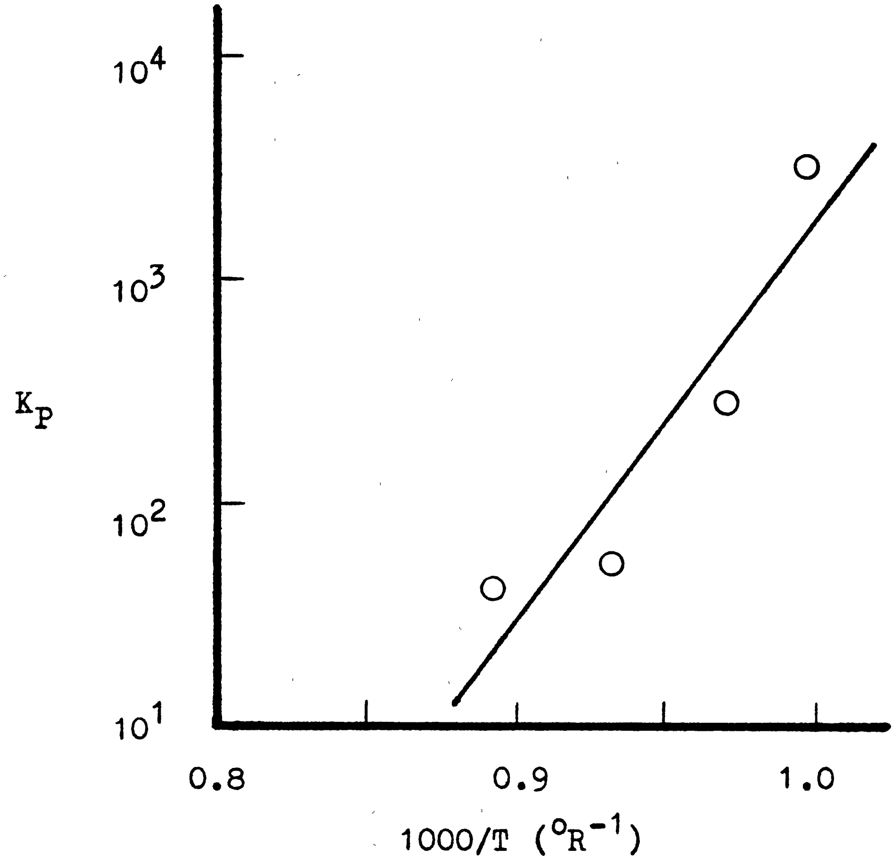


Figure 7. Plot of the Adsorption Equilibrium Constant of Products Against Reciprocal Temperature

$$K_B = K_{H2} = (2x10^{-93})e^{433000/RT} \qquad [4.11]$$

$$K_p = (1.9x10^{-16})e^{87000/RT} \qquad [4.12]$$

As mentioned before, the values of the parameters were selected from several possible sets of results, due to the multifarious results obtained when several different sets of initial guesses were used. The selections were based not only upon the goodness of fit to the data, but upon the trend displayed by the parameters according to temperature as well. In spite of this biased method of selection, the desired influence of temperature on the parameters could not be obtained. In fact, the results of the data fit at 590^{o}F were discarded altogether since no reasonably good fit to the data could be obtained, no matter what initial guesses for the parameters were used. This could be due to weaknesses in the data, since the data fits at the other temperatures were relatively good with respect to the APE.

The data fit at 662^{o}F was also very poor, as suggested by the high average percent error of the results (e.g. 12.49 percent). The average percent error of the concentrations for the data fit at 662^{o}F could be dropped down to 4.87 percent only by allowing negative values of the adsorption equilibrium constant of P, the products. Since the desired trend was displayed by the results given at 662^{o}F with respect to the other isothermal data fits, though, the results were retained.

Since the parameters in model I-1 could not be well correlated with the Arrhenius' equation form of temperature dependence, a polynomial fit was obtained. A third-degree polynomial in temperature was fit to four of five isotherms for the intrinsic parameters. The parameter isotherms at 590°F were not used in the correlations. The coefficients in the polynomial fits are given in Table VI.

The fact that more than one set of parameters could fit a given set of data with approximately equal accuracy indicates either model instability, due to the form of the equation, or a weakness in the method of regression used (33). Another explanation might be that the criterea for comparison of the data to the model predictions was not appropriate, as discussed earlier for the case of the global model. In fact, in a similar study to this one, this same intrinsic model was successfully fit to the same data using the following form (32),

$$\frac{1}{X}\ln\left(\frac{1}{1-X}\right) =$$

$$\frac{C_B\ W(100)kK_BK_A/K_p}{X(LHSV)C_{AO}V\rho_{oil}\left(\frac{Cpo}{C_{Ao}}+1\right)(1+K_BC_B)} + \frac{\left(1-\frac{K_A}{Kp}\right)}{(C_{po}/C_{Ao})} \qquad [4.13]$$

The consequential disadvantage of using the form suggested by eq. [4.10] is that values can be distinctly obtained for only two of the parameters k, K_A, K_B, K_p. For example,

TABLE VI

COEFFICIENTS IN THE CORRELATIONS FOR THE DATA FIT RESULTS FOR MODEL I-1

Intrinsic Model Parameter	c_1	c_2	c_3	c_4
k	0.2167472 E6	-0.6125365 E3	0.5758226 E0	-0.1800284 E-3
K_A	-0.4812131 E2	0.1354647 E0	-0.1270825 E-3	0.3974552 E-7
K_B	0.7215325 E7	-0.2009004 E5	0.1863637 E2	-0.5759635 E-2
K_P	0.4353594 E6	-0.1214055 E4	0.1127860 E1	-0.3490588 E-3

Note: The coefficients c_1, c_2, c_3, and c_4 refer to the following equation:

$$K = c_1 + c_2(T) + c_3(T)^2 + c_4(T)^3$$

estimates can be determined for k and K_B and the ratio of the third and fourth parameters, K_A/K_p.

Data Fit for Model I-2

Model I-2 in Table IV was derived for the case where the reactants adsorb on a single type of catalyst site. The derivation assumed that the products did not adsorb.

In fitting model I-2 to the given data sets, the initial guesses of the parameters played an even greater role. After much trial-and-error, initial guesses were reached which allowed three of the isothermal data sets to be fit. The model could not be fit using the isothermal data sets at the two highest temperatures (617 and 662°F). Surely, the isothermal data fits would have been obtained over the full range of temperatures if the appropriate first guesses of the parameters had been used.

The results of the isothermal data fits are given in Table VII for model I-2. Although the results obtained at 590°F are reported in the table, the worth of these results is questionable, due to the large average percent error of the concentrations. Thus, for both model I-1 and I-2, the results at 590°F were rejected due to the large average percent error at this point, which gives credence to the earlier suggestion that the data for this temperature might have been in error originally.

The Thiele modulus for this model was computed in the same way as for model I-1 (see eq. [4.8]). As for the

TABLE VII

ISOTHERMALLY-FIT PARAMETERS FOR MODEL I-2

Temperature (^{o}F)	k	K_A	K_P	APE
545	0.66583	0.020443	712.91	2.46
572	1.0761	0.030490	444.61	1.83
590*	12.170	1.2287	16795	17.85
617**	- - -	- - -	- - - -	- - -
662**	- - -	- - -	- - - -	- - -

* The results obtained at 590^{o}F were rejected due to excessively large APE. The information is included here for docummentary purposes.

** No data fit results could be obtained at 617 and 662^{o}F.

first intrinsic model considered, the values of η for this model were all very close to unity.

The advantage of this model as compared to model I-1 was that the final parameter estimates were not so sensitive to the initial guesses as were the final parameter estimates in model I-1. The corresponding disadvantage, it seems, is that the range was much narrower for the first guesses than that resulted in a successful data fit. This phenomenon was observed almost certainly due to the fact that only three parameters were used in model I-2. The three parameters were the reaction rate constant and two adsorption equilibrium constants. The improved average percent errors for the data fits using this model could be due to the reduced sensitivity of the parameters to the initial guesses.

Data Fit for Model I-3

For model I-3 no results at all were obtained. This model was the last one used in the data fit part of this study and consequentialy received the least amount of effort in attempts to fit the isothermal data sets. This model is for a single site adsorption mechanism with only hydrogen (component B) and products (component P) competing for catalyst sites. The surface reaction, which controls the mass transfer rate, is between adsorbed hydrogen and the dibenzothiophene (component A) at the liquid-solid interface. Since hydrogen sulfide is one of the products formed in HDS, this model is logical if hydrogen and hydrogen sulfide adsorb onto the same type of catalyst site.

Model I-3 contains three parameters, like model I-2. Thus, it is reasonable to expect the best initial guesses for the model parameters to be hard to pinpoint. However, if this model behaves similarly to model I-2 then at least the resulting final parameter values should be relatively stable.

Parameter Sensitivity Study

Simulated Data by Model I-1: General Considerations

The parameters of the global model (see eqs. [3.24] and [3.25]) were tested for sensitivity to variations in the intrinsic reaction kinetics and catalytic adsorption phenomena. The kinetic model given by model I-1 in Table IV was utilized to create the intrinsic reaction and catalytic adsorption perturbations.

With the intrinsic parameter values obtained via the previously mentioned data fit, the model was used to generate sets of simulated reactor data. Since the global model activation energy was one of the parameters to be investigated, it was necessary to use non-isothermal data. Thus the temperature effects of the intrinsic model parameters were correlated using a third-order polynomial in order to provide exact reproduction of those parameters (only four temperatures were used in the correlation). The non-isothermal operating conditions used in the computer runs are listed in Table VIII. The program listing for the parameter sensitivity study is given in Appendix G. Notice that the operating conditions do not include 590^{o}F, since no good data fits could be obtained for that isotherm. Thus, the simulated reactor data supplied to the global model consisted of the given operating conditions and the outlet stream concentrations generated by the intrinsic kinetic model, which also utilized the given operating conditions.

The intrinsic model was equipped with a method to simulate increases in the reaction rate or increased catalytic adsorption activity of particular components. This was accomplished by using coefficients to act as multipliers for the intrinsic model parameters. These "variation coefficients" were called VARK's in the computer program and were applied to the intrinsic model parameters as shown below:

$$k = k_{corr} \times \text{VARK} \tag{4.14}$$

$$K_A = K_{A,corr} \times \text{VARKA} \tag{4.15}$$

$$K_B = K_{B,corr} \times \text{VARKB} \tag{4.16}$$

$$K_p = K_{p,corr} \times \text{VARKP} \tag{4.17}$$

where the subscript "corr" refers to the respective parameter obtained directly from the correlations for that parameter. Notice that, for the special case where all VARK's are equal to unity, the intrinsic model parameters are used exactly as

TABLE VIII

NON-ISOTHERMAL DATA USED FOR PARAMETER SENSITIVITY STUDY

Data Point Number	Temperature (°F)	Pressure (psig)	LHSV (hr^{-1})
1	545	250	1
2	545	350	3
3	545	450	6
4	572	250	3
5	572	350	6
6	572	450	9
7	617	250	9
8	617	350	12
9	617	450	15
10	662	250	9
11	662	350	12
12	662	450	15

Note: The inlet concentration used for all data points was 2.43 wt % (DBT in tetraline).

they come from the correlations, i.e. exactly as they were determined from the isothermal data fits.

By changing the values of the VARK's, the values of the intrinsic model parameters could be varied at will. The limitation of the VARK values was set by the range of outlet stream concentrations which could be obtained from the intrinsic model. That is, if a VARK was set to too large a value, and the corresponding parameter was thus too large, then no solutions could be obtained from the intrinsic kinetic model. A few experimental computer runs with the VARK's showed that the range of VARK's between 0.3 and 3.0 was a practical limitation in most cases. Thus, by increasing the appropriate VARK, corresponding increases were made to occur in the intrinsic reaction rate constant or the adsorption equilibrium constant of a particular component, without affecting the other parameters.

An appealing aspect of the intrinsic model used in the parameter sensitivity study was the ability of the model to generate outlet stream concentrations even without the inclusion of one of the parameters. The alteration of the intrinsic model to formulate the mechanisms in which a particular component is not adsorbed involves simply removing the corresponding adsorption equilibrium constant from the given intrinsic model. Due to the simplicity of the alterations involved, the special cases in which each component is not adsorbed were considered separately, as variations to the parameter sensitivity study. The rate equations and the corresponding integrated forms are given in Table IX.

Before making the runs involving changes in the VARK's, the sensitivity of the global model parameters to initial guesses was checked. Thus, thirteen sets of initial guesses for the global model parameters were derived and are listed in Table X. The derivation of these estimates involved the stipulation of the operating conditions, the outlet stream concentration, and three of the four parameters to solve for the reaction rate constant. This method of derivation acted to insure that the initial guesses of the parameters would themselves allow the global model to predict plausible outlet stream concentrations.

The effect of the initial guesses are given in Table XI. Notice that two sets of results occur, depending upon the estimates used. Excluding the thirteenth set of initial guesses, when the initial guess involves the concentration order, N, equal to one or else N greater than two, the fitted value of N is equal to one. The effect of the initial guess of the pressure exponent, M, is displayed by the two sets of guesses where N equals two and also for the thirteenth set of initial guesses. Apparently, when the concentration order is guessed at values greater than two, the fitted value of N will be one unless the pressure exponent is also guessed at sufficiently high values.

The effect of the initial guesses was only tested for the case where all the VARK's were set equal to one. It was

TABLE IX

INTRINSIC KINETIC MODELS USED IN PARAMETER SENSITIVITY STUDY

Adsorption Mechanism	Rate Expression	Intrinsic Kinetic Model
All components adsorbed	$-r_A = \dfrac{kK_AK_Bc_Ac_B\eta}{(1+K_Ac_A+K_Pc_P)(1+K_Bc_B)}$	$f(c_A) = 0 = (1+K_Pc_{Po}+K_Pc_{Ao}M_P/M_A)\ln(c_{Ao}/c_A)$ $+ (K_A-K_PM_P/M_A)(c_{Ao}-c_A)$ $- \dfrac{kK_AK_Bc_B\eta}{1+K_Bc_B}\left(\dfrac{wM_A}{\rho_{oil}V(LHSV)}\right)$
Component A not adsorbed	$-r_A = \dfrac{kK_Bc_Ac_B\eta}{(1+K_Pc_P)(1+K_Bc_B)}$	$f(c_A) = 0 = (1+K_Pc_{Po}+K_Pc_{Ao}M_P/M_A)\ln(c_{Ao}/c_A)$ $- K_PM_P/M_A\ (c_{Ao}-c_A)$ $- \dfrac{kK_Bc_B\eta}{1+K_Bc_B}\left(\dfrac{wM_A}{\rho_{oil}V(LHSV)}\right)$
Component B not adsorbed	$-r_A = \dfrac{kK_Ac_Ac_B\eta}{(1+K_Ac_A+K_Pc_P)}$	$f(c_A) = 0 = (1+K_Pc_{Po}+K_Pc_{Ao}M_P/M_A)\ln(c_{Ao}/c_A)$ $+(K_A-K_PM_P/M_A)(c_{Ao}-c_A)$ $- kK_Ac_B\eta\left(\dfrac{wM_A}{\rho_{oil}V(LHSV)}\right)$
Component P not adsorbed	$-r_A = \dfrac{kK_AK_Bc_Ac_B\eta}{(1+K_Ac_A)(1+K_Bc_B)}$	$f(c_A) = 0 = \ln(c_{Ao}/c_A) + K_A(c_{Ao}-c_A)$ $- \dfrac{kK_AK_Bc_B\eta}{1+K_Bc_B}\left(\dfrac{wM_A}{\rho_{oil}V(LHSV)}\right)$

TABLE X

SETS OF INITIAL GUESSES USED FOR GLOBAL MODEL PARAMETERS

Estimate Set Number	k_o	E	M	N
1	5.943 E6	0.4 E5	0.40	0.50
2	5.700 E5	0.4 E5	0.80	0.50
3	1.940 E7	0.4 E5	0.40	0.80
4	1.870 E6	0.4 E5	0.80	0.80
5	4.290 E7	0.4 E5	0.40	1.00
6	4.120 E6	0.4 E5	0.80	1.00
7	9.470 E7	0.4 E5	0.40	1.20
8	9.100 E6	0.4 E5	0.80	1.20
9	2.270 E9	0.4 E5	0.40	2.00
10	2.180 E8	0.4 E5	0.80	2.00
11	1.220 E10	0.4 E5	0.40	3.00
12	1.174 E9	0.4 E5	0.80	3.00
13	6.940 E1	0.4 E5	3.00	2.50

Note: The data used to generate these results were the following:

$C=0.0150$; $C_o=0.0243$; $T=1050^oR$;
$P=350$ psia; LHSV= 9 hr^{-1}.

TABLE XI

THE EFFECT OF INITIAL GUESSES ON THE VALUES OF THE GLOBAL MODEL PARAMETERS

Estimate Set Number*	k_o	E	M	N	APE
1	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
2	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
3	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
4	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
5	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
6	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
7	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
8	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
9	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
10	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
11	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
12	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
13	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877

* Taken from Table XI.

assumed that the results obtained for this experiment applied over the full range of VARK's to be used. Thus, three sets of initial guesses were used in the computer runs involving the variations of the VARK's, in order to cover all possible values of the final fitted parameters of the global model. The sets of initial guesses used were the first, eleventh, and thirteenth given in Table VIII. These three sets of estimates are hereafter referred to as the half-order, third-order, and 2.5-order guesses, respectively, in reference to the concentration exponents. The results in Table XI are shown for the cases where the intrinsic model was used both with and without the variations involving the adsorption of the components. Both the third-order and the 2.5-order initial guesses were used to generate the information in the table.

The effect of the liquid holdup model calculations upon the global model parameters was also tested. The results are given in Table XII. Roughly, the inclusion of the liquid holdup calculations involves the use of a space time comprised of a temperature-dependent constant divided by the LHSV raised to the two-thirds power. This differs from the typical usage of the space time which is given simply by the reciprocal of the LHSV (see Chapter 3).

In the derivation of the global model (see Chapter 3) the liquid holdup constant of proportionality was shown to be absorbed into the global reaction rate constant. However, the observed effect produced by the inclusion of the liquid

TABLE XII

EFFECT OF LIQUID HOLDUP CALCULATIONS ON THE GLOBAL MODEL PARAMETERS

Intrinsic Model Used*	All Components Adsorbed	B Not Adsorbed	P Not Adsorbed
A. Runs without liquid holdup calculations:			
Third-Order Guesses -			
k_o	0.18591 E12	0.32089 E16	0.21259 E9
E	0.57811 E5	0.76877 E5	0.49503 E5
M	0.94035	1.06230	0.92306
N	1.75180	3.24890	1.00
APE	2.6053 %	0.2611 %	4.0302 %
2.5-Order Guesses -			
k_o	0.58737 E9	0.26433 E12	0.10439 E9
E	0.52759 E5	0.76078 E5	0.48955 E5
M	1.00370	1.05470	0.93380
N	1.00	0.81407	0.90133
APE	3.3533 %	0.2638 %	4.1090 %
B. Runs with liquid holdup calculations:			
Third-Order Guesses -			
k_o	0.55257 E8	- - - -	0.20783 E8
E	0.43212 E5	- - - -	0.39901 E5
M	0.52582	- - - -	0.43438
N	1.00	- - - -	1.00
APE	3.618 %	- - - -	6.0658 %

TABLE XII (CONTINUED)

Intrinsic Model Used	All Components Adsorbed	B Not Adsorbed	P Not Adsorbed
2.5-Order Guesses -			
k_o	0.32535 E6	0.16836 E11	- - - -
E	0.38906 E5	0.67169 E5	- - - -
M	0.58295	0.73948	- - - -
N	0.30168	0.87593	- - - -
APE	3.4877 %	0.2274 %	- - - -

* Refers to the intrinsic models given in Table X.

Note: No results were obtained for the situations indicated by dashes.

holdup calculations is that all of the global parameters are decreased. Generally, the global model parameters E, M, and N are changed by an order of magnitude less than the reaction rate constant. The fact that all four parameters are affected is undesirable, but does not greatly concern this work.

The results for the parameter sensitivity study were obtained by setting three of the VARK's equal to unity while varying the fourth. The three sets of initial guesses mentioned earlier were used to generate these results. The results acquired for each set of initial guesses used are described below.

Simulated Data by Model I-1: Half-Order Guesses

The results using the half-order guesses are shown in Table XIII. The results for 2.5-order estimates are not shown since the results are essentially the same as for the half-order guesses.

The effects of the changes in the VARK's upon the global model concentration order, N, is illustrated in Figure 8. Notice that N approaches one, which is the same as the intrinsic reaction order, for increases in all four of the intrinsic model parameters. This effect is most pronounced for increased adsorption of hydrogen, as seen for the VARKB curve.

The curve for VARKA is virtually super-imposed upon the

TABLE XIII

THE SENSITIVITY OF THE GLOBAL MODEL PARAMETERS USING HALF-ORDER INITIAL GUESSES

Variation Constant	k_o ((wt %)$^{1-N}$/hr/psig^M)	E (Btu/lbmol)	M	N	APE
<u>VARK</u>					
0.3	0.39090 E5	0.38860 E5	0.56896	0.00	1.2631
0.6	0.49052 E5	0.38296 E5	0.58594	0.00	2.2030
1.0	0.32535 E6	0.38296 E5	0.58295	0.30168	3.4897
1.5	0.11918 E8	0.41785 E5	0.53978	0.71504	4.9899
2.0	0.11011 E9	0.44019 E5	0.49301	0.87086	6.5373
3.0	0.12565 E10	0.46931 E5	0.42549	0.93782	10.5718
<u>VARKA</u>					
0.3	0.39171 E5	0.38865 E5	0.56900	0.00	1.2632
0.6	0.49091 E5	0.38298 E5	0.58595	0.00	2.2032
1.0	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
1.5	0.11872 E8	0.41780 E5	0.53982	0.71471	4.9898
2.0	0.10939 E9	0.44010 E5	0.49310	0.87043	6.5372
3.0	0.12450 E10	0.46917 E5	0.42561	0.93742	10.5664

TABLE XIII (CONTINUED)

Variation Constant	k_o	E	M	N	APE
VARKB					
0.3	0.66671 E4	0.34776 E5	0.55670	0.00	1.8099
0.6	0.21513 E5	0.36461 E5	0.58570	0.00	2.4414
1.0	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
1.5	0.40554 E9	0.46422 E5	0.49609	0.98998	4.6470
2.0*	0.17320 E10	0.48907 E5	0.49043	0.9900	6.0384
3.0*	0.57616 E11	0.54920 E5	0.43845	0.98985	13.9632
VARKP					
0.3	0.22794 E5	0.35584 E5	0.57041	0.00	4.2941
0.6	0.29710 E5	0.36374 E5	0.58631	0.00	3.9116
1.0	0.32535 E6	0.38906 E5	0.58295	0.30168	3.4877
1.5	0.40836 E7	0.41690 E5	0.57985	0.60813	3.0518
2.0	0.33008 E8	0.44079 E5	0.57825	0.85184	2.7000
3.0*	0.13013 E9	0.46170 E5	0.60269	0.99000	2.2773
	-------	-------	-------	-------	------
	0.15930 E9	0.46392 E5	0.59258	1.00	2.3007

* The results given in this table for half-order initial guesses were also obtained when 2.5-order initial guesses were used, except for the cases indicated by an asterisk. For the cases where VARKB equals 2.0 and 3.0, no fits were obtained. For VARKP equal to 3.0, the values given below the dashed lines were obtained.

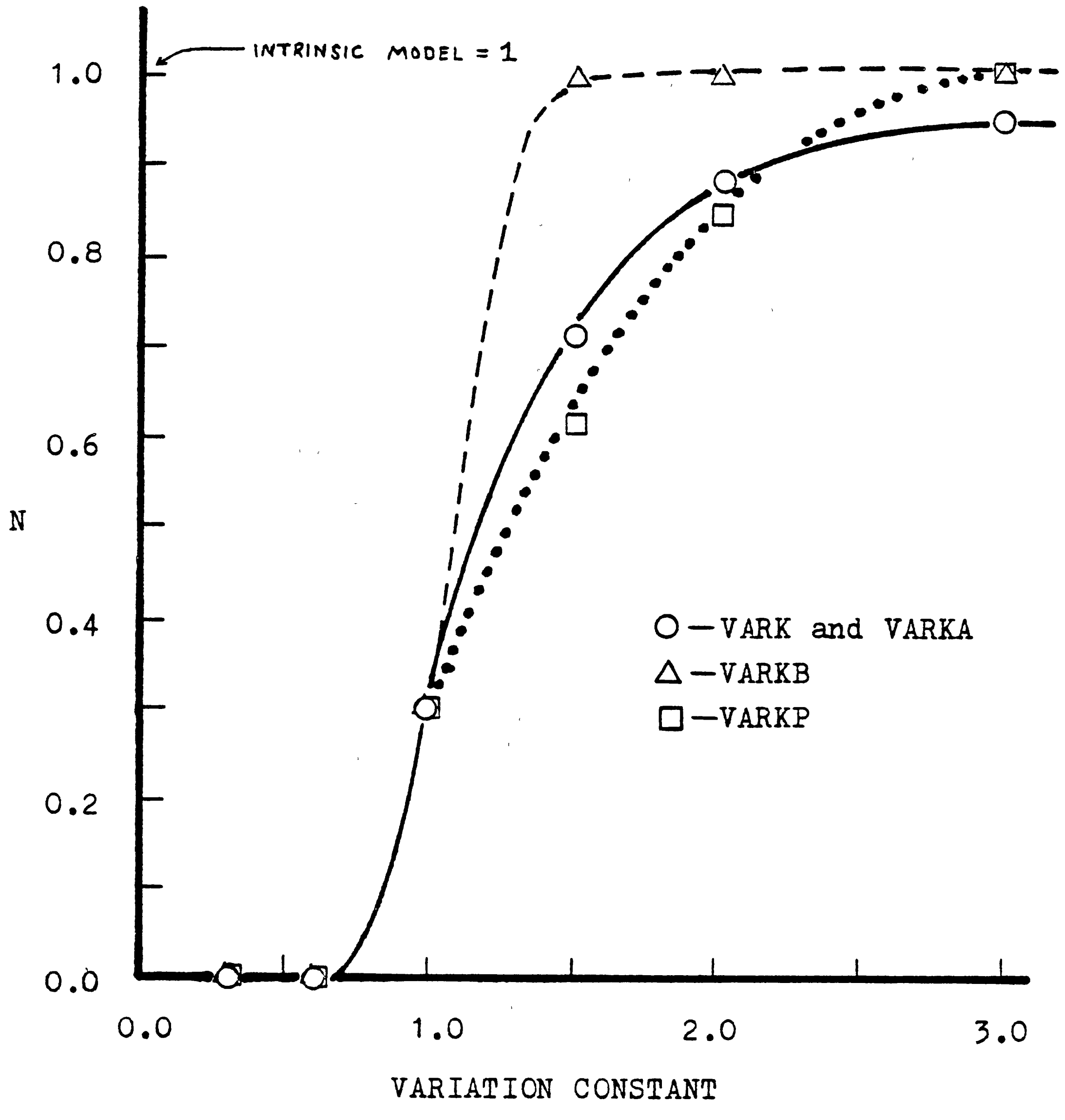


Figure 8. Effect of Variation Constants on N Using Half-Order Initial Guesses

curve for VARK. This characteristic is a consequence of the order of magnitude of the different terms in the intrinsic model. That is, the quantity including the difference between the inlet and outlet stream concentrations has typically about one-one hundredth the value of the quantity including the natural logarithm of these terms (see model I-1 in Table IV). Therefore, the adsorption equilibrium constant of DBT (component A) acts, in a mathematical way, similarly to the intrinsic reaction rate constant.

Observing Figure 9, which depicts the results for the sensitivity of M, the global hydrogen pressure order is seen to decrease with increased adsorption of DBT and hydrogen and with increased reaction rate constant of the intrinsic model. The adsorption of products, as seen by the curve for VARKP, does not appreciably affect M. Once again the curves for VARK and VARKA are practically the same. The order of hydrogen pressure is consistently between zero and one but decreases as the amount of hydrogen available on the catalyst is increased, as shown by increased values of K_B. A similar effect is produced by increased adsorption of DBT. The implication of these observations is that when the adsorption of either reacting component is increased, the effect of pressure on the global reaction rate decreases in significance.

The results for the changes in the VARK's upon the global model activation energy, E, and pre-exponential rate constant, k_o, are shown in Figures 10 and 11, respectively. However, these results are conveniently summarized by the

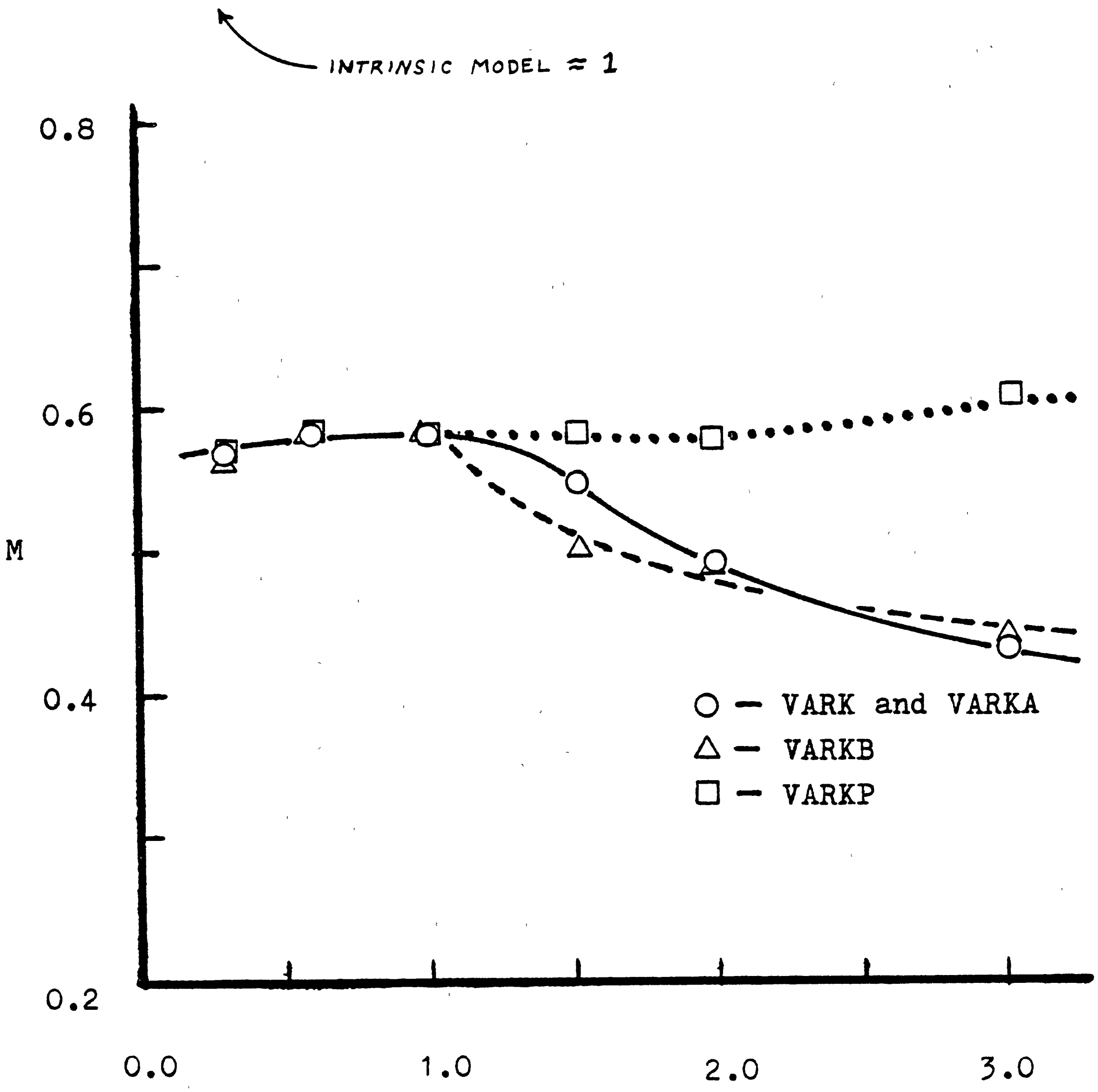


Figure 9. Effect of Variation Constants on M Using Half-Order Initial Guesses

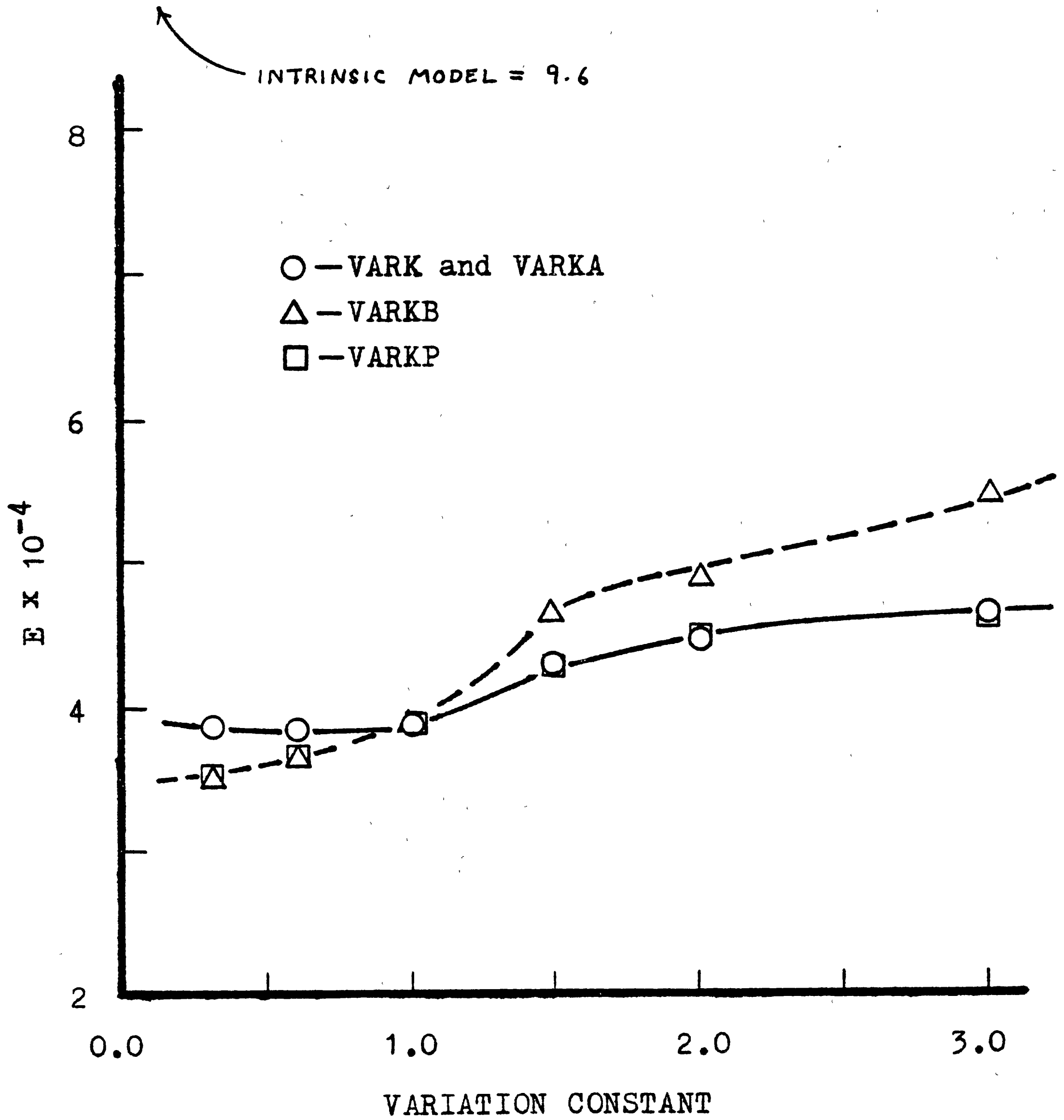


Figure 10. Effect of Variation Constants on E Using Half-Order Initial Guesses

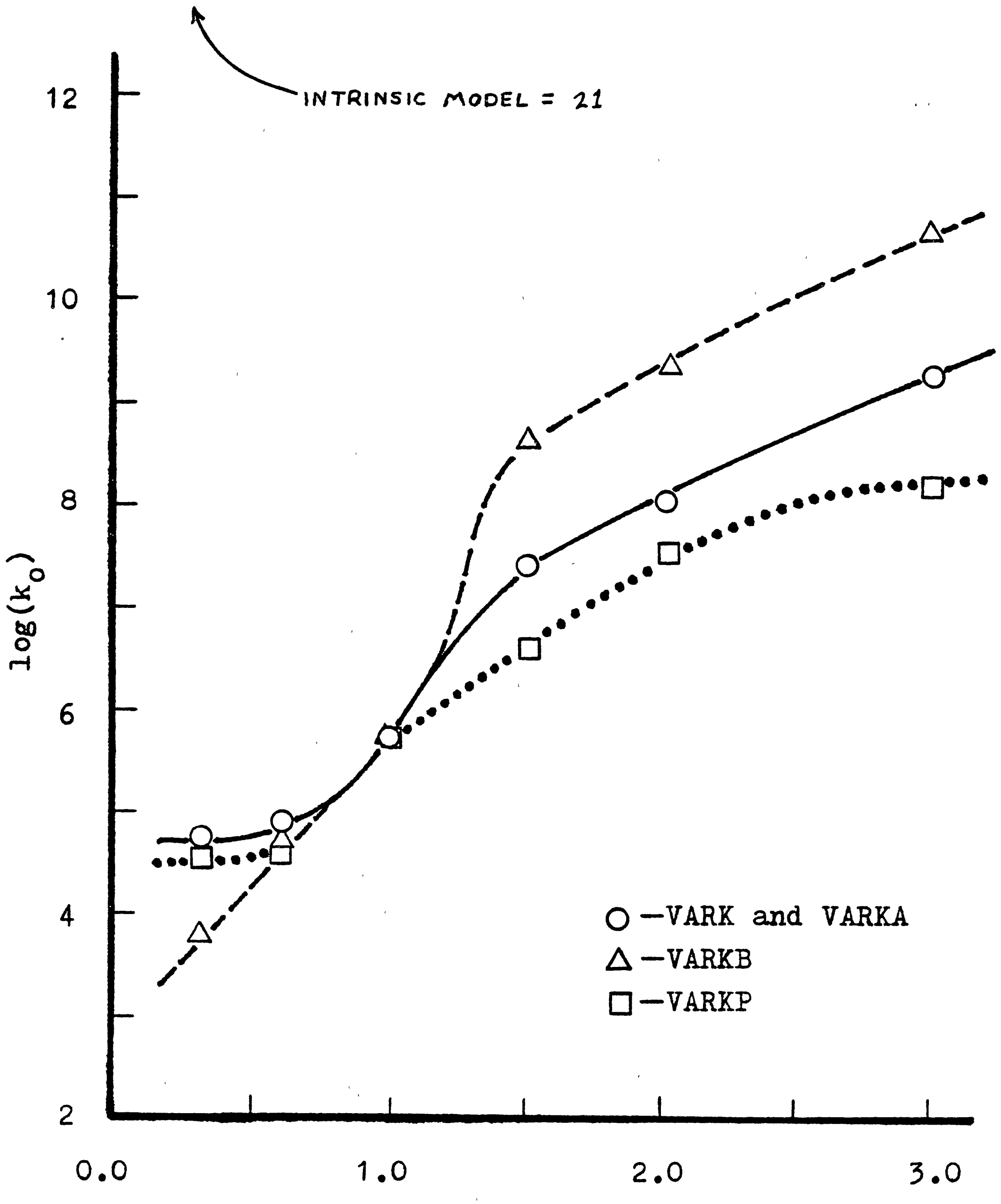


Figure 11. Effect of Variation Constants on k_o Using Half-Order Initial Guesses

graph of the combination of these terms, calculated via the Arrhenius equation using a temperature of 590^{O}F, given by Figure 12. This graph of the global reaction rate constant indicates that the increased adsorption of any component or an increase in the intrinsic reaction rate constant results in an increase in the global reaction rate constant. The curves also seem to be aproaching an assymptote, so that the increase in the observed reaction rate levels off at relatively high adsorption of any component or for a relatively fast intrinsic reaction rate. The assymptotic trend due to the adsorption phenomena is reasonable since the catalyst surface is approaching saturation of the adsorbed components. The leveling off of the global reaction rate constant at high intrinsic reaction rate constant values could possibly be attributed to a change in the controlling mass transfer resistance from surface reaction to either the adsorption of a component, say hydrogen, or else diffusion in the catalyst pores. The effects produced by increased adsorption of the products is less significant than for the other intrinsic model parameters.

Simulated Data by Model I-1:
Third-Order Guesses

The procedure used to obtain the results for half-order gueses was repeated to obtain similar results based upon third-order guesses. The results based upon third-order guesses are given in Table XIV. Using the third-order

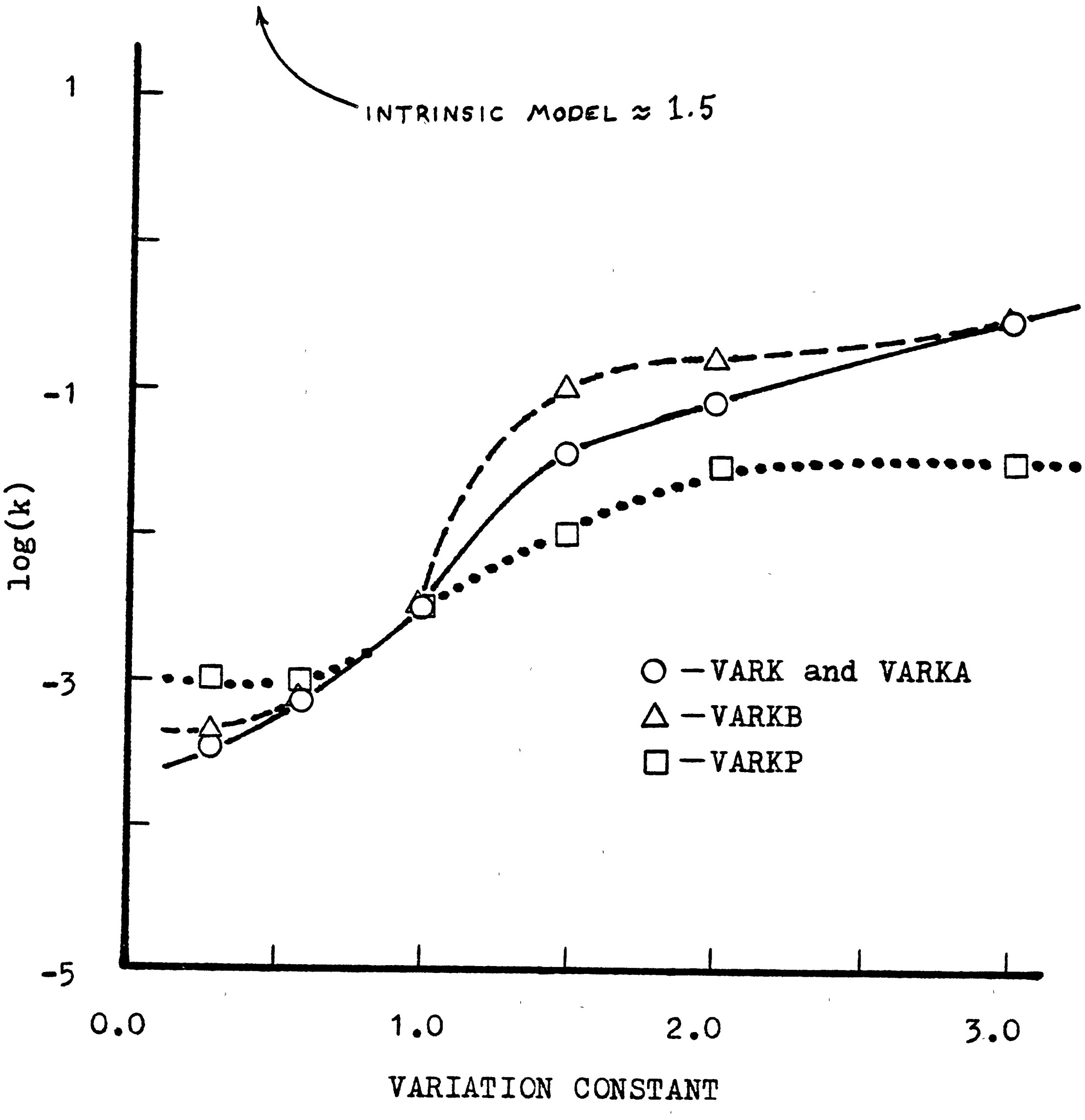


Figure 12. Effect of Variation Constants on k, Evaluated at 590°F, Using Half-Order Initial Guesses

TABLE XIV

THE SENSITIVITY OF THE GLOBAL MODEL PARAMETERS USING THIRD-ORDER INITIAL GUESSES

Variation Constant	k_o $((\text{wt }\%)^{1-N}/$ $\text{hr/psig}^M)$	E (Btu/lbmol)	M	N	APE
VARK					
0.3	0.23688 E10	0.51524 E5	0.96140	1.7620	0.9739
0.6	0.17220 E8	0.41977 E5	0.54236	1.00	2.3952
1.0	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
1.5	0.17204 E9	0.44447 E5	0.49589	1.00	5.0157
2.0	0.46258 E9	0.45562 E5	0.46458	1.00	6.5099
3.0	0.27970 E10	0.47799 E5	0.40488	1.00	10.1067
VARKA					
0.3	0.47650 E7	0.40723 E5	0.54693	1.00	1.3466
0.6	0.17242 E8	0.41979 E5	0.54237	1.00	2.3952
1.0	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
1.5	0.17184 E9	0.44445 E5	0.49689	1.00	5.0160
2.0	0.46163 E9	0.45559 E5	0.46459	1.00	6.5096
3.0	0.27854 E10	0.47791 E5	0.40487	1.00	10.1055

TABLE XIV (CONTINUED)

Variation Constant	k_o	E	M	N	APE
<u>VARKB</u>					
0.3	0.66671 E4	0.34776 E5	0.55670	0.00	1.8099
0.6	0.67996 E7	0.39858 E5	0.53776	1.00	2.8886
1.0	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
1.5	0.50754 E9	0.46659 E5	0.49108	1.0105	4.6268
2.0	0.91639 E11	0.53498 E5	0.38475	1.2730	5.9557
3.0	0.21986 E15	0.65066 E5	0.18523	1.4420	8.6933
<u>VARKP</u>					
0.3	0.22794 E5	0.35584 E5	0.57041	0.00	4.2941
0.6	0.39866 E8	0.42160 E5	0.49952	1.00	4.3225
1.0	0.55257 E8	0.43212 E5	0.52582	1.00	3.6182
1.5	0.77267 E8	0.44253 E5	0.54962	1.00	2.9755
2.0	0.10210 E9	0.45092 E5	0.56738	1.00	2.6202
3.0	0.92226 E9	0.48032 E5	0.57737	1.2251	2.1663

guesses for the parameters, the value of N was roughly one for the full range of VARK's used, as exhibited in Figure 13. Actualy, increased hydrogen adsorption produced a slight increase of N to about 1.7. This observation insinuates that the global concentration order is roughly equal to the intrinsic concentration order with respect to DBT. As for the case where half-order parameter guesses were used, the curves are virtually identical for VARK and VARKA.

The plot for M versus the VARK's is given by Figure 14. These results are only slightly different from those using half-order estimates (Figure 9). Increased adsorption of products has no apreciable effect upon the global pressure order. The effect produced by increased intrinsic reaction rate constant and DBT adsorption is slight, but indicates a trend for decreases in M. Increased hydrogen adsorption also results in a decrease in the order of pressure in the global model. The curves for VARK and VARKA are again the same.

The results for the activation energy and the pre-exponential rate constant in the global model, shown in Figures 15 and 16, are summarized by once again using the global reaction rate constant evaluated at 590°F, as seen in Figure 17. In Figure 17, the global reaction rate constant is shown to change negligibly in response to increased adsorption of products. The observed reaction rate constant increases for an increase in the other three intrinsic model parameters. Increased hydrogen adsorption generally affects k the most drastically.

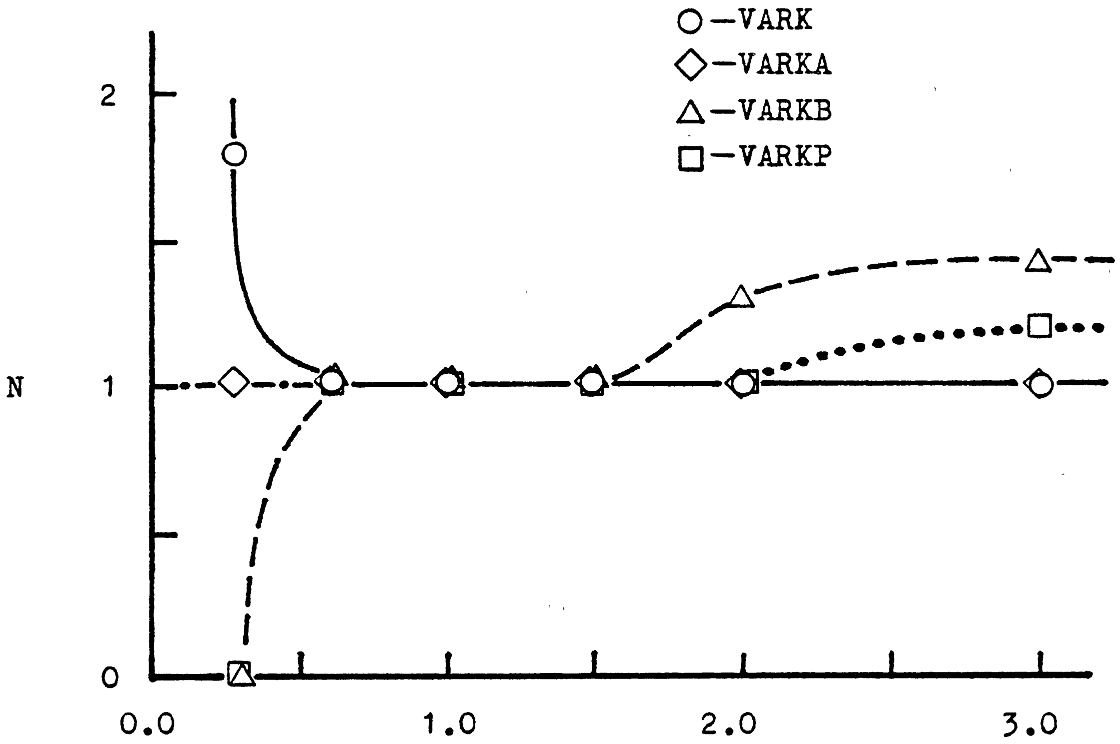


Figure 13. Effect of Variation Constants on N Using Third-Order Initial Guesses

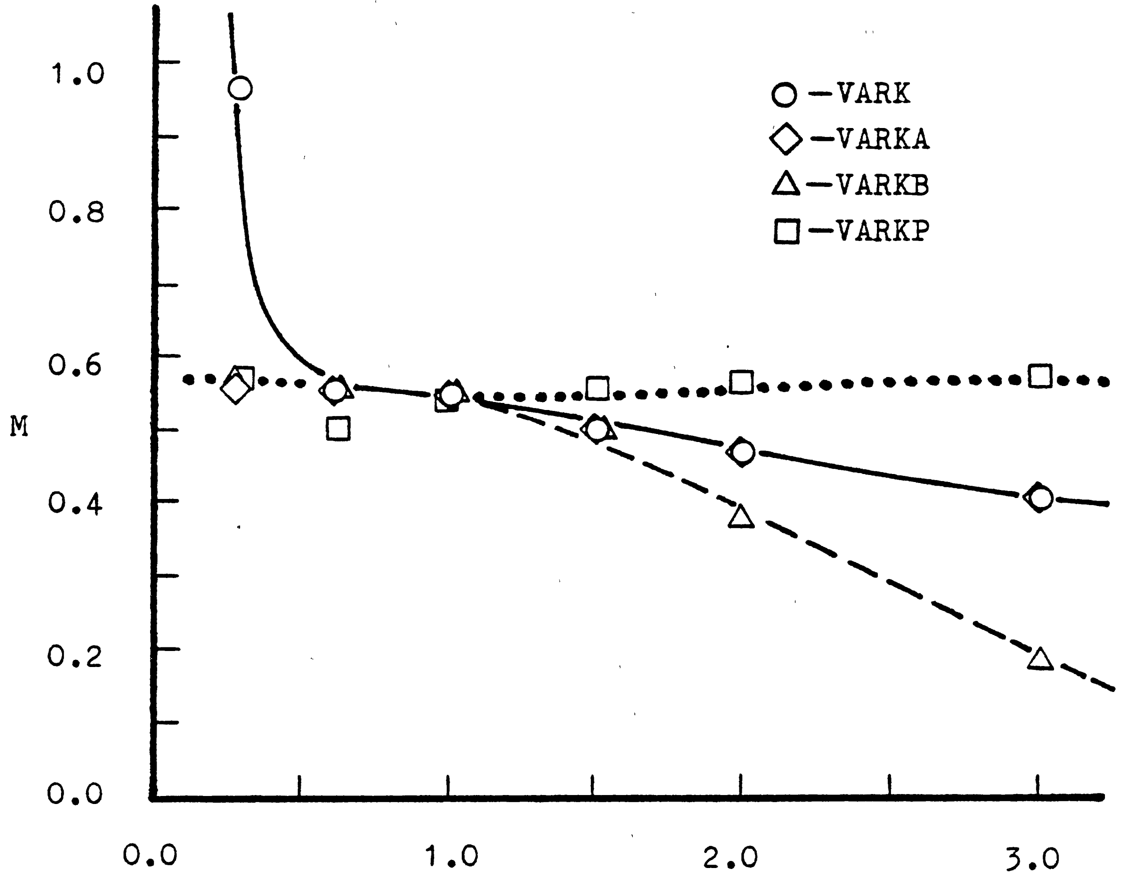


Figure 14. Effect of Variation Constants on M
Using Third-Order Initial Guesses

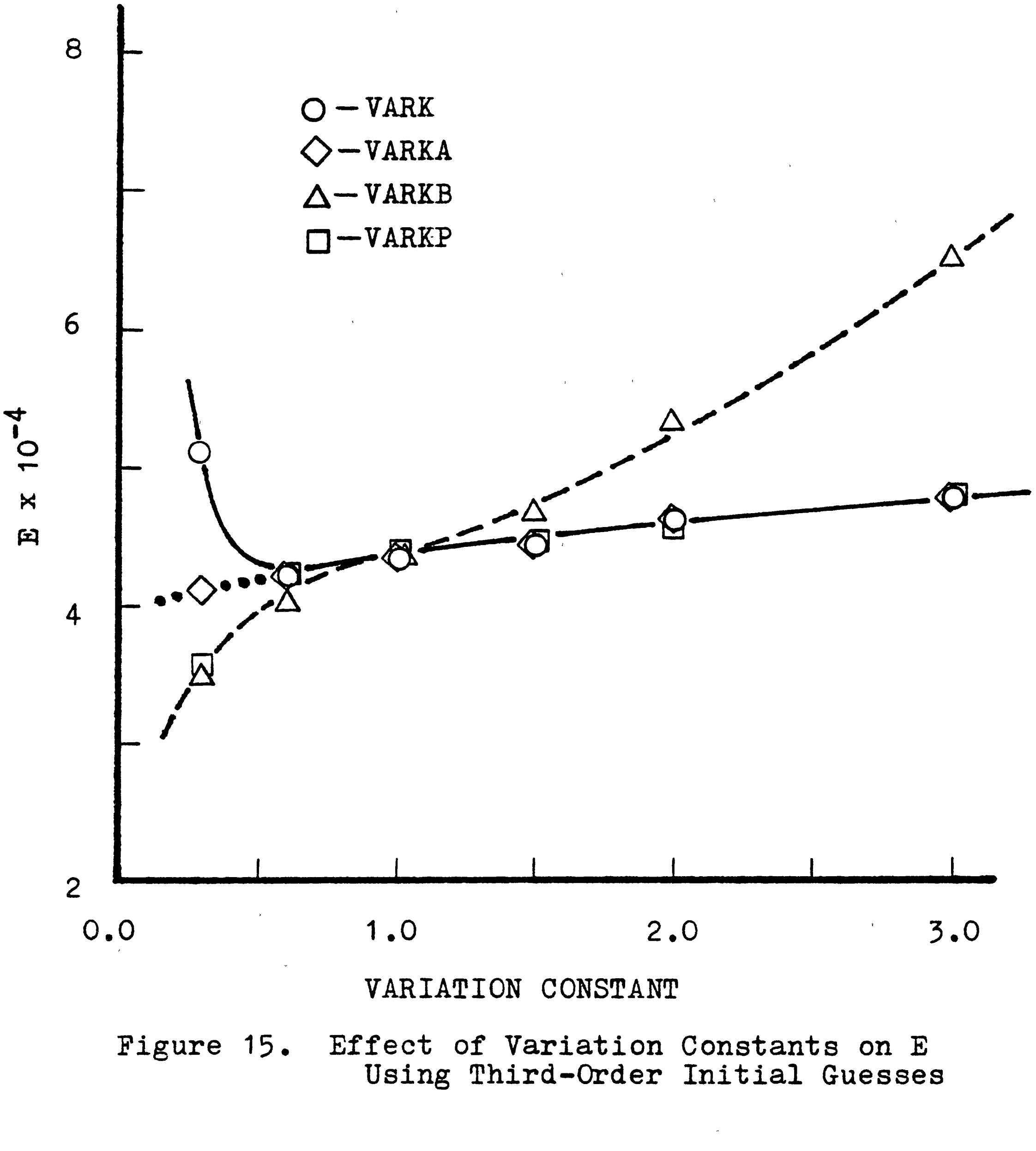


Figure 15. Effect of Variation Constants on E Using Third-Order Initial Guesses

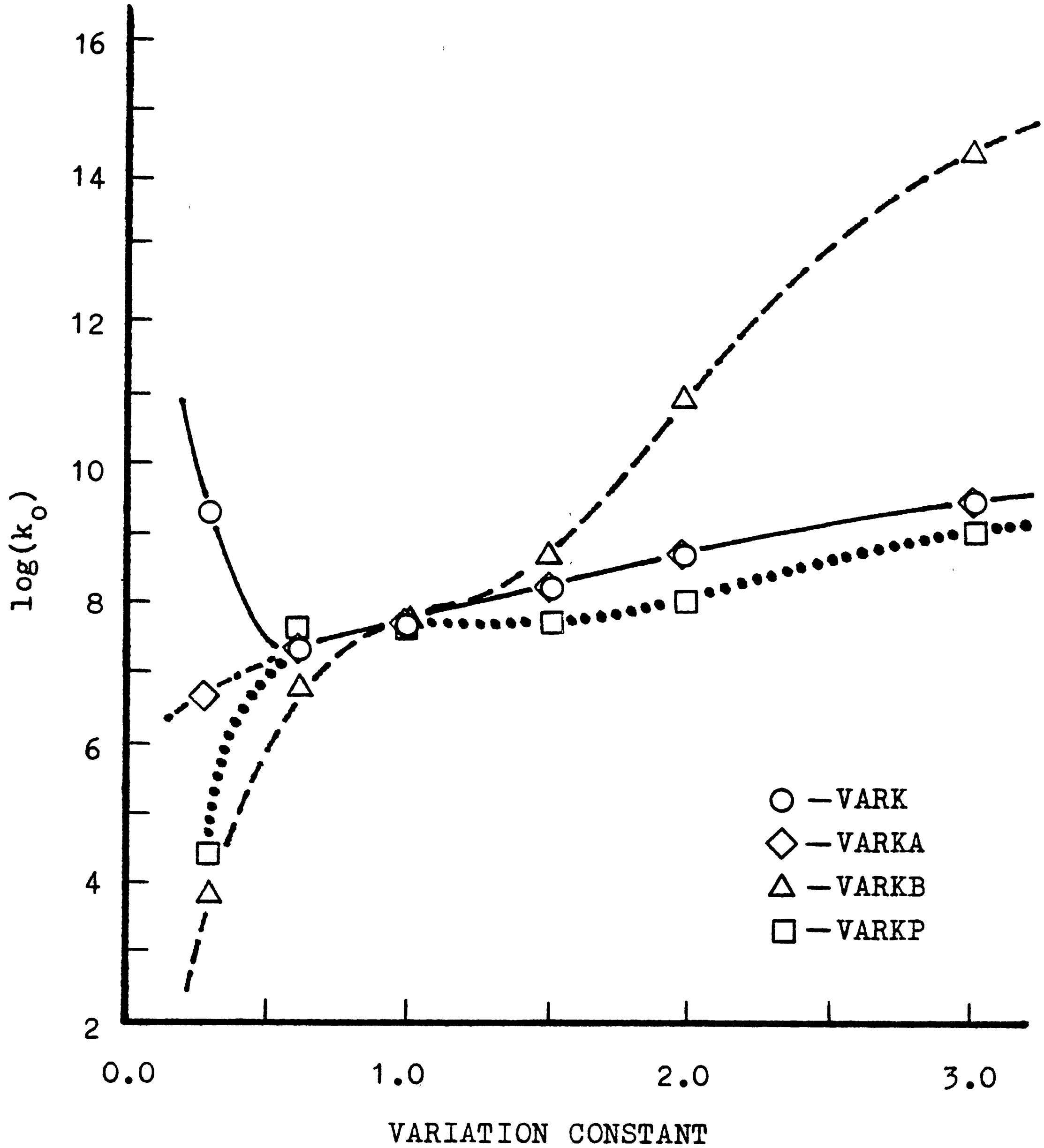


Figure 16. Effect of Variation Constants on k_o Using Third-Order Initial Guesses

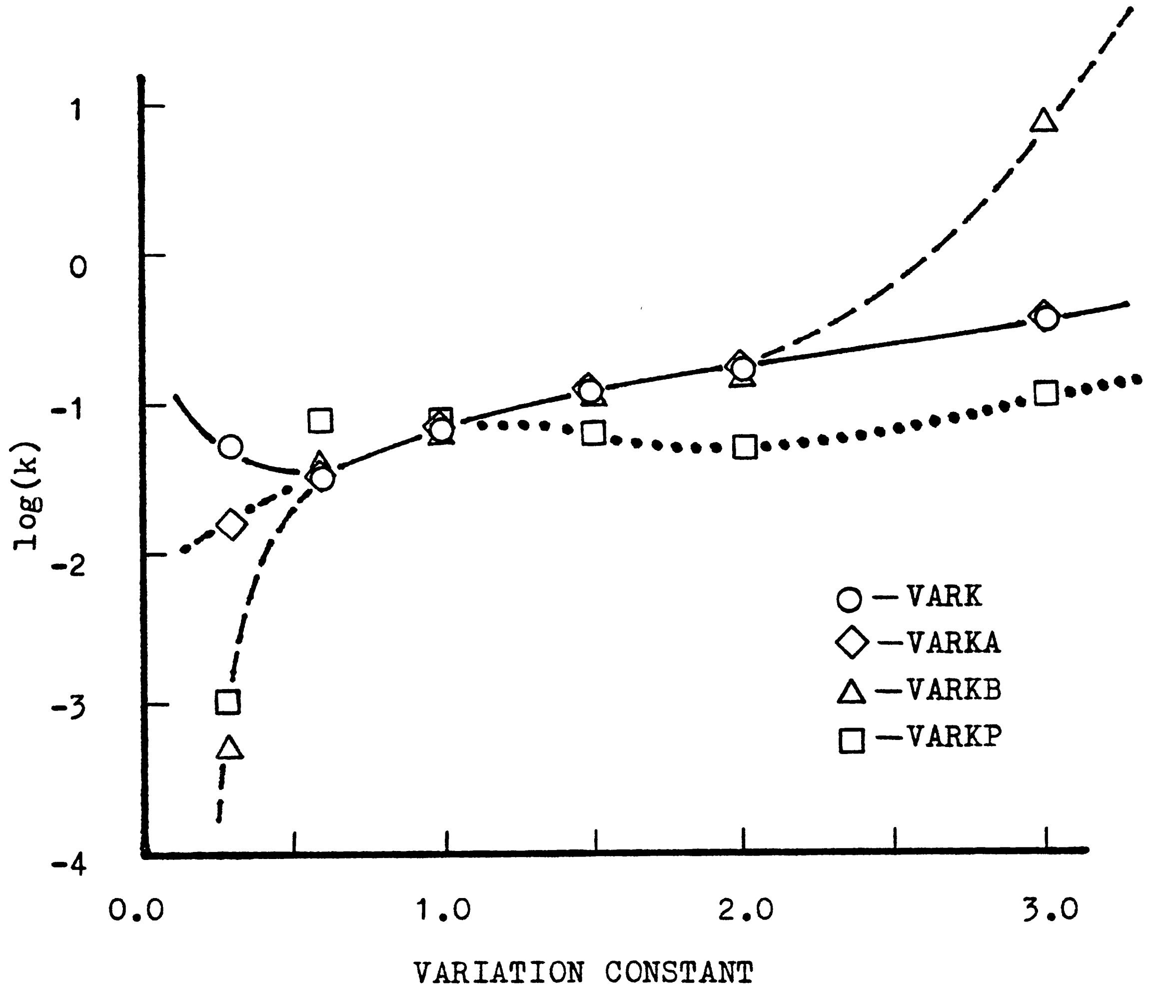


Figure 17. Effect of Variation Constants on k, Evaluated at 590°F, Using Third-Order Initial Guesses

Considering this intrinsic model and the corresponding results, a final comment should be made concerning E. For all three sets of initial guesses used, and with all VARK's set equal to unity, the global model value of E is barely over half that of the intrinsic model (eq. 5.3 E4 compared to 9.6 E4). This implies that pore diffusion is an important rate-determining step (28).

Simulated Data for No DBT Adsorbed

The parameter sensitivity study was continued using the variation of the intrinsic kinetic model in which DBT (component A) is not adsorbed. This mechanism leads to the second of the four models listed in Table IX. No results were collected for this model, however, since no concentrations could be calculated for the intrinsic model in this form.

Simulated Data for No Hydrogen Adsorbed

The intrinsic model variation corresponding to no hydrogen (component B) adsorbed was considered. The model for this mechanism is shown as the third model in Table IX. The relevant information describing the results of computer runs is given in Table XV. The effectiveness factor was computed in the same manner as before, except that the parameter K_B was removed from the computations. The values of η were still essentially one. Only the 2.5-order set of initial guesses were used to generate the results for this intrinsic

TABLE XV

THE SENSITIVITY OF THE GLOBAL MODEL PARAMETERS FOR NO HYDROGEN ADSORBED

Variation Constant	k_o ((wt %)$^{1-N}$/ hr/psig^{M})	E (Btu/lbmol)	M	N	APE
<u>VARK</u>					
0.3	0.26673 E10	0.67200 E5	0.73668	0.69582	0.0682
0.6	0.15688 E11	0.67223 E5	0.73668	0.98499	0.1366
1.0	0.16836 E11	0.67169 E5	0.73811	0.87593	0.2274
1.5	0.34257 E11	0.67176 E5	0.74176	0.96034	0.3410
2.0	0.60700 E11	0.67438 E5	0.73883	1.00	0.4556
3.0	0.72006 E11	0.67130 E5	0.74860	0.98950	0.6863
<u>VARKA</u>					
0.3	0.44633 E10	0.67220 E5	0.73677	0.83185	0.0681
0.6	0.73595 E10	0.67181 E5	0.73780	0.78655	0.1364
1.0	0.16836 E11	0.67169 E5	0.73948	0.87593	0.2274
1.5	0.34600 E11	0.67176 E5	0.74178	0.96322	0.3409
2.0	0.66072 E11	0.67216 E5	0.74446	1.0585	0.4542
3.0	0.71759 E11	0.67122 E5	0.74861	0.98999	0.6857

TABLE XV (CONTINUED)

Variation Constant	k_o	E	M	N	APE
VARKP					
0.3	0.16717 E11	0.67168 E5	0.73947	0.87412	0.2274
0.6	0.16741 E11	0.67168 E5	0.73947	0.87449	0.2274
1.0	0.16836 E11	0.67169 E5	0.73948	0.87593	0.2274
1.5	0.16695 E11	0.67168 E5	0.73947	0.87374	0.2274
2.0	0.16763 E11	0.67169 E5	0.73948	0.87479	0.2274
3.0	0.16690 E11	0.67168 E5	0.73947	0.88364	0.2274

Note: The parameter estimates given here were arrived at after the regression routine had reached the maximum number of iterations allowed (200 iterations).

model. The APE's for this model are all less than 0.7%. However, in every case reported in Table XV, the data-fitting procedure was cut short by MARQ. This was due to an excessive number of iterations required by MARQ to reach the best estimates of the parameters.

The graph of Figure 18 is for the effect of the VARK's on N. The trends produced by increasing the intrinsic reaction rate constant and the DBT adsorption equilibrium constant are to cause the global reaction order to become one, thereby equalling the intrinsic reaction order. Increasing the adsorption of products does not affect the global reaction order over the range of VARKB used.

The effect of the VARK's upon the global pressure order was slight for the case of VARK and VARKA, as shown by Figure 19. Increasing the intrinsic reaction rate constant or the adsorption of DBT shows some trend for increasing M, however. Variation of VARKP showed no effect upon M.

Figure 20 verified that the activation energy was not affected by changes in any of the VARK's. Thus, the plot for the global reaction rate constant, computed according to the Arrhenius relation using E and k_o and evaluated at 590^oF, showed the same trends as displayed by the pre-exponential rate constant, which are given in Figure 21.

The plot for the global reaction rate constant as a function of the VARK's is given in Figure 22. This figure is unique in that the curves for VARK and VARKA are not the same. In fact, the curve for VARKA shows that increased

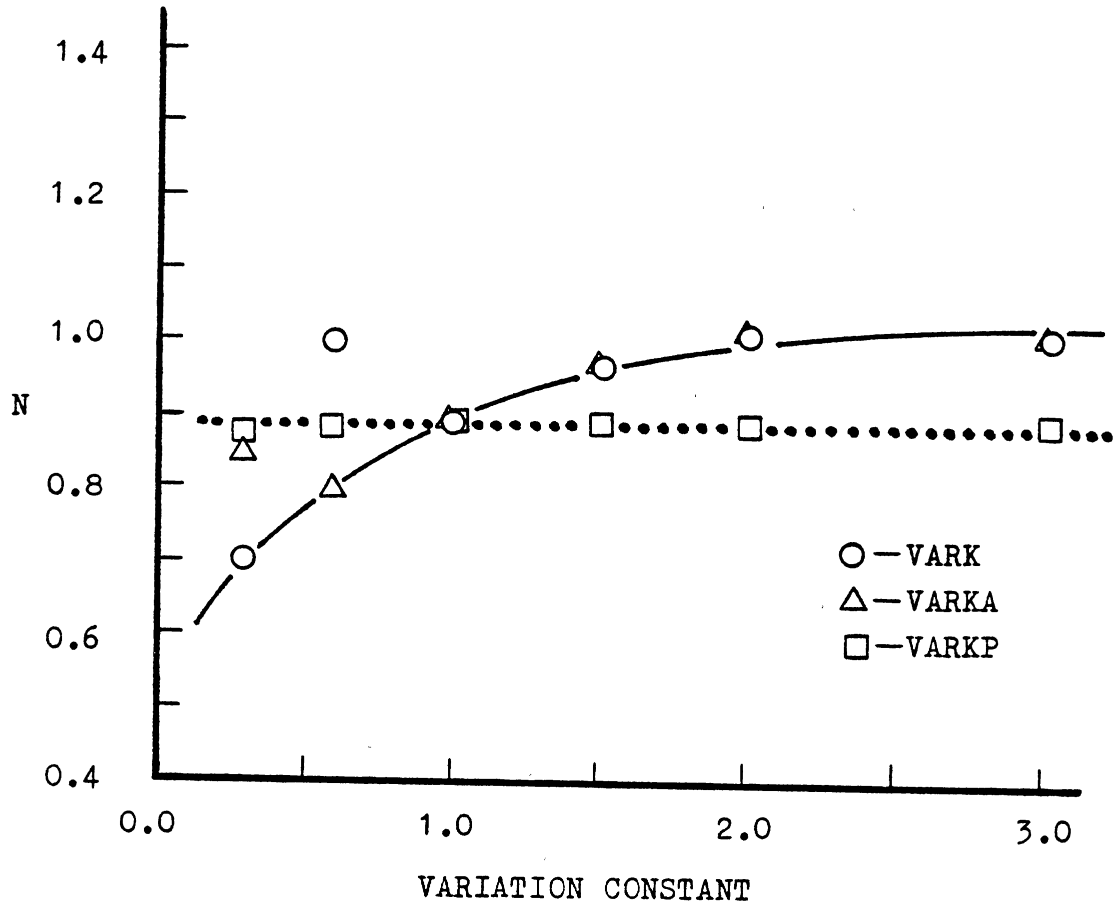


Figure 18. Effect of Variation Constants on N for No Hydrogen Adsorbed

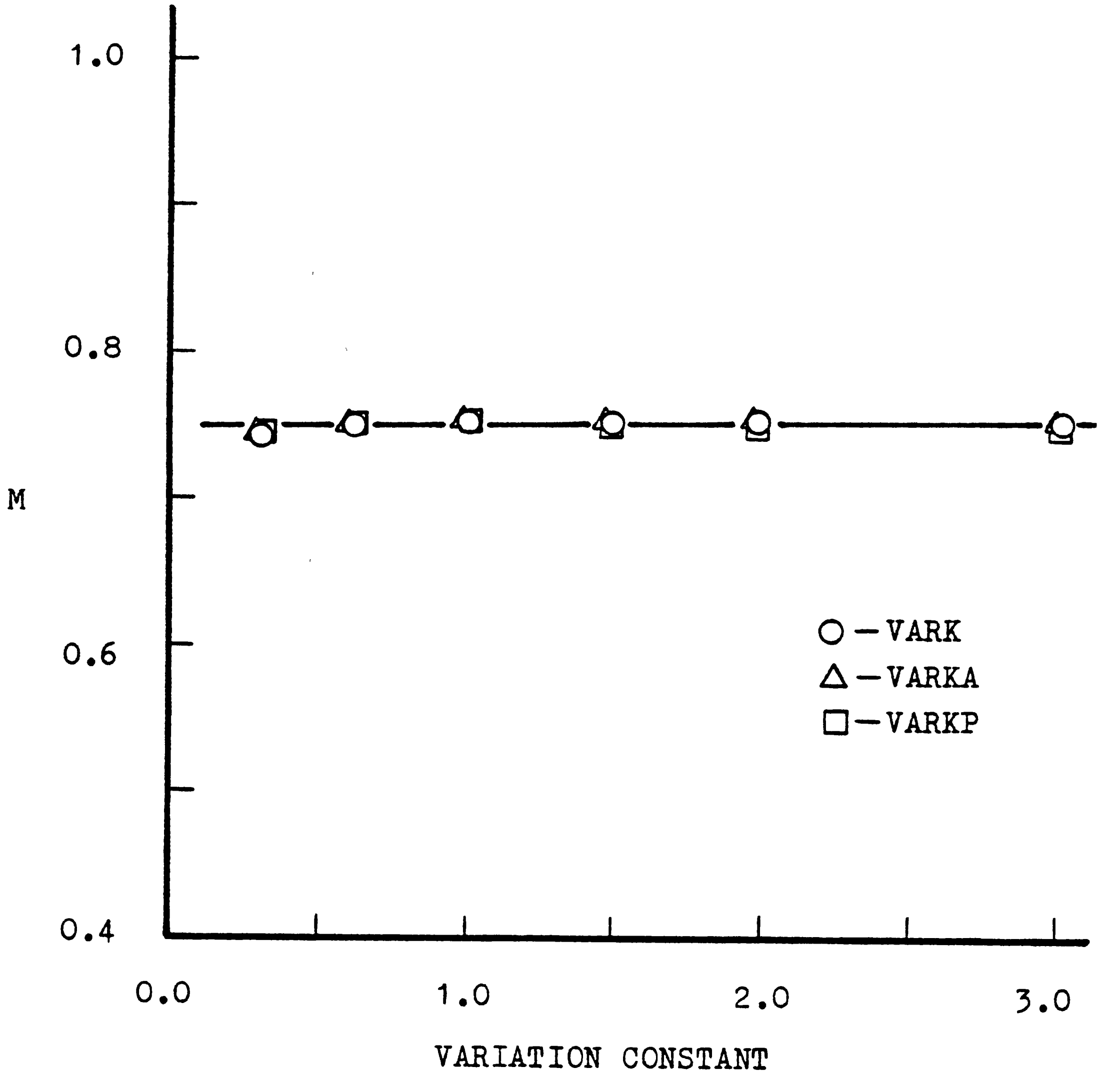


Figure 19. Effect of Variation Constants on M for No Hydrogen Adsorbed

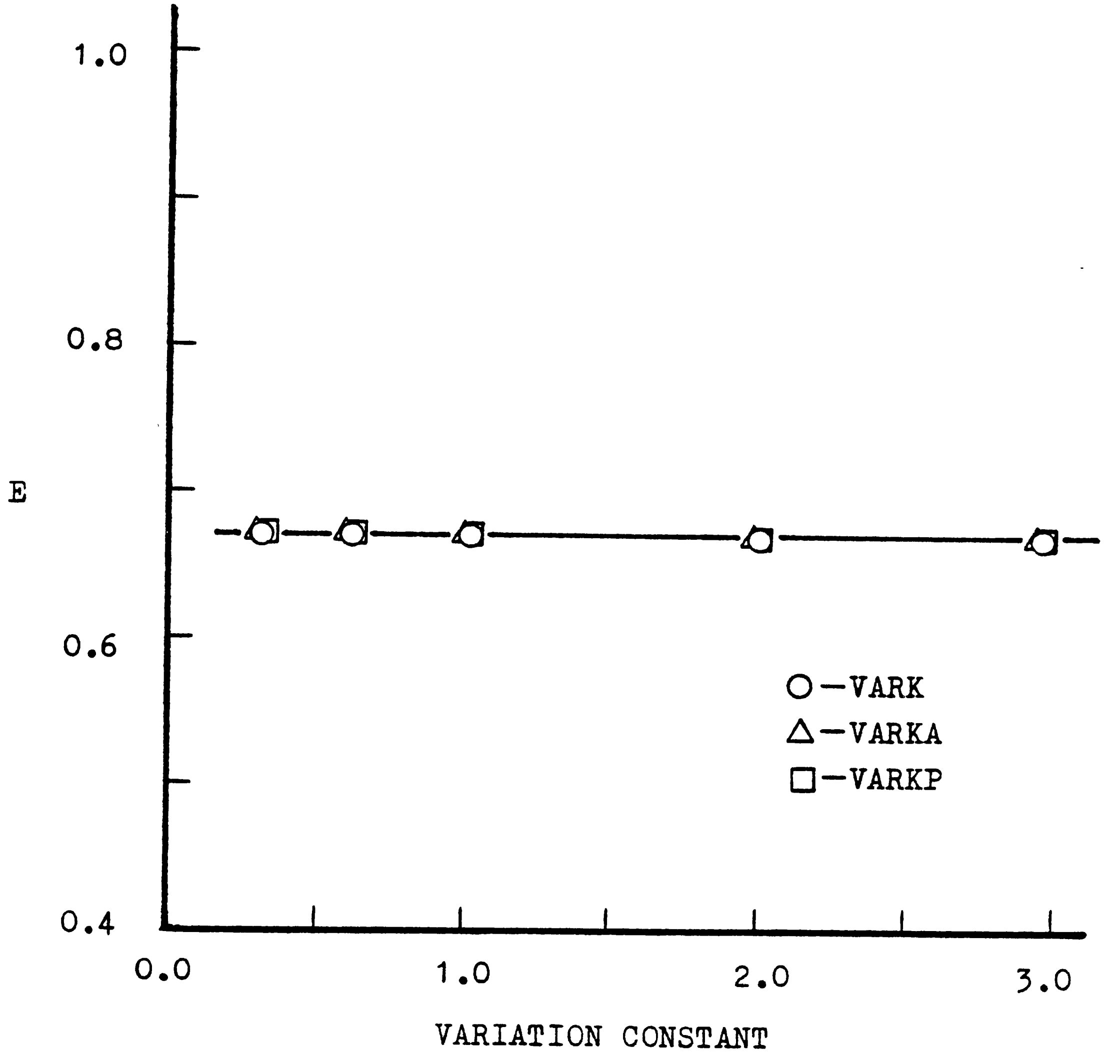


Figure 20. Effect of Variation Constants on E for No Hydrogen Adsorbed

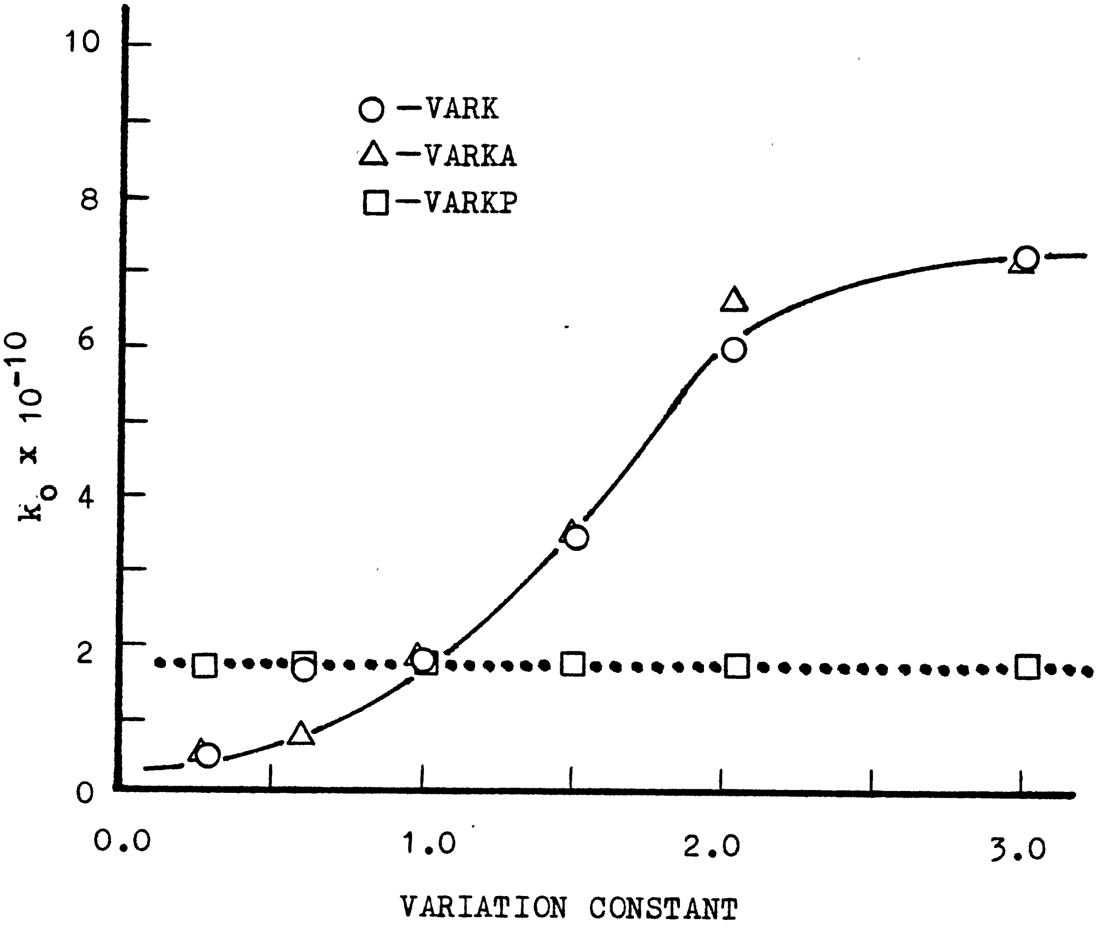


Figure 21. Effect of Variation Constants on k_o for No Hydrogen Adsorbed

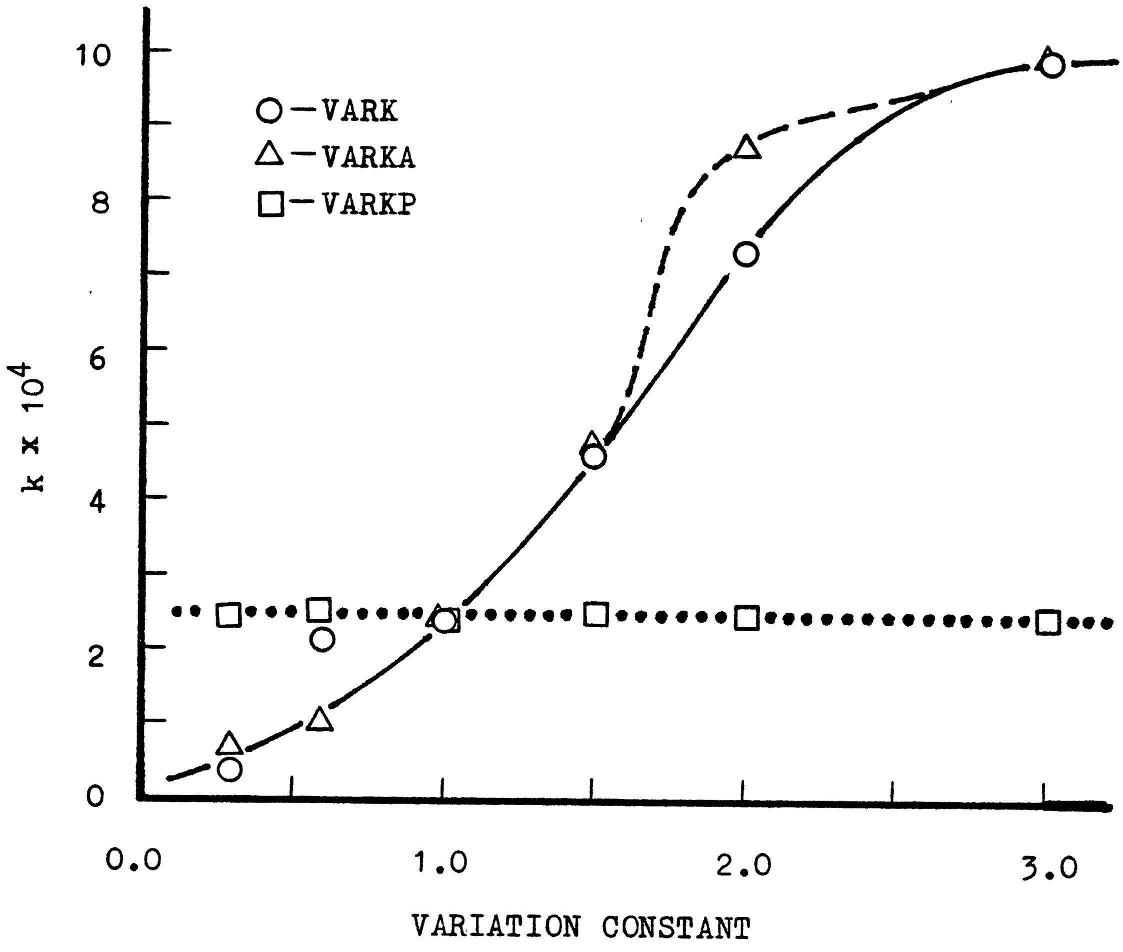


Figure 22. Effect of Variation Constants on k, Evaluated at 590°F, for No Hydrogen Adsorbed

adsorption of DBT causes a corresponding increase in the global reaction rate constant to a point, after which the effect levels off. This effect has been noted for the other intrinsic models used as well. However, no such levelling off occurs for increases in the intrinsic reaction rate constant, instead, the increasing trend continues.

If the adsorption of hydrogen had been the cause of the levelling off in the earlier models the lack of hydrogen adsorption for this model might account for the continued increase in the reaction rate constant. That is, if in the other models the controlling mechanism was switching from surface reaction to adsorption of hydrogen, as speculated. Increased adsorption of products has no effect on the reaction rate constant.

Simulated Data for No Products Adsorbed

The last intrinsic model considered in the parameter sensitivity study is given by the fourth model in Table IX. This model assumes no adsorption of products. The effectiveness factor was computed using the relationship given by eq. [4.8]. The third-order initial guesses were used to obtain the results. Table XVI gives the results for this model. Notice in the table that the concentration order is typically one for all VARK's.

In Figure 23, the concentration order is shown to remain constant. Figure 24 shows the global pressure order to decrease with respect to increases in each of the three

TABLE XVI

THE SENSITIVITY OF THE GLOBAL MODEL PARAMETERS FOR NO PRODUCTS ADSORBED

Variation Constant	k_o ((wt %)$^{1-N}$/ hr/psig^M)	E (Btu/lbmol)	M	N	APE
<u>VARK</u>					
0.3	0.29572 E7	0.39151 E5	0.50633	1.00	1.7078
0.6	0.82184 E7	0.39493 E5	0.47554	1.00	3.4934
1.0	0.20783 E8	0.39901 E5	0.43438	1.00	6.0658
1.5	0.86676 E4	0.32872 E5	0.56737	0.00	7.5750
2.0	0.93564 E8	0.40644 E5	0.34960	1.00	13.8943
3.0	0.20651 E9	0.40985 E5	0.30627	1.00	23.5981
<u>VARKA</u>					
0.3	0.29646 E7	0.39157 E5	0.50638	1.00	1.7080
0.6	0.82285 E7	0.39496 E5	0.47555	1.00	3.4936
1.0	0.20783 E8	0.39901 E5	0.43438	1.00	6.0658
1.5	0.86669 E4	0.32872 E5	0.56735	0.00	7.5744
2.0	0.93415 E8	0.40641 E5	0.34961	1.00	13.8933
3.0	0.20608 E9	0.40982 E5	0.30626	1.00	23.5990

TABLE XVI (CONTINUED)

Variation Constant	k_o	E	M	N	APE
VARKB					
0.3	0.35403 E4	0.32722 E5	0.50512	0.00	2.3660
0.6	0.94511 E4	0.33918 E5	0.52896	0.00	3.6090
1.0	0.20783 E8	0.39901 E5	0.43438	1.00	6.0660
1.5	0.16150 E9	0.42934 E5	0.38715	1.00	7.9970
2.0	0.10727 E10	0.45706 E5	0.32830	1.00	9.7504
3.0	0.46229 E11	0.51465 E5	0.20284	0.98996	15.0473

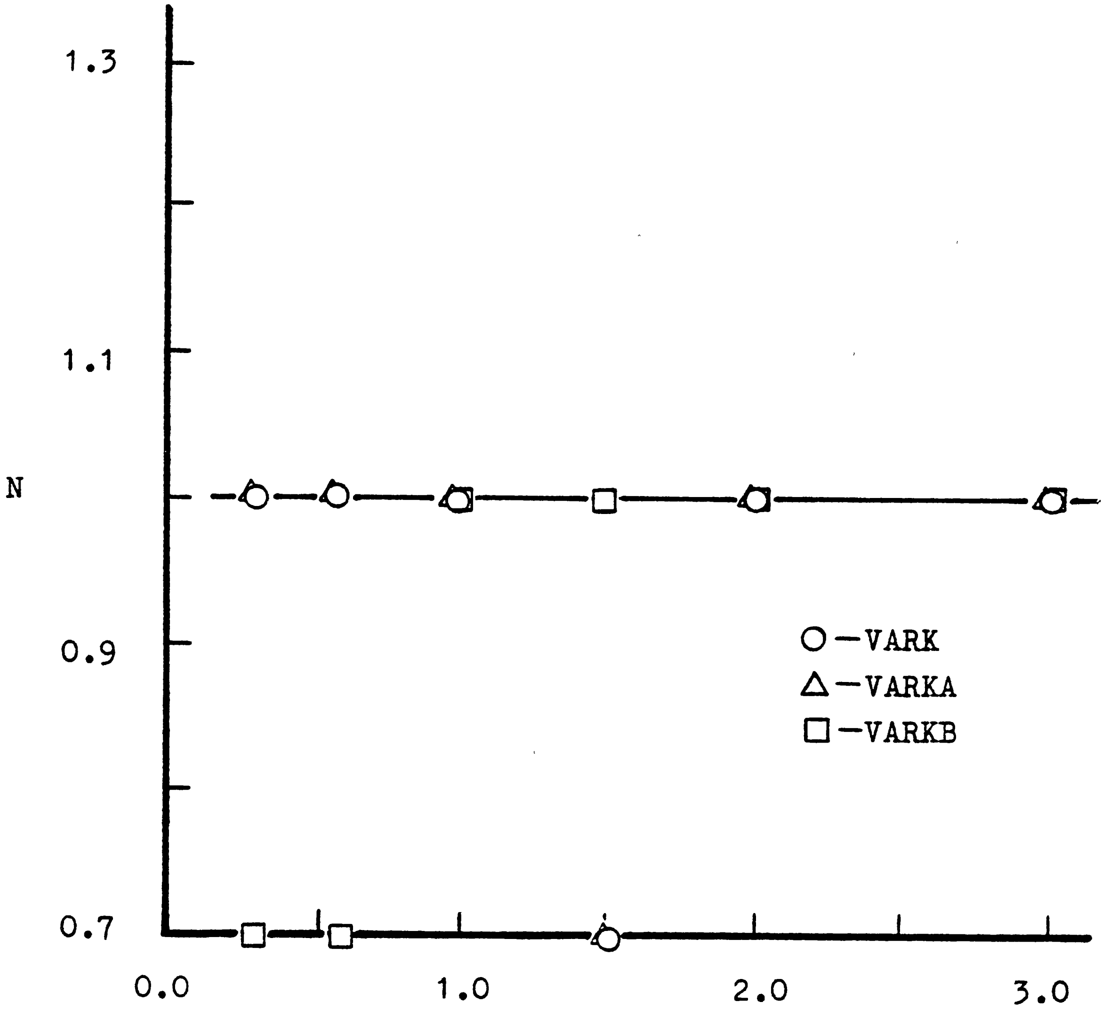


Figure 23. Effect of Variation Constants on N for No Products Adsorbed

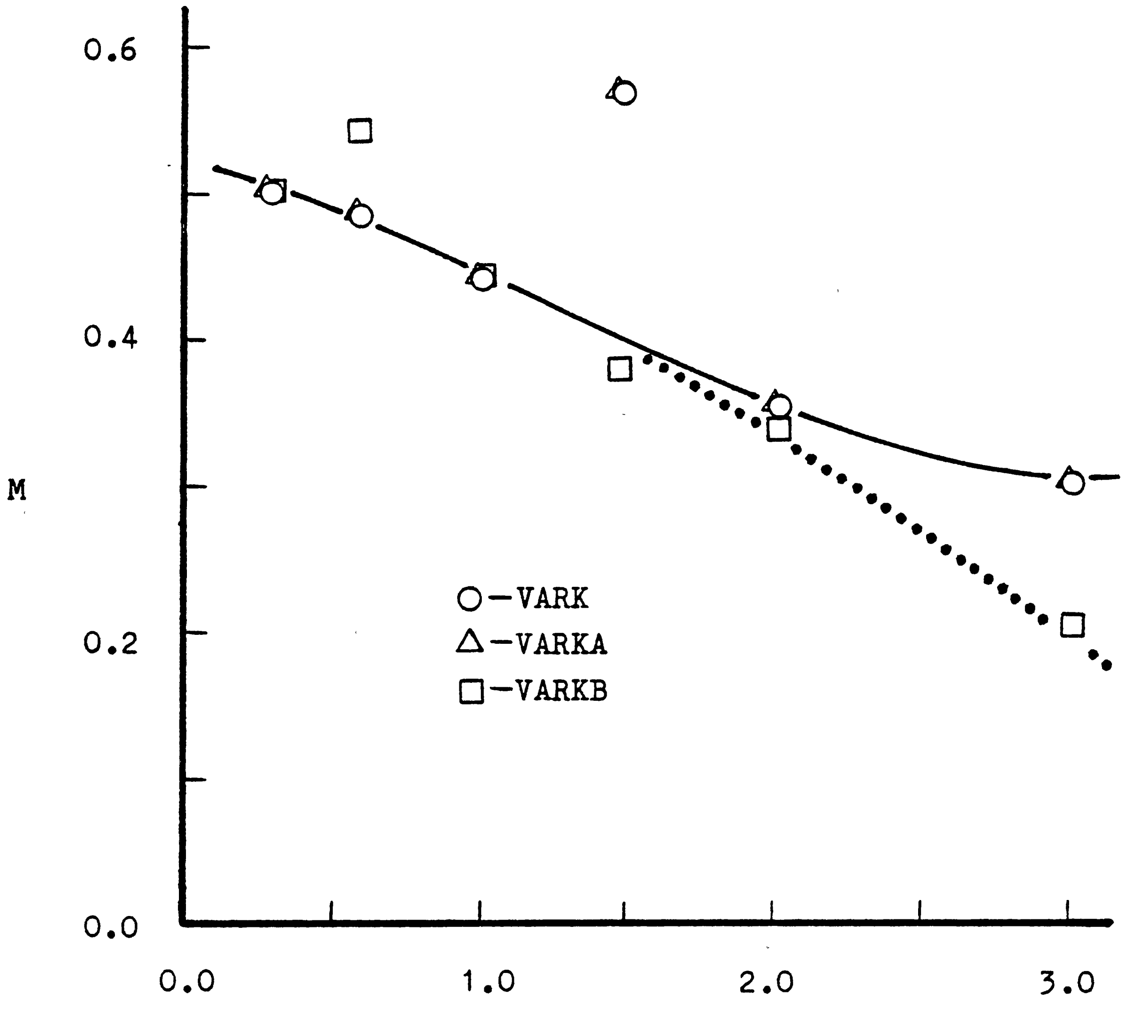


Figure 24. Effect of Variation Constants on M for No Products Adsorbed

intrinsic model parameters. This observation has been seen to hold true for all of the intrinsic models considered which include the adsorption equilibrium constant of hydrogen. The curves for VARK and VARKA, which are identical, level off after a point. The effect of hydrogen adsorption is seen to affect M most dramatically.

The figures illustrating the effect of the VARK's on the activation energy and pre-exponential constant of the global model are, respectively, Figures 25 and 26. The global reaction rate constant was evaluated at 590^{o}F and using the results for E and k_o. The graph for the global reaction rate constant versus the VARK's is given by Figure 27. The curves are shown to practically coincide for all three intrinsic model parameters and show an increase in the observed reaction rate constant results from increases in the intrinsic model parameters. At the high end of the VARK values, though, the global reaction rate constant continues to increase with the adsorption of hydrogen. For the same range, an assymptotic effect is seen in the curves for VARK and VARKA.

A parameter sensitivity study was carried out for one other intrinsic model. The model was an erroneous form of the first intrinsic model listed in Table IX. The results for this model are presented in Appendix B.

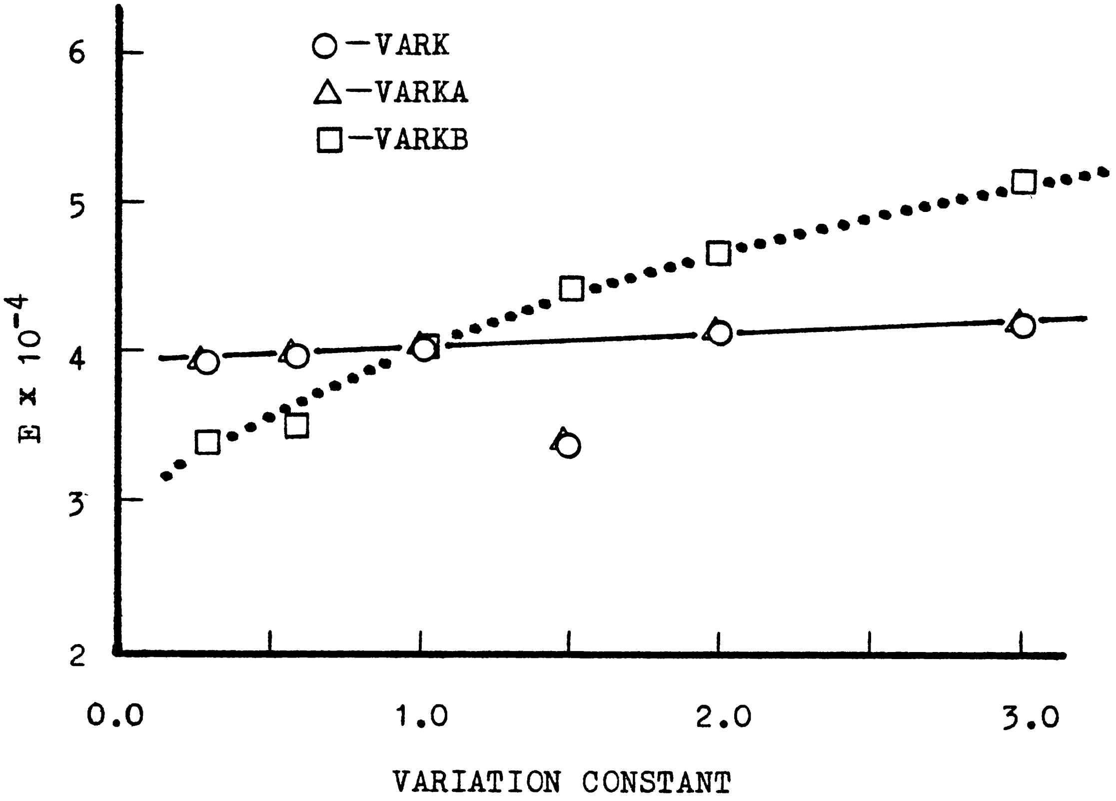


Figure 25. Effect of Variation Constants on E for No Products Adsorbed

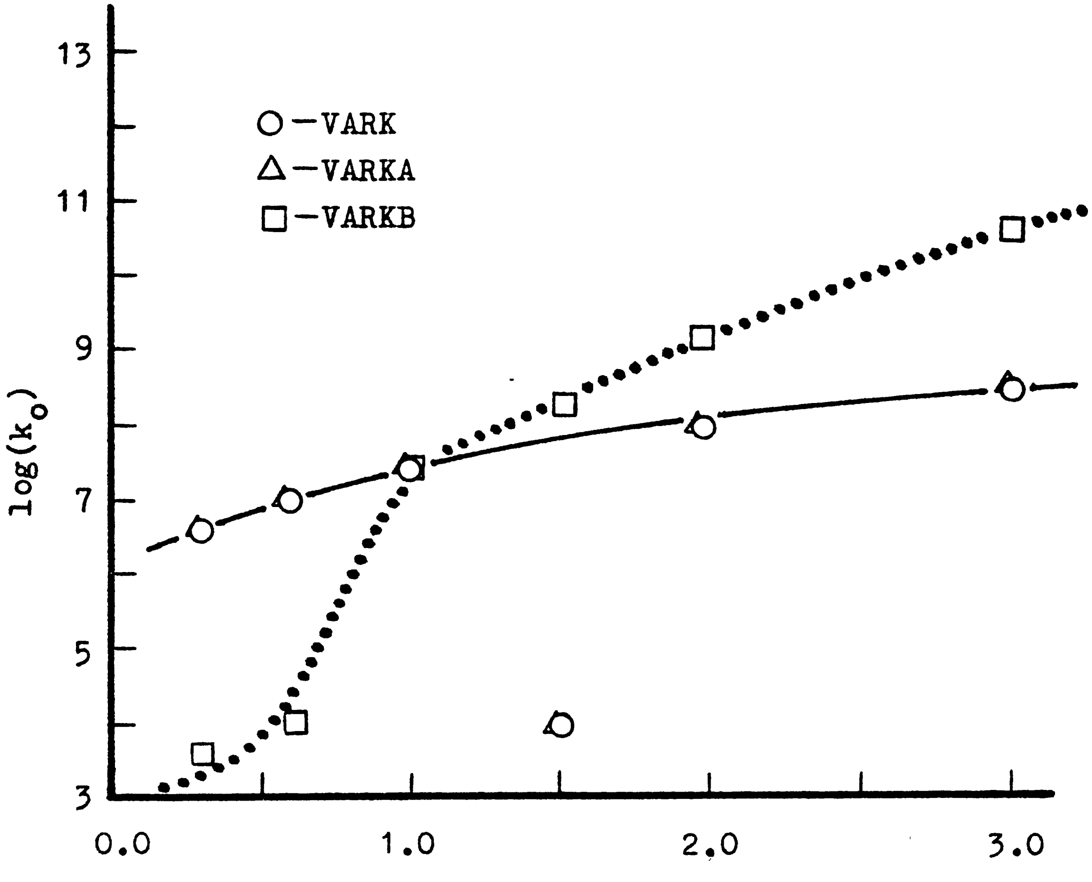


Figure 26. Effect of Variation Constants on k_o for No Products Adsorbed

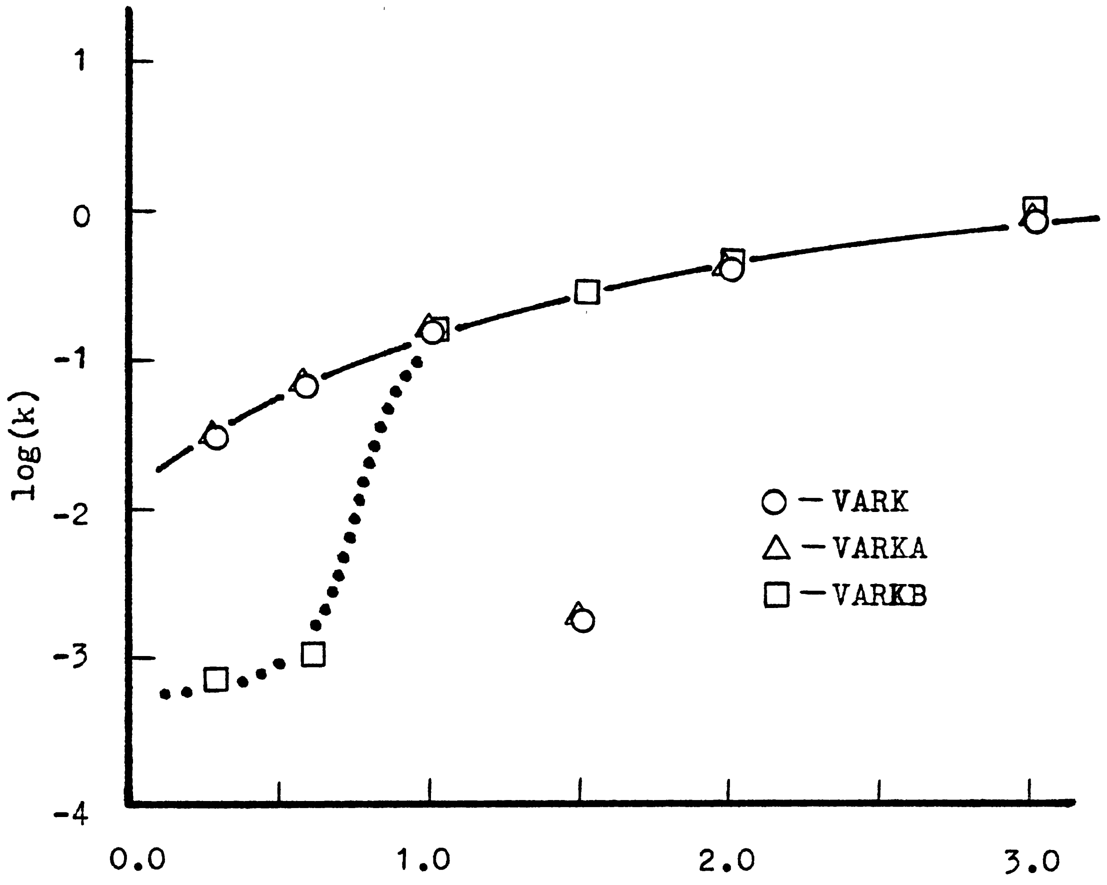


Figure 27. Effect of Variation Constants on k, Evaluated at 590°F, for No Products Adsorbed

CHAPTER V

SUMMARY AND CONCLUSIONS

In order to become more familiar with the aspects of the kinetic modelling of coal-derived liquids hydrotreating, a literature survey was carried out. The most widely-used kinetic models for this purpose are apparently the simple power law types of models, which only describe the overall observed phenomena. These "global" models are capable of describing the hydrotreating data over limited ranges of operating conditions, but are unreliable if scale-up or extrapolation to new operating conditions is the goal. In the literature, several forms of global kinetic expressions were encountered. These factors combined to give discrepant results when the hydroprocessing studies in the literature were compared to one another.

Two global models were fit to data for the HDS of a coal-derived liquid in order to evaluate their ability to describe the kinetic data. One model contained three parameters and the other used four parameters. As expected, the four-parameter model was capable of describing the data more accurately than the three-parameter model. However, data fits using the former model were possible only by stipulating the value of the fourth parameter, so that all four parameters were not allowed to vary independently in the regression process. The reason the stipulation of the fourth parameter was necessary was probably that the initial guesses for the model parameters were not close enough to the final, fitted values of the parameters.

Kinetic models were then developed to describe the intrinsic effects of hydrotreatment systems. These intrinsic models were based on a model compound system which considered the HDS of dibenzothiophene (DBT), a hetrocyclic compound representative of the sulfur-containing compounds in coal-derived liquids. Of the three models developed, one contained four parameters while the other two had three parameters, not including the parameters used to account for non-isothermal effects. The models were fit to literature data obtained at five isotherms, so that the temperature dependence of the parameters in the models were correlated separately.

Data fit results were obtained for only two of the three intrinsic models. Of these two models, only one, the four-parameter model, was fit to the complete range of temperatures contained in the isothermal data sets. The other model was successfully fit to only three of the isotherms and probably could have been fit to the remaining two isotherms if adequate initial guesses for the model parameters had been used. The remaining intrinsic model was not fit to any of the isothermal data sets.

A parameter sensitivity study was conducted using the four-parameter global model. The parameters studied were the global reaction rate constant, comprised of the pre-exponential constant (k_o) and the activation energy (E), the pressure exponent (M), and the heteroatom concentration order (N). These parameters were evaluated in their response to perturbations in the intrinsic mass transfer effects, which were generated from the four-parameter intrinsic model and variations thereof. The intrinsic model variations consisted of the special cases in which (a) hydrogen was not adsorbed and (b) products were not adsorbed. The perturbations of the intrinsic model parameters thus investigated were those corresponding to the intrinsic reaction rate constant and the adsorption equilibrium constants of DBT, hydrogen, and the products.

The interpretation of the results of the parameter sensitivity study was complicated by the dependence of the fitted estimates of the global model parameters upon the initial guesses of those parameters. This phenomenon was probably due to some weakness in the application of the method of regression, which was Marquardt's method. The conclusions drawn from the study are consequentially less specific than desired, although some useful conclusions may still be drawn.

The conclusions developed from the results of this work are:

1. The procedures set forth in this study adequately establish a method by which a four-parameter intrinsic model may be fit to isothermal kinetic data for single-component hydroprocessing systems. Previous studies found in the

literature were capable of utilizing models incorporating no more than three parameters.

2. The stability with respect to the initial guesses of the parameters is much worse in the four-parameter models than in the three-parameter models (isothermal conditions).

3. The parameters of the four-parameter global model behaved similarly in response to changes in the parameters of each of the intrinsic models used, with one exception. The variation of the intrinsic model in which hydrogen adsorption was neglected was the exception. The remaining conclusions apply to the models in which hydrogen adsorption is considered.

4. The global model concentration order, N, has values between zero and two in response to changes in the intrinsic model parameters. This implies that the global concentration order is in the same range as the first-order intrinsic model.

5. The global model hydrogen pressure exponent, M, decreases with increases in the intrinsic reaction rate constant, DBT adsorption and hydrogen adsorption. Increased adsorption of products does not affect M.

6. The value of M is always between zero and one in response to increases in the intrinsic model parameters. This compares to first-order concentration dependence for liquid phase hydrogen in the intrinsic model. Thus, the effect of hydrogen pressure in the global model is less significant than in the intrinsic model.

7. The global model activation energy, E, increases in response to increases in each of the intrinsic model parameters. This effect is also observed for the global model pre-exponential constant, k_o.

8. The global reaction rate constant is increased in response to increases in the intrinsic model parameters. The effects upon k level off at high values of the intrinsic model parameters. This might be due to a switch in the controlling mechanism from surface reaction to hydrogen adsorption.

9. Increases in the equilibrium adsorption of hydrogen are seen to affect each of the global model parameters the most strongly. Hydrogen adsorption is probably an important rate-determining step in the HDS of DBT.

10. The global concentration order is approximately equal to one and is independent of intrinsic model parameter changes when hydrogen adsorption is neglected. Thus, the global concentration order is essentially equal to the intrinsic reaction order for this special case.

As a recommendation, the procedures utilized in this work should be extended to derive and evaluate intrinsic models based on two and more component systems. This model could, for example, provide a kinetic model for the simultaneous HDS and HDN of the reacting components. Such models should be capable of describing multicomponent hydroprocessing kinetics more adequately. A complete intrinsic model describing the reactions of each component in coal-derived liquids may not be necessary if an adequate model is developed based upon only a few reacting components. This program of development would be a great aid in omitting much of the empiricism currently required for the design of coal-derived liquids hydroprocessing systems.

Additionally, some reactor data should be made available to verify the results of the parameter sensitivity study. Thus, comparisons could be made between model predictions and experimental results. This information could provide an invaluable aid in selecting the operating conditions and catalysts used in the design of industrial hydroprocessing equipment.

Finally, if this work is to be extended, a more specific form of Marquardt's method should be used in providing the regressions, as compared to the generalized form used in this work. If Marquardt's method were properly programmed, the sensitivity of the parameters to the initial guesses should not pose such a problem.

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APPENDICES

APPENDIX A

DERIVATION OF AN INTRINSIC MODEL BASED UPON LANGMUIR-HINSHELWOOD KINETICS

The derivation of the rate expression corresponding to a specific reaction/adsorption mechanism is given here. The derivation follows the Langmuir-Hinshelwood rules for reactions on solid catalyst surfaces. The surface reaction occurs between adsorbed reactants A and B, which combine irreversibly to form product P. A dual site adsorption mechanism is considered in which A and P compete for one type of site, designated an L type site, and B adsorbs on an M type site. The overall mass transfer rate is controlled by the surface reaction.

The mass transfer steps involved, which occur in series, are:

1. Liquid phase reactants A and B, with respective concentrations C_A and C_B, diffuse to the liquid-solid interface at the catalyst pellet surface.

2. The reactants adsorb onto the catalyst surface. Reactant A adsorbs onto an L site and B adsorbs onto an M site.

3. The adsorbed A and B molecules react to form a P molecule, which is adsorbed onto an L site.

4. The P molecule desorbs from the catalyst surface.

5. Products P diffuses from the liquid-solid interface into the bulk liquid phase, where P then has concentration C_P.

The adsorption steps mentioned above are assumed to occur reversibly, but not the surface reaction step. Also, the mass transfer resistance in the liquid phase is assumed to be negligible, so that the concentrations at the liquid/solid interface are equivalent to concentrations in the bulk liquid phase.

If l is used to denote a vacant L site and m likewise for a vacant M site, the adsorption/reaction steps may be consecutively expressed as follows:

$$A+l \rightleftharpoons Al \qquad [A.1]$$

$$B+m \rightleftharpoons Bm \qquad [A.2]$$

$$Al+Bm \rightarrow Pl+m \qquad [A.3]$$

$$Pl \rightleftharpoons P+l \qquad [A.4]$$

The corresponding rate expressions may then be given:

$$r_A=0=k_A(C_A/M_A)C_l-k_A'(C_A{}^s/M_A) \qquad [A.5]$$

$$r_B=0=k_B(C_B/M_B)C_m-k_B'(C_B{}^s/M_B) \qquad [A.6]$$

$$-r_A=\overset{*}{k}(C_A{}^s/M_A)(C_B{}^s/M_B) \qquad [A.7]$$

$$r_P=0=k_P'(C_P{}^s/M_P)-k_P(C_P/M_P)C_l \qquad [A.8]$$

where

r_A, r_B, r_P = net adsorption rates, mols "i"/catalyst mass/time.

$-r_A$ = rate of reaction of A, mols A/catalyst mass/time.

C_A, C_B, C_P = bulk liquid phase concentrations, mass of "i"/mass of liquid.

C_A^s, C_B^s, C_P^s = adsorbed species concentrations, mass of "i"/catalyst mass.

C_l, C_m = concentrations of vacant adsorption sites, mols of sites/catalyst mass.

k_A, k_B, k_P = adsorption rate coefficients, mass of liquid/mols of sites/time.

k^* = surface reaction rate coefficient, catalyst mass/mole B/time.

k_A', k_B', k_P' = desorption rate coefficients, 1/time.

M_A, M_B, M_p = molecular weight of species "i"

Now eq. [A.5] may be rearranged to yield

$$C_A^s = K_A^* C_A C_l, \quad K_A^* = k_A/k_A' \qquad [A.9]$$

where K_A^* is the adsorption equilibrium constant in units of mass of liquid per mols of L sites. Taking similar action on eqs. [A.6] and [A.8] gives

$$C_B^s = K_B^* C_B C_m, \quad K_B^* = k_B/k_B' \qquad [A.10]$$

$$C_P^s = K_P^* C_P C_l, \quad K_P^* = k_P/k_P' \qquad [A.11]$$

In eq. [A.10], K_B^* has the units of mass of liquid per mols of M sites. Similarly, K_P^* has the units of mass of liquid per mols of L sites in eq. [A.11]. The adsorbed species concentrations given by eqs. [A.9] and [A.10] may now be utilized in eq. [A.7] to get

$$-r_A = k^*(K_A^*/M_A)(K_B^*/M_B)C_AC_BC_1C_m \qquad [A.12]$$

Elimination of the quantities C_1 and C_m from eq. [A.12] is facilitated by noting that the number of molal L sites per given amount of catalyst mass, N_1, is constant, which is also true for the total number of occupied and vacant M sites per catalyst mass, N_m. Thus,

$$N_1 = C_1+C_A^s/M_A+C_P^s/M_P \qquad [A.13]$$

$$N_m = C_m+C_B^s/M_B \qquad [A.14]$$

Upon substituting eq. [A.9] for C_A^s and eq. [A.11] for C_P^s, eq. [A.13] can be altered to give

$$C_1 = \frac{N_1}{1+K_A^*C_A/M_A+K_P^*C_P/M_P} \qquad [A.15]$$

Similarly, using eq. [A.10] in eq. [A.14],

$$C_m = \frac{N_m}{1+K_B^*C_B/M_B} \qquad [A.16]$$

Now eq. [A.12] may be expressed in terms of the measurable liquid phase concentrations, C_A and C_B, after combination with eqs. [A.15] and [A.16], which yields

$$-r_A = \frac{k^*(K_A^*/M_A)(K_B^*/M_B)N_l N_m C_A C_B}{(1+K_A^*C_A/M_A+K_P^*C_P/M_P)(1+K_B^*C_B/M_B)} \qquad [A.17]$$

This equation can be put into a simpler form by defining new adsorption equilibrium constants and a new reaction rate constant, as follows:

$$k = k^* N_l N_m \qquad [A.18]$$

$$K_A = K_A^*/M_A \qquad [A.19]$$

$$K_B = K_B^*/M_B \qquad [A.20]$$

$$K_P = K_P^*/M_P \qquad [A.21]$$

The units of the new constants are, consequently,

k = (mols of L sites)(mols of M sites)/mols B/catalyst mass/time.

K_A = (liquid mass)(mols A)/mols of L sites/mass of A.

K_B = (liquid mass)(mols B)/mols of M sites/mass of B.

K_P = (liquid mass)(mols P)/mols of L sites/mass of P.

Therefore, eq. [A.17] becomes

$$-r_A = \frac{kK_AK_BC_AC_B}{(1+K_AC_A+K_PC_P)(1+K_BC_B)} \qquad [A.22]$$

When the diffusion of the reactants through the pores of the catalyst offers an important mass transfer resistance consideration, the observed rate of reaction will not be as high as it is without pore diffusion effects. The loss in reaction rate due to this resistance may be compensated for by using the effectiveness factor, η, as a multiplier on the right-hand side of eq. [A.22]. Thus, when inner pore diffusion resistance is not negligible, eq. [A.22] is rewritten as

$$-r_A = \frac{kK_AK_BC_AC_B\eta}{(1+K_AC_A+K_PC_P)(1+K_BC_B)} \qquad [A.23]$$

Thus, eq. [A.23] is the final rate equation used to describe the postulated adsorption/reaction mechanism. The use of this rate equation in the development of an intrinsic kinetic model is illustrated below.

The rate equation given by eq. [A.23] is one of a few considered in this work. The rate equations are used to describe the hydrotreatment kinetics of coal-derived liquid model compound systems. This work concerns the use of a trickle-bed reactor to process the reacting system.

To begin the development of a process model utilizing eq. [A.23], consider an incremental mass of catalyst in a trickle-bed reactor, shown in Figure 28. If the reactor is trickle-bed reactor, shown in Figure 28. If the reactor is assumed to operate at near-plug flow conditions and with negligible evaporation of liquid, the material balance on the incremental mass for component A, the liquid reactant, may be written for steady-state and isothermal operation as

$$\text{input} - \text{output} + \text{generation} = 0 \qquad [A.24]$$

or

$$F_A-(F_A+dF_A)+dW(r_A) = 0 \qquad [A.25]$$

In eq. [A.25], dW is the incremental mass of catalyst in the reactor and r_A is the reaction rate of A, as given by eq. [A.23]. The material balance expressed by eq. [A.25] may now be simplified to give

$$dF_A = dW(r_A) \qquad [A.26]$$

Now, defining X_A as the fractional molar conversion of A, eq. [A.27], which follows, may be applied:

$$F_A = F_{Ao}(1-X_A) \qquad [A.27]$$

differentiating,

$$dF_A = -F_{Ao}dX_A \qquad [A.28]$$

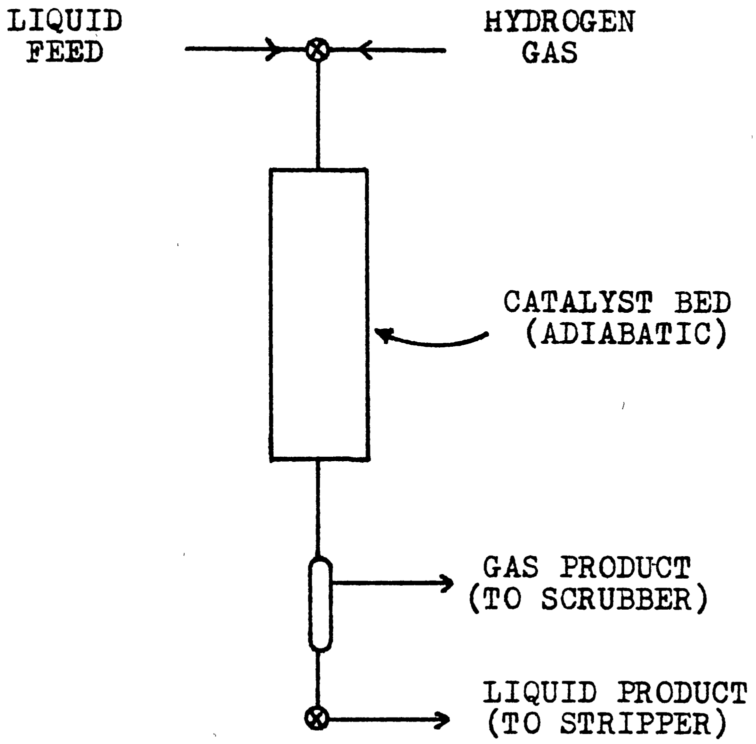

Figure 28. Trickle-Bed Reactor

where F_{Ao} is the molar feed rate of A at the reactor inlet. Combining eqs. [A.26] and [A.28] and integrating gives

$$\int_{0}^{W} dW/F_{Ao} = \int_{X_{Ao}}^{X_A} dX_A/(-r_A) \qquad [A.29]$$

or, after integrating,

$$W/F_{Ao} = \int_{X_{Ao}}^{X_A} dX_A/(-r_A) \qquad [A.30]$$

In order to facilitate the integration that follows, the fractional conversion can be related to the concentration of A as follows:

$$X_A = 1 - \frac{C_A/M_A}{C_{Ao}/M_A} = 1 - C_A/C_{Ao} \qquad [A.31]$$

where C_A = concentration of A in liquid, mass of A/ mass of liquid

C_{Ao} = inlet concentration of A, mass of A/ mass of liquid

Differentiating eq. [A.31] then gives

$$dX_A = -dC_A/C_{Ao} \qquad [A.32]$$

Substitute eq. [A.32] into [A.30] to get

$$WC_{Ao}/F_{Ao} = \int_{C_A}^{C_{Ao}} dC_A/(-r_A) \qquad [A.33]$$

The reason for the change of variables is evident after the introduction of eq. [A.23] into eq. [A.33] which yields

$$\eta\left(\frac{WC_{Ao}}{F_{Ao}}\right)\left(\frac{kK_AK_BC_B}{1+K_BC_B}\right) = \int_{C_A}^{C_{Ao}} (1+K_AC_A+K_PC_P)\frac{dC_A}{C_A} \qquad [A.34]$$

Notice that C_B, which represents the hydrogen dissolved in the liquid phase of the reactor, has been removed from the integral since this concentration is presumed to be constant throughout the reactor (i.e., the hydrogen is saturated in the liquid phase). The reaction rate constant and adsorption equilibrium constants have also been removed since the reactor model is for isothermal operation. Finally, η has been taken out from under the integral mainly to avoid complicating the evaluation of the integral and since the effectivenes factor should be essentially constant, although strictly speaking the effectiveness factor is a function of C_A. The integral in eq. [A.34] cannot be evaluated unless C_P is related to C_A. This relation provided by making overall reactor component balances on A and P. Thus, for component A,

$$\text{input} - \text{output} + \text{generation} = 0 \qquad [A.35]$$

where

$$\text{input} = C_{Ao}\,\rho_{oil}v_{oil}/M_A \qquad [A.36]$$

$$\text{output} = C_A \rho_{oil} v_{oil}/M_A \qquad [A.37]$$

$$\text{generation} = W(r_A) \qquad [A.38]$$

thus,

$$C_{Ao} \rho_{oil} v_{oil}/M_A - C_A \rho_{oil} v_{oil}/M_A + W(r_A) = 0 \qquad [A.39]$$

In eq. [A.39], ρ_{oil} is the density of the flowing liquid in units of mass per volume, and v_{oil} is the volumetric feed rate of the flowing liquid. Making a component P balance,

$$C_{Po} \rho_{oil} v_{oil}/M_P - C_P \rho_{oil} v_{oil}/M_P + W(r_P) = 0 \qquad [A.40]$$

Now, from the stoichiometry of the reaction, notice that the moles reacted by A is equivalent to the molar production rate of P. Thus,

$$W(r_P) = -W(r_A) \qquad [A.41]$$

This relationship allows eqs. [A.39] and [A.40] to be combined to yield the following

$$C_{Po} \rho_{oil} v_{oil}/M_P - C_P \rho_{oil} v_{oil}/M_P = C_A \rho_{oil} v_{oil}/M_A - C_{Ao} \rho_{oil} v_{oil}/M_A \qquad [A.42]$$

Dividing through by ($\rho_{oil} v_{oil}$) and rearranging gives

$$C_P = C_{Po} + (C_{Ao} - C_A)M_P/M_A$$

[A.43]

This is the sought after relation between C_P and C_A, which may be inserted into eq. [A.34] to give

$$\eta\left(\frac{WC_{Ao}}{F_{Ao}}\right)\left(\frac{kK_AK_BC_B}{1+K_BC_B}\right) = \int_{C_A}^{C_{Ao}} \left(1+K_AC_A+K_PC_{Po}+K_PC_{Ao}\frac{M_P}{M_A} - K_PC_A\frac{M_P}{M_A}\right) dC_A/C_A$$

[A.44]

Evaluation of the integral then gives

$$\eta\left(\frac{WC_{Ao}}{F_{Ao}}\right)\left(\frac{kK_AK_BC_B}{1+K_BC_B}\right) = \left(K_A-K_P\frac{M_P}{M_A}\right)(C_{Ao}-C_A) + \left(1+K_pC_{po}+K_pC_{Ao}\frac{M_P}{M_A}\right)\ln {}^{C_{Ao}}/_{C_A}$$

[A.45]

Now the LHSV (liquid-hourly space velocity) may be used in the equation via the following definition of LHSV,

$$\mathrm{LHSV} = \frac{F_{Ao}M_A}{\rho_{oil}C_{Ao}V}$$

[A.46]

where V is the volume of packed reactor. Rearrangement gives

$$\frac{C_{Ao}}{F_{Ao}} = \frac{M_A}{\rho_{oil}V(\mathrm{LHSV})}$$

[A.47]

Insertion of eq. [A.47] into eq. [A.45] gives

$$\left(\frac{\eta\, WM_A}{{}_{oil}V(LHSV)}\right)\left(\frac{kK_AK_BC_B}{1+K_BC_B}\right) = \left(K_A-K_p\frac{M_p}{M_A}\right)(C_{Ao}-C_A)$$
$$+\ \left(1+K_pC_{po}+K_pC_{Ao}\frac{M_p}{M_A}\right)\ln {C_{Ao}}/{C_A} \qquad [A.48]$$

As a final step, this last equation may be rearranged to a mathematical form which better affords numerical solution,

$$f(C_A)=0=\left(K_A-K_p\frac{M_p}{M_A}\right)(C_{Ao}-C_A)+\left(1+K_pC_{po}\right.$$
$$\left.+K_pC_{Ao}\frac{M_p}{M_A}\right)\ln\frac{C_{Ao}}{C_A}-\left(\frac{kK_AK_BC_B}{1+K_BC_B}\right)\frac{\eta\, WM_A}{\rho_{oil}V(LHSV)} \qquad [A.49]$$

APPENDIX B

EVALUATION OF AN ALTERNATIVE INTRINSIC MODEL

Using the procedures described earlier for the data fit technique and the parameter sensitivity study, the intrinsic model given by eq. [B.1] was evaluated.

$$\begin{aligned} f(C_A) = 0 = {} & (1+K_AC_A+K_PC_PM_P/M_A)\ln(C_{Ao} / C_A) \\ & + (K_A-K_PM_P/M_A)(C_{Ao}-C_A) \\ & + \frac{kK_AK_PC_B}{(1+K_BC_B)}\left(\frac{\eta\, w\, M_A}{\rho_{oil}V(LHSV)}\right) \end{aligned} \qquad [B.1]$$

The model given by eq. [B.1] is exactly the same as model I-1 (Table IV) except that the K_B in model I-1 has been replaced by K_P in the term containing η. The derivation leading to eq. [B.1] utilized the same adsorption/reaction mechanism as that used to arrive at model I-1. Thus, the K_P in eq. [B.1] was considered to be an error.

The "error" was not discovered until a full set of results had been obtained for the model. The fact that results could be obtained for this model suggests that there may be some mechanism to which eq. [B.1] corresponds. This matter was not investigated.

Data Fits

The intrinsic model given by eq. [B.1] was fit to the same sets of kinetic data as model I-1. That is, the HDS data for dibenzothiophene. The data fits were obtained using five computer runs corresponding to five different isotherms. These data fit results are given in Table XVII.

TABLE XVII

DATA FIT RESULTS FOR EQUATION [B.1]

Temperature (°F)	k	K_A	K_B	K_P
545	2.850	0.05517	1547.0	79.960
572	12.672	0.24094	995.9	4.7540
590*	47.2	0.344	15437	23.0
	------	-------	------	------
	20.521	0.2886	573.2	4.200
617	37.971	0.3068	36.037	2.815
662	94.61	0.3979	0.15 E-7	1.5027

*The actual data fit results given at 590°F were not used in the parameter sensitivity study. The parameter values given below the dashed line were obtained via the correlations used to generate the intrinsic model parameters in the parameter sensitivity study.

In order to be able to generate kinetic data at 590°F for the parameter sensitivity study, the data fits were correlated using a third-degree polynomial in temperature. Thus, the parameters in the intrinsic model were correlated with temperature as follows:

$$k = k_1 + k_2(T)^2 + k_4(T)^3 \tag{B.2}$$

$$K_A = K_{A1} + K_{A2}(T) + K_{A3}(T)^2 + K_{A4}(T)^3 \tag{B.3}$$

$$K_B = K_{B1} + K_{B2}(T) + K_{B3}(T)^2 + K_{B4}(T)^3 \tag{B.4}$$

$$K_P = K_{P1} + K_{P2}(T) + K_{P3}(T)^2 + K_{P4}(T)^3 \tag{B.5}$$

The data fit results at 590°F were not used in the correlations. Rather, the correlations were used in the parameter sensitivity study to interpolate for what the parameter values at 590°F "should" have been. The coefficients used in the correlations are given in Table XVIII.

Parameter Sensitivity Study

The intrinsic model, eq. [B.1], was used in conjunction with the global model to test the sensitivity of the global model parameters to intrinsic phenomena. The global model used was the same as in the parameter sensitivity studies described earlier.

TABLE XVIII

COEFFICIENTS IN THE CORRELATIONS FOR THE DATA FIT RESULTS FOR EQUATION [B.1]

Intrinsic Model Parameter	c_1	c_2	c_3	c_4
k	-0.4506919 E5	0.1323324 E3	-0.1298443	0.4258204 E-4
K_A	-0.8628306 E3	0.2410342 E1	-0.2243952 E-2	0.6964405 E-6
K_B	-0.2289296 E7	0.6652735 E4	-0.6418989 E1	0.2057172 E-6
K_P	0.4045352 E6	-0.1127905 E4	0.1047687 E1	-0.3242128 E-3

Note: The coefficients c_1, c_2, c_3, c_4 refer to the following equation:

$$K = c_1 + c_2(T) + c_3(T)^2 + c_4(T)^3$$

Two sets of results were obtained during this investigation, according to two sets of initial guesses used. Similar problems were encountered with model I-1, and so are not explained here. The results for 2.5-order initial guesses are given in Table XIX. The results for first-order initial guesses are listed in Table XX.

The results are not discussed in further detail here since they were not used in drawing conclusions in this work. However, the fact that results were obtained for this model was important in that the results verify the adequacy of the procedure used in evaluating four-parameter intrinsic models other than model I-1.

TABLE XIX

SENSITIVITY OF THE GLOBAL MODEL PARAMETERS FOR 2.5-ORDER INITIAL GUESSES, EQ. [B.1]

Variation Constant	k_o ((wt %)$^{1-N}$/ hr/psig^M)	E (Btu/lbmol)	M	N	APE
VARK					
0.1	0.22364 E4	0.34058 E5	0.47656	0.0	0.42016
0.4	0.75785 E4	0.34438 E5	0.51906	0.0	1.3028
0.8	0.10178 E5	0.34214 E5	0.55003	0.0	2.4334
1.0	0.75703 E5	0.35259 E5	0.53885	0.31781	2.9775
1.5	0.34082 E7	0.38078 E5	0.47725	0.77284	4.2403
2.0	0.36802 E8	0.40402 E5	0.42109	0.94422	5.651
3.0	0.36441 E9	0.43157 E5	0.34874	0.98997	8.859
4.0	0.18784 E10	0.45491 E5	0.29136	0.97299	12.726
5.0*	-------	-------	-------	-------	------
VARKA					
0.1	0.23579 E4	0.34182 E5	0.47847	0.0	0.4196
0.4	0.77817 E4	0.34498 E5	0.51989	0.0	1.304
0.8	0.10237 E5	0.34227 E5	0.55021	0.0	2.4369
1.0	0.75703 E5	0.35259 E5	0.53385	0.31781	2.9775
2.0	0.31598 E8	0.40220 E5	0.42363	0.93246	5.627
3.0	0.34833 E9	0.43056 E5	0.34691	0.98997	8.827
4.0	0.14449 E10	0.45105 E5	0.29553	0.96289	12.5465

TABLE XIX (CONTINUED)

Variation Constant	k_o	E	M	N	APE
<u>VARKB</u>					
0.1	0.11140 E4	0.28375 E5	0.62663	0.17405	1.8566
0.4	0.39512 E4	0.30741 E5	0.58644	0.16539	2.3376
0.8	0.25981 E5	0.33734 E5	0.54900	0.24444	2.828
1.0	0.75703 E5	0.35259 E5	0.53385	0.31781	2.976
2.0	0.46927 E8	0.43601 E5	0.47245	0.89241	3.580
3.0	0.71173 E9	0.48741 E5	0.47795	1.0	3.9488
4.0	0.22142 E10	0.51905 E5	0.51986	0.9900	4.169
5.0	0.11389 E11	0.55423 E5	0.51828	1.0	4.3522
<u>VARKP</u>					
0.1	0.82682 E4	0.36430 E5	0.43013	0.0	0.8186
0.4	0.15263 E5	0.35404 E5	0.46961	0.0	2.5303
0.8	0.12432 E5	0.34447 E5	0.53239	0.0	2.8060
1.0	0.75703 E5	0.35259 E5	0.53385	0.31781	2.9775
2.0	0.12670 E11	0.56419 E5	0.20623	2.4174	13.3860
3.0	0.10080 E11	0.51312 E5	0.48055	1.0	45.8420
4.0	0.42875 E14	0.67719 E5	0.45540	1.0	70.5200
5.0*	-------	-------	-------	------	-------

* No solutions for the outlet concentration could be determined at VARK, VARKA, and VARKP equal to 5.0.

TABLE XX

SENSITIVITY OF THE GLOBAL MODEL PARAMETERS FOR FIRST-ORDER INITIAL GUESSES, EQ. [B.1]

Variation Constant	k_o $((\text{wt }\%)^{1-N}/\text{hr/psig}^M)$	E (Btu/lbmol)	M	N	APE
<u>VARK</u>					
0.1	0.12137 E6	0.34468 E5	0.46611	1.0	0.4290
0.4	0.74955 E6	0.36139 E5	0.48073	1.0	1.4006
0.8	0.39048 E7	0.37670 E5	0.47585	1.0	2.454
1.0	0.67697 E7	0.38295 E5	0.46838	1.0	2.959
2.0	0.63570 E8	0.40925 E5	0.40904	1.0	5.657
3.0	0.45330 E9	0.43415 E5	0.33971	1.0	8.935
4.0	0.26339 E10	0.45825 E5	0.28063	1.0	12.300
5.0	0.98362 E10	0.47624 E5	0.23667	1.0	16.098
<u>VARKA</u>					
0.1	0.12836 E6	0.34598 E5	0.46803	1.0	0.4285
0.4	0.98200 E6	0.36213 E5	0.48155	1.0	1.4008
0.8	0.39434 E7	0.37690 E5	0.47600	1.0	2.4540
1.0	0.67697 E7	0.38295 E5	0.46838	1.0	2.959
2.0	0.61075 E8	0.40850 E5	0.40911	1.0	5.636
3.0	0.41656 E9	0.43260 E5	0.34019	1.0	8.869
4.0	0.22964 E10	0.45565 E5	0.28100	1.0	12.229
5.0	0.82737 E10	0.47286 E5	0.23638	1.0	15.484

TABLE XX (CONTINUED)

Variation Constant	k_o	E	M	N	APE
VARKB					
0.1	13015 E6	0.30517 E5	0.54298	1.0	2.810
0.4	0.63506 E6	0.33515 E5	0.50385	1.0	2.808
0.8	0.33579 E7	0.36846 E5	0.47592	1.0	2.888
1.0	0.67697 E7	0.38295 E5	0.46838	1.0	2.959
2.0	0.10203 E9	0.44230 E5	0.46236	1.0	3.548
3.0	0.71173 E9	0.48741 E5	0.47795	1.0	3.949
4.0	0.32556 E10	0.52382 E5	0.49836	1.0	4.195
5.0	0.11389 E11	0.55423 E5	0.51828	1.0	4.352
VARKP					
0.1	0.46285 E6	0.36918 E5	0.42022	1.0	0.8260
0.4	0.20370 E7	0.37240 E5	0.43005	1.0	2.6261
0.8	0.48943 E7	0.37950 E5	0.45684	1.0	3.2120
1.0	0.67697 E7	0.38295 E5	0.46838	1.0	2.959
2.0	0.50492 E8	0.41332 E5	0.49570	1.0	15.914
3.0	0.10080 E11	0.51312 E5	0.48055	1.0	45.842
4.0*	0.42875 E14	0.67719 E5	0.45540	1.0	70.52
5.0*	0.68955 E18	0.86537 E5	0.39931	1.0	75.60

---

*Reached maximum allowed number of iterations in routine MARQ (200 iterations).

APPENDIX C

A DISCUSSION OF EFFECTIVENESS FACTORS

By definition, the effectiveness factor is the ratio of the reaction rate with pore diffusion effects included to the rate which would exist if there were no pore diffusion resistance (7, 28, 29). Although the basic definition of η is almost universally accepted as stated above, the application of effectiveness factors is apparently not in such general agreement.

$$\eta = (3/\kappa^2)(\kappa \coth \kappa - 1)$$

where $\kappa = R_c(k/D_{eff})^{1/2}$, dimensionless

R_c = catalyst particle radius, cm.

k = reaction rate constant, sec^{-1}.

D_{eff} = effective diffusivity, cm^2/sec. [C.1]

The effective diffusivity, D_{eff}, which appears in [C.1] can be calculated from the following equation (20).

$$D_{eff} = \frac{\epsilon D_{AB}}{\tau}\left(1 - \frac{a}{R_p}\right)^4 \qquad [C.2]$$

where ϵ = internal voidage fraction

τ = tortuosity factor

a = molecular size parameter

R_p = average pore radius of catalyst

On the other hand, other authors (20, 30) suggest the use of the effectiveness factor given by eq. [C.3].

$$\eta = (\tanh \phi / \phi) \qquad \text{[C.3]}$$

where $\phi = K/3$, dimensionless.

in which H is the same as defined in eq. [C.1]. The effectiveness factor given by eq. [C.3] is actually derived for slab geometry using a mass balance on an incremental area inside of a single cylindrical pore. This type of effectiveness factor is supposed to be better for general use than eq. [C.1] since the parameter , called the Thiele modulus, has been generalized (20, 30). This generalized Thiele modulus is given by eq. [C.4].

$$\phi = \frac{V_p}{S_x}\sqrt{\frac{N+1}{2}\,\frac{k(C^s)^{N-1}}{D_{eff}}} \quad ,N>-1 \qquad \text{[C.4]}$$

where V_p/S_x = ratio of particle volume to surface area for solid, nonporous catalyst, cm.

N = reaction order

C^s = concentration of reactant at surface of catalyst, arbitrary units.

In eq. [C.4], the product $k(C^s)^{N-1}$ should have the combined units of reciprocal seconds. Using this generalized modulus, the curves for η versus ϕ for any reaction order are in close agreement for any type of geometry, e.g. slab versus spherical. There are, however, exceptions to this general agreement of the curves which are related to the mathematical form of the chosen rate expression (31). In fact, the exceptional cases referred to are for rate expressions of the LHHW type. Since the effectiveness factors used in the mathematical model are not derived from the basic LHHW rate expressions, though, the exceptional cases are of no concern to this work.

The fact that eqs. [C.1] and [C.3] predict about the same effectiveness factors over the entire range of η, i.e. from zero to one, is shown numerically by Table XXI. At both low and high the agreement is very close. Even at the worst point of comparison, which is in the medium range of values, the two equations still compare to within twenty percent of each other. Therefore, the type of effectiveness factor given by eq. [C.3] is used for the intrinsic kinetic model developed in this work.

TABLE XXI

COMPARISON OF EFFECTIVENESS FACTORS*

	equation [3.16]		equation [3.18]	
k	κ	η	Φ	η
10	0.20089	0.997300	0.066965	0.998507
50	0.44921	0.986787	0.140740	0.992593
100	0.63529	0.974082	0.211762	0.985315
500	1.42054	0.886991	0.473514	0.931407
1000	2.00895	0.804702	0.669649	0.873217
5000	4.49215	0.519333	1.497381	0.604171
10000	6.35285	0.397898	2.117618	0.458752
50000	14.20541	0.196320	4.735137	0.211155
100000	20.08948	0.141899	6.696492	0.149332
500000	44.92146	0.065297	14.973800	0.066783

* The parameters in this table are defined in their respective equations. The values used to compute the results given here were: $D_{eff} = 0.758819 \times 10^{-5}$ cm^2/s ; $R_c = 0.01$ cm.

APPENDIX D

LISTING OF THE MODIFIED MARQUARDT NONLINEAR REGRESSION ROUTINE

```
$JOB            ,LIBLIST
      EXTERNAL EXFIT,DELMN
      JX=1
      DELN=DABS(DELMN(JX))
      CALL FUNK(FIT)
      CALL STSET
      CALL STEPT(EXFIT)
      STOP
      END

$ENTRY
      SUBROUTINE EXFIT(FITM)
      DOUBLE PRECISION FIT,X
      DIMENSION FITM(10)
          COMMON/CDAT/ FIT(300),Y(300),YSIG(300),NPTS
        COMMON/CSTEP/X(20),XMAX(20),XMIN(20),DELTX(20),   DELMN(20),
     *     ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),
     *     NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW
       RETURN
       END
      SUBROUTINE STSET                                                  STSETM 1
C                                                                       STSETM 2
C   SUBROUTINE UPDATED MAY 1981 BY J. CHANDLER, OSU COMPUTER SCIENCE    STSETM 2
C   DEPARTMENT--J. HANSON UCC USER SERVICES                             STSETM 2
C                                                                       STSETM 2
C   STSET SETS SOME INPUT QUANTITIES TO DEFAULT VALUES, FOR MARQ.       STSETM 3
C                                                                       STSETM 4
C   NOTE..........                                                      STSETM 5
C   THIS VERSION OF STSET MAY ALSO BE USED WITH STEPIT, SIMPLEX,        STSETM 6
C   STP, MAUFE, AND MINF.                                               STSETM 7
C                                                                       STSETM 8
C   USAGE.....                                                          STSETM 9
C   CALL STSET.  THEN SET SOME INPUT QUANTITIES (NV AND NPTS, AT LEAST) STSETM10
C   AND RESET ANY OF THOSE SET IN STSET (BETTER VALUES OF X, ETC.)      STSETM11
C   BEFORE CALLING MARQ OR THE STEPT-MARQ INTERFACE ROUTINE.            STSETM12
C                                                                       STSETM13
      DOUBLE PRECISION XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,FLAME,FNL,        STSETM14
     *     RELDF,RELMN,FZERO,HUGE      ,X                               STSETM15
C                                                                       STSETM16
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20),       STSETM17
     *     ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),                     STSETM18
     *     NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW                 STSETM19
      COMMON /NLLS4/ FLAMB,FNL,RELDF,RELMN,METHD,KALCF,KORDF,MAXIT,     STSETM20
     *     LEQU,MXSUB,MXUPD                                             STSETM21
C                                                                       STSETM22
C                            KW ...  LOGICAL UNIT NUMBER OF THE PRINTER STSETM23
      KW=6                                                              STSETM24
      NVMAX=20                                                          STSETM25
C                            THE USER MUST SET NV AFTER CALLING STSET.  STSETM26
      NV=-1                                                             STSETM27
      HUGE=1.E30                                                        STSETM28
      FZERO=0.                                                          STSETM29
      NTRAC=0                                                           STSETM30
      NFMAX=32767                                                       STSETM31
      MAXIT=20                                                          STSETM32
      MXSUB=25                                                          STSETM33
      METHD=1                                                           STSETM34
      KALCF=0                                                           STSETM35
      KORDF=1                                                           STSETM36
```

```
 32           LEQU=0                                                                        STSETM37
 33           NFLAT=1                                                                       STSETM38
 34           MATRX=106                                                                     STSETM39
 35           NXTRA=0                                                                       STSETM40
 36           FLAMB=1.                                                                      STSETM41
 37           FNU=10.                                                                       STSETM42
 38           RELDF=1.E-8                                                                   STSETM43
 39           RELMN=1.E-8                                                                   STSETM44
        C                                                                                   STSETM45
 40           DO 10 JX=1,NVMAX                                                              STSETM46
 41              X(JX)=RZERO                                                                STSETM47
 42              XMAX(JX)=HUGE                                                              STSETM48
 43              XMIN(JX)=-HUGE                                                             STSETM49
 44           [illegible]                                                                   STSETM50
 45           [illegible](JX)=RZERO                                                         STSETM51
 46              MASK(JX)=0                                                                 STSETM52
 47     10    CONTINUE                                                                      STSETM53
        C                                                                                   STSETM54
 48           RETURN                                                                        STSETM55
 49           END                                                                           STSETM56
**WARNING**  COMMON BLOCK CSTEP  HAS A DIFFERENT LENGTH THAN WAS SPECIFIED IN A PREVIOUS SUBPROGRAM;GRE
 50           SUBROUTINE STEPT (FUNK)                                                       STMARQ 1
        C                                                                                   STMARQ 2
        C  UPDATED MAY 1981 BY J.P. CHANDLER, OSU DEPARTMENT OF COMPUTING                   STMARQ 2
        C  AND INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES                           STMARQ 2
        C                                                                                   STMARQ 2
        C  INTERFACE TO MAKE MARQ LOOK LIKE STEPT.                                          STMARQ 3
        C                                                                                   STMARQ 4
        C  TO USE THIS ROUTINE, SET THE VALUES OF LPDMA AND LPDMB, AND SET                  STMARQ 5
        C  THE DIMENSIONS OF THE ARRAYS P, FITSV, FIT, Y, AND YSIG.                         STMARQ 6
        C  NORMALLY THE DIMENSIONS ARE....                                                  STMARQ 7
        C     P(LPDMA,LPDMB), FITSV(LPDMA), FIT(LPDMA), Y(LPDMA), YSIG(LPDMA),              STMARQ 8
        C  WHERE LPDMA IS .GE. NPTS AND LPDMB IS .GE. NV.                                   STMARQ 9
        C                                                                                   STMARQ10
        C  COMMON/CDAT/ DOES NOT APPEAR IN ANY ROUTINE OF THE MARQ PACKAGE                  STMARQ11
        C  OTHER THAN THIS ONE, SO THIS IS THE ONLY ROUTINE THAT MUST BE                    STMARQ12
        C  RECOMPILED WHEN THE DIMENSIONS OF THE ARRAYS ARE CHANGED.                        STMARQ13
        C                                                                                   STMARQ14
        C  THE FOLLOWING EXTERNAL STATEMENT IS REQUIRED BY SOME COMPILERS                   STMARQ15
        C  (WATFIV, FOR EXAMPLE) AND FORBIDDEN BY OTHERS (MODCOMP II).                      STMARQ16
 51           EXTERNAL FUNK                                                                 STMARQ17
        C                                                                                   STMARQ18
 52           DOUBLE PRECISION FIT,FITSV          ,Y,YSIG,P                                 STMARQ19
        C                                                                                   STMARQ20
 53           DIMENSION P(300,20),FITSV(300)                                                STMARQ21
 54           COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS                                  STMARQ22
        C                                                                                   STMARQ23
 55           LPDMA=300                                                                     STMARQ24
 56           LPDMB=20                                                                      STMARQ25
        C                                                                                   STMARQ26
 57           CALL MARQ (FUNK,Y,YSIG,NPTS,FIT,FITSV,P,LPDMA,LPDMB)                          STMARQ27
        C                                                                                   STMARQ28
 58           RETURN                                                                        STMARQ29
 59           END                                                                           STMARQ30
**WARNING**  COMMON BLOCK CDAT   HAS A DIFFERENT LENGTH THAN WAS SPECIFIED IN A PREVIOUS SUBPROGRAM;GRE
 60           SUBROUTINE MARQ (FUNK,Y,YSIG,NPTS,FIT,FITSV,P,LPDMA,LPDMB)                     MARQ    1
        C                                                                                    MARQ    2
        C  MARQ 3.0          A.N.S.I. STANDARD FORTRAN          MAY 1981                     MARQ    3
```

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C                 DEPARTMENT OF COMPUTING AND INFORMATION SCIENCES
C                 OKLAHOMA STATE UNIVERSITY, STILLWATER, OKLAHOMA 74074
C
C     MARQ PERFORMS A NONLINEAR LEAST SQUARES FIT OF A USER-SUPPLIED
C     FUNCTION TO A GIVEN SET OF DATA, USING MARQUARDT-S METHOD, OR THE
C     GAUSS-NEWTON METHOD, OR A MODIFIED GAUSS-NEWTON METHOD.
C
C    UPDATE ADDED TO WATFIV LIBRARY BY J. HANSON, UCC USER SERVICES
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C     INPUT QUANTITIES.....  FUNK,X(*),XMAX(*),XMIN(*),DELMN(*),NF,NTRAC,
C                            MASK(*),MATRX,NFMAX,NFLAT,KW,
C                            Y(*),YSIG(*),NPTS,LFCCL,
C                            FLAMB,FNU,RELDF,METHD,KALCP,KORDP,
C                            MAXIT,LEQU,MXSLE
C
C     OUTPUT QUANTITIES....  X(*),FOBJ,ERR(*,*),KFLAG,FIT(*)
C     SCRATCH VECTOR.......  DEL1X(*)
C     UNUSED QUANTITIES (INCLUDED FOR COMPATIBILITY WITH STEPIT COMMON)....
C                                  JVARY,NXTRA,NCREP,KERFL
C
C        FUNK         --  THE NAME OF THE SUBROUTINE CALLED TO OBTAIN
C                             THE FITTED VALUES IF KALCP=0
C
C        X(JX)        --  THE JX-TH PARAMETER
C        XMAX(JX)     --  THE UPPER LIMIT FOR X(JX)
C        XMIN(JX)     --  THE LOWER LIMIT FOR X(JX)
C        DELMN(JX)    --  THE CONVERGENCE TOLERANCE FOR X(JX)
C        FOBJ         --  RETURNS THE FINAL VALUE OF PHI, THE WEIGHTED
C                             SUM OF SQUARES (PHI IS BEING MINIMIZED AS A
C                             FUNCTION OF THE X(JX))
C
C        NV           --  THE NUMBER OF PARAMETERS
C        NTRAC        --  USER PRINT CONTROL
C                             =-3, NO OUTPUT EXCEPT FATAL ERROR MESSAGES
C                             =-2, NO OUTPUT EXCEPT DIAGNOSTIC MESSAGES
C                             =-1, STANDARD OUTPUT EXCEPT FINAL FIT VALUES
C                             = 0, STANDARD OUTPUT
C                             = 1, ALSO PRINTS RESULTS OF EACH ITERATION
C                             = 2, ALSO PRINTS THE COEFFICIENT MATRIX, GSAV
C                             = 3, ALSO PRINTS THE JACOBIAN MATRIX, P
C        MATRX        --  NONZERO IF STATISTICAL ERRORS ARE TO BE COMPUTED
C        MASK(JX)     --  NONZERO IF X(JX) IS TO BE HELD FIXED
C        NFMAX        --  THE MAXIMUM NUMBER OF FUNCTION COMPUTATIONS
C        NFLAT        --  NONZERO IF THE SEARCH IS TO TERMINATE WHEN TWO
C                             ITERATIONS GIVE IDENTICAL VALUES OF PHI
C
C        KW           --  THE LOGICAL UNIT NUMBER OF THE PRINTER
C        ERR(JX,KX)   --  RETURNS THE ERROR MATRIX
C        KFLAG        --  RETURNED .GT. ZERO FOR A NORMAL EXIT,
C                             RETURNED .LT. ZERO FOR AN ABNORMAL EXIT
C
C        Y(JPT)       --  THE JPT-TH DATA ORDINATE
C        YSIG(JPT)    --  THE EXPECTED ERROR IN Y(JPT)
C        NPTS         --  THE NUMBER OF DATA OBSERVATIONS
C        FIT(JPT)     --  THE JPT-TH FITTED VALUE
C        FITSV        --  A SCRATCH VECTOR OF NPTS VALUES
C        P(JPT,JX)    --  THE FIRST PARTIAL DERIVATIVE
C                             OF FIT(JPT) WITH RESPECT TO X(JX)
C        LPDMA        --  THE FIRST DIMENSION OF THE ARRAY CONTAINING P
```

```
C                    (LPCOL MUST BE .GE. NPTS IF KALCP IS .GE. ZERO)
C     LPCMB     --  THE SECOND DIMENSION OF THE ARRAY CONTAINING P
C                    (LPCMB MUST BE .GE. NV)
C     FLAMB     --  MARQUARDT-S LAMBDA. THE RELATIVE AMOUNT BY WHICH
C                     THE DIAGONAL COEFFICIENTS OF THE NORMAL
C                     EQUATIONS ARE AUGMENTED
C     FNU       --  MARQUARDT-S NU. THE FACTOR BY WHICH FLAMB IS
C                     CHANGED
C     RELDF     --  DETERMINES THE MAGNITUDE OF THE DIFFERENCING STEP
C     RELMN     --  RELATIVE CONVERGENCE CRITERION USED FOR EACH X(J)
C                     FOR WHICH DELMN(J) IS ZERO
C     METHD     --  DETERMINES THE METHOD USED
C                     =-1, MODIFIED GAUSS-NEWTON METHOD
C                     = 0, GAUSS-NEWTON METHOD
C                     = 1, MODIFIED FORM OF MARQUARDT-S METHOD
C                     = 2, MARQUARDT-S METHOD
C     KALCP     --  DETERMINES WHICH ROUTINE IS CALLED TO COMPUTE THE
C                     JACOBIAN MATRIX OF FIRST PARTIAL DERIVATIVES
C                     =-1, ONE ROW OF P RETURNED BY DERIV OR CALCD.
C                              DERIV CALLS FCFX
C                     = 0, ALL OF P RETURNED BY DERIV OR CALCD.
C                              DERIV CALLS FUNK
C                     = 1, ALL OF P RETURNED BY DERIV OR CALCD.
C                              DERIV CALLS FCFX
C     NORDF     --  DETERMINES HOW P IS TO BE CALCULATED
C                     = 1, FIRST ORDER APPROXIMATION USED BY DERIV
C                     = 2, SECOND ORDER APPROXIMATION USED BY DERIV
C                     = 3, ANALYTICAL DERIVATIVE SUPPLIED BY CALCD
C     MAXIT     --  THE MAXIMUM NUMBER OF ITERATIONS TO BE PERFORMED
C     LEQU      --  SAVES STORAGE IF ALL YSIG(JPT) ARE THE SAME
C                     =1 IF ALL YSIG(JPT) ARE EQUAL (IN THIS CASE
C                          ONLY YSIG(1) IS REFERENCED)
C                     =0 OTHERWISE
C     MXSUB     --  THE MAXIMUM NUMBER OF SUBITERATIONS PERMITTED
C     MXLPD     --  NOT USED AT PRESENT
C
C  MODIFICATIONS TO MARQUARDT-S METHOD...
C    1.  THE QUANTITY (1+LAMBDA) IS NOT ALLOWED TO INCREASE BY MORE
C          THAN A FACTOR OF FNULM. IN ANY SINGLE CHANGE.
C    2.  WHEN CUTSTEPS ARE USED IN A LINE SEARCH (WHEN THE ANGLE
C          GAMMA .LT. GAMMA SUB ZERO), THE VALUE OF LAMBDA IS INCREASED.
C  IN BOTH THE MODIFIED MARQUARDT-S METHOD AND THE MODIFIED
C  GAUSS-NEWTON METHOD, A HALF STEP IS ATTEMPTED FOLLOWING EACH
C  SUCCESSFUL STEP.  THIS AVOIDS ONE FORM OF VERY SLOW CONVERGENCE.
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C  THE FOLLOWING EXTERNAL STATEMENT IS REQUIRED BY SOME COMPILERS
C  (WATFIV, FOR EXAMPLE) AND FORBIDDEN BY OTHERS (MODCOMP II).
      EXTERNAL FUNK
C
      DOUBLE PRECISION F,Y,YSIG,H,SCALE,XMAX,XMIN,DELTX,DELMN,
     *     ERR,FOBJ,FLAMB,FNU,RELDF,GSQRT,ARG,CRIT,FLDEF,RELMN,
     *     RLTOL,FACCL,HLCE,RZERO,RUNIT,RTWO,DELM,FMGN,FCUT,
     *     STFAC,PTERM,SCALJ,SA,PIVOT,EM,SUM,COSIN,SB,SC,HH,
     *     FRMIN,XMX,XMN,DENOM,FFAC,UPFAC,RLFAC,FSFAC,RMSDV,
     *     SDVMX,QMAX1,QMIN1,CABS,ARGB
      DOUBLE PRECISION X,XSAVE,XTEMP,GRAD,FIT,FITSV,
     *                 XSAV,SIG,FTERM,PHI,PHNEW,PHALF,XLIM
C
```

```
C   THE DIMENSIONS OF THE VECTORS AND MATRICES (AS OPPOSED TO ARRAYS)
C   ARE....
C         F(NPTS,NACTV) (OR F(1,NACTV) IF KALCP.EQ.-1),
C         FITSV(NPTS) (OR FITSV(1) IF KALCP.EQ.-1),
C         X(NV),XMAX(NV),XMIN(NV),DELMN(NV),ERR(NV,NV+1),
C         XSAVE(NV),H(NV),MASKT(NV),
C         GRAD(NACTV),SCALE(NACTV),
C         Y(NPTS),FIT(NPTS),YSIG(NPTS) (OR YSIG(1) IF LEQU.NE.0),
C   WHERE NACTV IS THE NUMBER OF ACTIVE (UNMASKED) X(J).
C
      DIMENSION P(LPDMA,LPDMB)
      DIMENSION Y(1),YSIG(1),FIT(1),FITSV(1)
      DIMENSION XSAVE(20),H(20),GRAD(20),MASKT(20),XTEMP(20)
C
C   USER COMMON.....
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20),
     *      ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),
     *      NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW
C
C   MARQ COMMON.....
      COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDR,MAXIT,
     *      LEQU,MXSUB,MXUPD
C
C   SET THE LIBRARY FUNCTIONS FOR DOUBLE PRECISION (DSQRT, DABS, DMAX1,
C   DMIN1) OR FOR SINGLE PRECISION (SQRT, ABS, AMAX1, AMIN1).
C
      QSQRT(ARG)=DSQRT(ARG)
      QABS(ARG)=DABS(ARG)
      QMAX1(ARG,ARGB)=DMAX1(ARG,ARGB)
      QMIN1(ARG,ARGB)=DMIN1(ARG,ARGB)
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C   SET FIXED QUANTITIES ....
C
C   NVMAX IS THE MAXIMUM PERMISSIBLE VALUE OF NV.  IT IS ALSO THE
C   DIMENSION OF THE ARRAYS X, XMAX, XMIN, MASK, DELMN,
C   XSAVE, H, MASKT, GRAD, AND SCALE, AND THE FIRST DIMENSION OF ERR.
C   THE SECOND DIMENSION OF ERR IS NVMAX+1.
C
      NVMAX=20
C                                  CRIT ...  COSINE OF MARQUARDT-S CRITICAL
C                                                ANGLE, GAMMA SUB ZERO
      CRIT=.70711
C                                  FLDEF ...  DEFAULT VALUE FOR FLAMB
      FLDEF=1.
C                                  RLTOL ...  TOLERANCE FOR A WARNING MESSAGE
      RLTOL=1.E-4
C                                  FACCL ...  ACCELERATION FACTOR FOR FCUT
      FACCL=2.
C                                  FNULM ...  LIMIT ON THE FACTOR BY WHICH
C                                       (1+FLAMB) MAY CHANGE
      FNULM=2.
C                                  HUGE ...  A VERY LARGE REAL NUMBER
C                                       (DEFAULT VALUE FOR XMAX AND -XMIN)
      HUGE=1.E30
C
      RZERO=0.
      RUNIT=1.
      RTWO=2.
```

```
C                                                                       MARQ 181
C     NO FLOATING POINT CONSTANTS ARE USED BEYOND THIS POINT.           MARQ 182
C                                                                       MARQ 183
      KFLAG=0                                                           MARQ 184
      NCREP=0                                                           MARQ 185
      ITER=0                                                            MARQ 186
      PHI=HUGE                                                          MARQ 187
      SC=HUGE                                                           MARQ 188
C                                                                       MARQ 189
      IF(NTRAC.GE.-1) WRITE(KW,10)                                      MARQ 190
   10 FORMAT(49H1MARQ....  BEGIN NONLINEAR LEAST SQUARES SOLUTION)      MARQ 191
      NACTV=-99                                                         MARQ 192
      IF(NV.GT.0 .AND. NV.LE.NVMAX .AND. NV.LE.LPDMB .AND.              MARQ 193
     *      NPTS.GE.1 .AND. (KALCF.LT.0 .OR. NPTS.LE.LPDMA)) GO TO 20   MARQ 194
      KFLAG=-1                                                          MARQ 195
      GO TO 60                                                          MARQ 196
C                                                                       MARQ 197
C     CHECK SOME INPUT QUANTITIES, AND SET THEM TO DEFAULT VALUES IF    MARQ 198
C     DESIRED.                                                          MARQ 199
C                                    NACTV ...  NUMBER OF ACTIVE X(J)   MARQ 200
   20 NACTV=0                                                           MARQ 201
      DO 50 JX=1,NV                                                     MARQ 202
        DELN=QABS(DELMN(JX))                                            MARQ 203
        IF(MASK(JX))50,30,50                                            MARQ 204
   30   NACTV=NACTV+1                                                   MARQ 205
        IF(DELN.EQ.RZERO) DELN=GABS(RELMN*X(JX))                        MARQ 206
        IF(DELN.EQ.RZERO) DELN=RELMN                                    MARQ 207
        IF(XMAX(JX).GT.XMIN(JX)) GO TO 40                               MARQ 208
        XMAX(JX)=HUGE                                                   MARQ 209
        XMIN(JX)=-HUGE                                                  MARQ 210
   40   X(JX)=GMAX1(XMIN(JX),GMIN1(XMAX(JX),X(JX)))                     MARQ 211
   50   DELMN(JX)=DELN                                                  MARQ 212
C                                                                       MARQ 213
      IF(NACTV.GT.0) GO TO 80                                           MARQ 214
      KFLAG=-2                                                          MARQ 215
   60 CONTINUE                                                          MARQ 216
      WRITE(KW,70)NV,NVMAX,NACTV,NPTS,LPDMA,LPDMB,KALCP                 MARQ 217
   70 FORMAT(//29H ILLEGAL INPUT VALUE IN MARQ.,4X,5H NV =,I3,4X,       MARQ 218
     *   8H NVMAX =,I3,4X,8H NACTV =,I3/10X,7H NPTS =,I5,4X,8H LPDMA =, MARQ 219
     *   I5,4X,8H LPDMB =,I5,4X,8H KALCP =,I3)                          MARQ 220
      GO TO 1300                                                        MARQ 221
   80 CONTINUE                                                          MARQ 222
      IF(NTRAC.LT.-1) GO TO 150                                         MARQ 223
      WRITE(KW,90)(MASK(J),J=1,NV)                                      MARQ 224
   90 FORMAT(/10H MASK    = ,I7,7I13/(4X,8I13))                         MARQ 225
      WRITE(KW,100)(X(J),J=1,NV)                                        MARQ 226
  100 FORMAT(/10H X       = ,8E13.5/(10X,8E13.5))                       MARQ 227
      WRITE(KW,110)(XMAX(J),J=1,NV)                                     MARQ 228
  110 FORMAT(/10H XMAX    = ,8E13.5/(10X,8E13.5))                       MARQ 229
      WRITE(KW,120)(XMIN(J),J=1,NV)                                     MARQ 230
  120 FORMAT(/10H XMIN    = ,8E13.5/(10X,8E13.5))                       MARQ 231
      WRITE(KW,130)(DELMN(J),J=1,NV)                                    MARQ 232
  130 FORMAT(/10H DELMN   = ,8E13.5/(10X,8E13.5))                       MARQ 233
      WRITE(KW,140)NV,NPTS,LPDMA,LPDMB,NTRAC,METHD,KALCP,KORDF,         MARQ 234
     *      NFLAT,NFMAX,MAXIT,MXSUE,CRIT,RELCF,RELMN                    MARQ 235
  140 FORMAT(//5H NV =,I4,5X,7H NPTS =,I6,5X,8H LPDMA =,I6,5X,          MARQ 236
     *   8H LPDMB =,I4,5X,8H NTRAC =,I2,5X,8H METHD =,I3,5X,8H KALCF =, MARQ 237
     *   I3//8H KORDF =,I2,5X,8H NFLAT =,I2,5X,8H NFMAX =,I7,5X,        MARQ 238
     *   8H MAXIT =,I5,5X,8H MXSUE =,I4//7H CRIT =,E12.5,5X,8H RELCF =, MARQ 239
     *   E12.5,5X,8H RELMN =,E12.5)                                     MARQ 240
```

```
  150 JVARY=0
C
C  SET FMGN.  IF NECESSARY. RESET FLAMB AND/OR FACCL.
C
      FMGN=RUNIT
      UPNU=FNU
      DOWNU=FNU
      IF(FLAMB.LE.RZERO) FLAMB=FLOFF
      IF(METHD.LE.0) FLAMB=RZERO
      IF(METHD.NE.1) FACCL=RUNIT
C
C  COMPUTE THE INITIAL GOODNESS OF FIT OF THE MODEL TO THE DATA.
C  CALL FUNC TO CALCULATE THE VECTOR OF FITTED VALUES.
C
      CALL FUNC (FUNK.Y.YSIG.NPTS.FIT.PHI)
C
C                                    NF ...  EQUIVALENT NUMBER OF CALLS TO FUNC
      NF=1
      IF(NTRAC.GE.-1) WRITE(KW.160)PHI.FLAMB
  160 FORMAT(//27H PHI (THE SUM OF SQUARES) =.E15.8.57X.9H LAMBDA =.
     *   E12.5//1H )
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C  BEGIN THE NEXT ITERATION.
C  THIS IS THE ENTRY POINT AFTER A SUCCESSFUL STEP IF THE CONVERGENCE
C  CRITERION IS NOT MET.
C
  170 JSUB=0
      FCUT=RTWO
      ITER=ITER+1
      IF(NTRAC.GE.1) WRITE(KW.180)ITER.FMGN.FLAMB
  180 FORMAT(//16H BEGIN ITERATION.I5.44X.7H FMGN =.E12.5.15X.
     *   9H LAMBDA =.E12.5)
      IF(NTRAC.GE.3) WRITE(KW.190)
  190 FORMAT(/28H P (THE JACOBIAN MATRIX)..../1H )
C
C                                    INITIALIZE FOR THIS ITERATION.
      STFAC=RUNIT
      DO 200 JX=1.NACTV
        GRAD(JX)=RZERO
        DO 200 KX=1.JX
  200     ERR(JX.KX)=RZERO
C
C  CALL DERIV (OR CALCD) TO COMPUTE THE JACOBIAN MATRIX. P.
C  DERIV IS CALLED NPTS TIMES IF KALCP=-1.
C
      SIG=YSIG(1)
      DO 270 JPT=1.NPTS
        KPT=JPT
        IF(KALCP.LT.0) GO TO 210
        IF(JPT.NE.1) GO TO 230
  210   KPT=1
        IF(KORDF.LE.2) GO TO 220
        CALL CALCD (JPT.P.LPDMA.LPDMB)
        GO TO 230
  220   CALL DERIV (JPT.FUNK.NPTS.FIT.FITSV.P.LPDMA.LPDMB)
  230   CONTINUE
        IF(NTRAC.GE.3) WRITE(KW.240)JPT.(P(KPT.JX).JX=1.NACTV)
  240   FORMAT(1X.I3.2X.6E15.7/(6X.6E15.7))
```

```
C                                                                       MARQ 301
C     COMPUTE QSAV AND GRAD.                                            MARQ 302
C     QSAV, WHICH IS STORED IN ONE HALF OF THE ARRAY ERR(*,*), IS PT*P. MARQ 303
C     GRAD(*) IS HALF THE GRADIENT OF PHI.                              MARQ 304
C                                                                       MARQ 305
          IF(LEQL.EQ.0) SIG=YSIG(JPT)                                   MARQ 306
          FTERM=(FIT(JPT)-Y(JPT))/SIG**2                                MARQ 307
          DO 260 JX=1,NACTV                                             MARQ 308
            GRAD(JX)=GRAD(JX)+P(KPT,JX)*FTERM                           MARQ 309
            PTERM=P(KPT,JX)/SIG**2                                      MARQ 310
            DO 250 KX=1,JX                                              MARQ 311
  250         ERR(JX,KX)=ERR(JX,KX)+P(KPT,KX)*PTERM                     MARQ 312
  260       CONTINUE                                                    MARQ 313
  270     CONTINUE                                                      MARQ 314
C                                   RESTORE FIT IF IT WAS DESTROYED IN DERIV.  MARQ 315
      IF(KCRDF.NE.2) GO TO 290                                          MARQ 316
      IF(KALCP.NE.0) GO TO 280                                          MARQ 317
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                              MARQ 318
      NF=NF+1                                                           MARQ 319
  280 NF=NF+NACTV                                                       MARQ 320
  290 NF=NF+NACTV                                                       MARQ 321
C                                                                       MARQ 322
C     COMPUTE THE SCALE FACTORS AND STORE THEM IN DELTX(*).  SCALE GRAD.  MARQ 323
C                                                                       MARQ 324
      DO 300 JX=1,NACTV                                                 MARQ 325
        SCALJ=QSQRT(ERR(JX,JX))                                         MARQ 326
        IF(SCALJ.EQ.RZERO) SCALJ=RUNIT                                  MARQ 327
        DELTX(JX)=SCALJ                                                 MARQ 328
  300   GRAD(JX)=GRAD(JX)/SCALJ                                         MARQ 329
      IF(NTRAC.GE.1) WRITE(KW,310)(GRAD(JX),JX=1,NACTV)                 MARQ 330
  310 FORMAT(/21H   SCALED GRADIENT = ,6E15.7/(21X,6E15.7))             MARQ 331
C                                                                       MARQ 332
C     SCALE QSAV.  THE DIAGONAL ELEMENTS OF QSAV ARE SCALED TO UNITY.   MARQ 333
C                                                                       MARQ 334
      DO 355 JX=1,NACTV                                                 MARQ 335
        DO 350 KX=1,JX                                                  MARQ 336
          SA=ERR(JX,KX)/(DELTX(JX)*DELTX(KX))                           MARQ 337
          IF(KX.NE.JX) GO TO 320                                        MARQ 338
          IF(SA.EQ.RZERO) GO TO 330                                     MARQ 339
          SA=RUNIT                                                      MARQ 340
          GO TO 350                                                     MARQ 341
  320     IF(QABS(SA).LT.RUNIT-RLTOL) GO TO 350                         MARQ 342
  330     CONTINUE                                                      MARQ 343
          IF(NTRAC.GE.-2) WRITE(KW,340)JX,KX,SA,ITER                    MARQ 344
  340     FORMAT(38H ********  POSSIBLY DANGEROUS VALUE OF ,            MARQ 345
     1      16H COEFFICIENT.....5X,6H QSAV(,I3,1H,,I3,3H) =,E15.7,9X,   MARQ 346
     1      10H ITERATION,I5)                                           MARQ 347
  350     ERR(JX,KX)=SA                                                 MARQ 348
  355 CONTINUE
      IF(NTRAC.LT.2) GO TO 380                                          MARQ 349
      WRITE (KW,360)                                                    MARQ 350
  360 FORMAT(/49H QSAV (PT*P, SCALED, WHERE P IS THE JACOBIAN).../1H )  MARQ 351
      DO 370 JX=1,NACTV                                                 MARQ 352
  370   WRITE(KW,240)JX,(ERR(JX,KX),KX=1,JX)                            MARQ 353
  380 DO 390 JX=1,NV                                                    MARQ 354
  390   XSAVE(JX)=X(JX)                                                 MARQ 355
C                                   INITIALIZE MASKT AND NACT.          MARQ 356
  400 NACT=NACTV                                                        MARQ 357
      DO 410 JX=1,NV                                                    MARQ 358
  410   MASKT(JX)=MASK(JX)                                              MARQ 359
```

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C                                                                       MARQ 360
C  COPY GSAV INTO G AND GRAD INTO H. AND SET THE DIAGONAL ELEMENTS OF G.MARQ 361
C  THIS IS THE ENTRY POINT FOR SUBITERATIONS IN WHICH FLAMB IS          MARQ 362
C  INCREASED OR CONSTRAINTS ARE IMPOSED.                                MARQ 363
C                                                                       MARQ 364
  420 KRANK=0                                                           MARQ 365
      JG=0                                                              MARQ 366
      JT=0                                                              MARQ 367
      DO 450 JX=1,NV                                                    MARQ 368
         IF(MASK(JX).NE.0) GO TO 450                                    MARQ 369
         JG=JG+1                                                        MARQ 370
         IF(MASKT(JX).NE.0) GO TO 450                                   MARQ 371
         JT=JT+1                                                        MARQ 372
         H(JT)=-GRAD(JG)                                                MARQ 373
         KG=0                                                           MARQ 374
         KT=0                                                           MARQ 375
         DO 440 KX=1,JX                                                 MARQ 376
           IF(MASK(KX).NE.0) GO TO 440                                  MARQ 377
           KG=KG+1                                                      MARQ 378
           IF(MASKT(KX).NE.0) GO TO 440                                 MARQ 379
           KT=KT+1                                                      MARQ 380
           SA=ERR(JG,KG)                                                MARQ 381
           IF(KX.NE.JX .OR. SA.EQ.RZERO) GO TO 430                      MARQ 382
           SA=RUNIT+FLAMB                                               MARQ 383
           KRANK=KRANK+1                                                MARQ 384
  430      ERR(KT,JT+1)=SA                                              MARQ 385
  440      CONTINUE                                                     MARQ 386
  450    CONTINUE                                                       MARQ 387
C                                                                       MARQ 388
C  SOLVE THE NORMAL EQUATIONS FOR H, THE CORRECTION VECTOR.             MARQ 389
C                                                                       MARQ 390
      NSMAL=0                                                           MARQ 391
      NMU=NACT-1                                                        MARQ 392
      IF(NMU.EQ.0) GO TO 490                                            MARQ 393
C                                                                       MARQ 394
C                                      REDUCE THE SYSTEM TO TRIANGULAR FORM,   MARQ 395
C                                             UTILIZING THE SYMMETRY OF THE MATRIX.  MARQ 396
      DO 480 J=1,NMU                                                    MARQ 397
         PIVOT=ERR(J,J+1)                                               MARQ 398
         IF(PIVOT.EQ.RZERO) GO TO 480                                   MARQ 399
         JPU=J+1                                                        MARQ 400
         DO 470 K=JPU,NACT                                              MARQ 401
           EM=ERR(J,K+1)/PIVOT                                          MARQ 402
           IF(EM.EQ.RZERO) GO TO 470                                    MARQ 40
           DO 460 L=K,NACT                                              MARQ 404
  460        ERR(K,L+1)=ERR(K,L+1)-ERR(J,L+1)*EM                        MARQ 405
  470      H(K)=H(K)-H(J)*EM                                            MARQ 406
  480    CONTINUE                                                       MARQ 407
C                                      DO THE BACK SOLUTION.            MARQ 408
  490 DO 530 JINV=1,NACT                                                MARQ 409
         J=(NACT+1)-JINV                                                MARQ 410
         PIVOT=ERR(J,J+1)                                               MARQ 411
         IF(PIVOT.LE.RZERO) NSMAL=NSMAL+1                               MARQ 412
         IF(PIVOT.NE.RZERO) GO TO 500                                   MARQ 413
         H(J)=RZERO                                                     MARQ 414
         GO TO 530                                                      MARQ 415
  500    SUM=RZERO                                                      MARQ 416
         IF(J.EQ.NACT) GO TO 520                                        MARQ 417
         JPU=J+1                                                        MARQ 418
         DO 510 K=JPU,NACT                                              MARQ 419
```

```
  510       SUM=SUM+ERR(J,K+1)*H(K)
  520    H(J)=(H(J)-SUM)/PIVOT
  530    CONTINUE
C
C  IF THE COEFFICIENT MATRIX WAS RANK DEFICIENT, PRINT A MESSAGE.
C
      MRANK=NACT-NSMAL
      IF(MRANK.EQ.NACT) GO TO 560
      COSIN=HUGE
      IF(NTRAC.GE.-2) WRITE(KW,540)MRANK,NACT,ITER
  540 FORMAT(/41H RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.,9X,7H RANK =,
     *   I4,7X,18H ORDER OF MATRIX =,I4,9X,10H ITERATION,I5)
      IF(MRANK.GT.0) GO TO 550
      KFLAG=-4
      GO TO 1200
  550 IF(METHD.GT.0 .AND. MRANK.LT.KRANK) GO TO 860
C
C  UNPACK AND DE-SCALE THE CORRECTION VECTOR H.
C  COMPUTE THE INNER PRODUCTS SA, SB, AND SC.
C
  560 SA=RZERO
      SB=RZERO
      SC=RZERO
      KX=NV
      KQ=NACTV
      KT=NACT
      DO 590 JX=1,NV
        HH=RZERO
         IF(MASK(KX).NE.0) GO TO 580
         IF(MASKT(KX).NE.0) GO TO 570
        HH=H(KT)
        SA=SA-HH*GRAD(KQ)
        SB=SB+HH*HH
        SC=SC+GRAD(KQ)**2
        HH=HH*FMGN/DELTX(KQ)
        KT=KT-1
  570   KQ=KQ-1
  580   H(KX)=HH
  590   KX=KX-1
C
C  ADD THE CORRECTION VECTOR TO THE PARAMETER VECTOR AND
C  CHECK FOR CONSTRAINT VIOLATIONS.
C  THIS IS THE ENTRY POINT FOLLOWING A CUTSTEP.
C
  600 CONTINUE
      IF(NTRAC.GE.1) WRITE(KW,610)(H(JX),JX=1,NV)
  610 FORMAT(/7X,14H CORRECTION = ,6E15.7/(21X,6E15.7))
      NACSV=NACT
      FFMIN=FUNIT
      NLCOP=0
      JXLIM=0
  620 DO 720 JX=1,NV
        IF(MASKT(JX).NE.0) GO TO 720
        XSAV=XSAVE(JX)
        XMX=XMAX(JX)
        XMN=XMIN(JX)
        HH=H(JX)
        IF((XSAV.LT.XMN .OR. HH.LE.RZERO) .AND.
     *      (XSAV.GT.XMX .OR. HH.GE.RZERO)) GO TO 640
        MASKT(JX)=1
```

```
                                                                         MARQ 480
            NACT=NACT-1                                                  MARQ 481
            X(JX)=XSAV                                                   MARQ 482
            IF(NTRAC.GE.-1) WRITE(KW,630)JX,XSAV,ITER                    MARQ 483
     630    FORMAT(/8H FIX  X(,I3,4H) = ,E12.5,22H TEMPORARILY, TO AVOID,  MARQ 484
    *        24H VIOLATING A CONSTRAINT.,26X,10H ITERATION,I5)           MARQ 485
            GO TO 720                                                    MARQ 486
     640    XLIM=XSAV+FH*FRMIN                                           MARQ 487
            IF(JX.NE.JXLIM) GO TO 650                                    MARQ 488
            IF(KBND)680,660,660                                          MARQ 489
     650    X(JX)=XLIM                                                   MARQ 490
            IF(XLIM.LE.XMX) GO TO 670                                    MARQ 491
     660    X(JX)=XMX                                                    MARQ 492
            JEND=1                                                       MARQ 493
            GO TO 690                                                    MARQ 494
     670    IF(XLIM.GE.XMN) GO TO 720                                    MARQ 495
     680    X(JX)=XMN                                                    MARQ 496
            JEND=-1                                                      MARQ 497
     690    IF(JX.NE.JXLIM) GO TO 710                                    MARQ 498
            IF(NTRAC.LT.-1) GO TO 720                                    MARQ 499
            WRITE(KW,700)JX,X(JX),FRMIN,ITER                             MARQ 500
     700    FORMAT(/26H CONSTRAINT VIOLATED BY X(,I3,                    
    *        20H).   VALUE RESET TO ,E15.8,24H USING CUTSTEP FACTOR = ,E12.5MARQ 501
    *        ,3X,6H ITER.,I5)                                            MARQ 502
            GO TO 720                                                    MARQ 503
     710    IF(NLOCP.NE.0) GO TO 720                                     MARQ 504
            DENOM=XLIM-XSAV                                              MARQ 505
            IF(DENOM.EQ.RZERO) GO TO 720                                 MARQ 506
            FRAC=(X(JX)-XSAV)/DENOM                                      MARQ 507
            IF(FRAC.GE.FRMIN) GO TO 720                                  MARQ 508
            FRMIN=FRAC                                                   MARQ 509
            JXLIM=JX                                                     MARQ 510
            KBND=JEND                                                    MARQ 511
     720    CONTINUE                                                     MARQ 512
C                                                                        MARQ 513
C     IF THE PROPOSED STEP WOULD VIOLATE ANY ALREADY ACTIVE CONSTRAINTS, MARQ 514
C     FIX THOSE COMPONENTS OF H EQUAL TO ZERO AND RECOMPUTE THE          MARQ 515
C     OTHER COMPONENTS.                                                  MARQ 516
C                                                                        MARQ 517
          IF(NACT.GT.0) GO TO 740                                        MARQ 518
          KFLAG=3                                                        MARQ 519
          IF(NTRAC.LT.-2) GO TO 1200                                     MARQ 520
          WRITE(KW,730)                                                  MARQ 521
      730 FORMAT(////47H APPARENT CONSTRAINED OPTIMUM LIES IN A CORNER.) MARQ 522
          GO TO 1200                                                     MARQ 523
      740 IF(NACT.LT.NACSV) GO TO 420                                    MARQ 524
          IF(NLOOP.NE.0) GO TO 750                                       MARQ 525
          NLOOP=1                                                        MARQ 526
          IF(JXLIM.NE.0) GO TO 620                                       MARQ 527
      750 CONTINUE                                                       MARQ 528
          IF(NTRAC.GE.1) WRITE(KW,760)(X(JX),JX=1,NV)                    MARQ 529
      760 FORMAT(/16X,5H X = ,6E15.7/(21X,6E15.7))                       MARQ 530
C                                                                        MARQ 531
C     CALCULATE THE NEW FITTED VALUES.                                   MARQ 532
C                                                                        MARQ 533
          CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHNEW)                         MARQ 534
          NF=NF+1                                                        MARQ 535
          IF(PHNEW-PHI)930,770,790                                       MARQ 536
C                                                                        MARQ 537
C     THE NEW VALUE OF PHI IS EXACTLY EQUAL TO THE OLD VALUE.            MARQ 538
C     CHECK FOR CONVERGENCE UNDER THE NFLAT OPTION.                      MARQ 539
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```
C                                                                        MARQ 540
  770 IF(NFLAT.EQ.0) GO TO 930                                           MARQ 541
      KFLAG=2                                                            MARQ 542
      IF(NTRAC.LT.-1) GO TO 830                                          MARQ 543
      WRITE(KW,780)                                                      MARQ 544
  780 FORMAT(//45H CONVERGENCE ACHIEVED UNDER THE NFLAT OPTION.)         MARQ 545
      GO TO 830                                                          MARQ 546
C                                                                        MARQ 547
C  THE NEW VALUE OF PHI IS GREATER THAN THE OLD VALUE.                   MARQ 548
C                                                                        MARQ 549
  790 CONTINUE                                                           MARQ 550
      IF(NTRAC.GE.1) WRITE(KW,800)PHI,PHNEW                              MARQ 551
  800 FORMAT(/23X,10H OLD PHI =,E15.8,5X,10H NEW PHI =,E15.8)            MARQ 552
C                                                                        MARQ 553
C  CHECK WHETHER JSUB HAS EXCEEDED MXSUB.                                MARQ 554
C                                                                        MARQ 555
      JSUB=JSUB+1                                                        MARQ 556
      IF(JSUB.GT.MXSUB) GO TO 810                                        MARQ 557
      IF(METHD)880,1090,850                                              MARQ 558
  810 KFLAG=-1                                                           MARQ 559
      IF(NTRAC.GE.-1) WRITE(KW,820)MXSUB                                 MARQ 560
  820 FORMAT(//43H EXCEEDED MAXIMUM NUMBER OF SUBITERATIONS =,I3,        MARQ 561
     *   9H IN MARQ.)                                                    MARQ 562
C                                    RESTORE X TO THE BASE POINT.        MARQ 563
  830 DO 840 JX=1,NV                                                     MARQ 564
  840   X(JX)=XSAVE(JX)                                                  MARQ 565
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                               MARQ 566
      GO TO 1200                                                         MARQ 567
C                                                                        MARQ 568
C  THE NEW FIT IS WORSE THAN THE OLD FIT.  COMPUTE COSIN, THE COSINE     MARQ 569
C  OF THE ANGLE BETWEEN THE SCALED GRADIENT AND THE SCALED CORRECTION    MARQ 570
C  VECTOR.                                                               MARQ 571
C                                                                        MARQ 572
  850 DENOM=SB*SC                                                        MARQ 573
      IF(DENOM.LE.RZERO) GO TO 880                                       MARQ 574
      COSIN=SA/DSQRT(DENOM)                                              MARQ 575
      IF(COSIN.GT.CRIT) GO TO 880                                        MARQ 576
C                                                                        MARQ 577
C  COSIN IS NOT GREATER THAN CRIT.  INCREASE THE VALUE OF LAMBDA.        MARQ 578
C                                                                        MARQ 579
  860 UPFAC=UPNU                                                         MARQ 580
      UPNU=DMIN1(UPNU*FTWO,FNU)                                          MARQ 581
      IF(METHD.EQ.1) UPFAC=DMIN1(UPFAC,FNULM*FUNIT/FLAMB)                MARQ 582
      FLAMB=FLAMB*UPFAC                                                  MARQ 583
      IF(NTRAC.GE.1) WRITE(KW,870)JSUB,COSIN,FLAMB                       MARQ 584
  870 FORMAT(/18H **** SUBITERATION,I3,4X,17H INCREASE LAMBDA.,4X,       MARQ 585
     *   13H COS(GAMMA) =,E12.5,26X,9H LAMBDA =,E12.5)                   MARQ 586
C                                                                        MARQ 587
C                                 GO BACK AND FORM THE NORMAL EQUATIONS  MARQ 588
C                                   USING A LARGER VALUE OF LAMBDA.      MARQ 589
      GO TO 400                                                          MARQ 590
C                                                                        MARQ 591
C  COSIN IS GREATER THAN CRIT.  CUT THE MAGNITUDE OF THE STEP, H.        MARQ 592
C                                                                        MARQ 593
  880 STFAC=STFAC/FCUT                                                   MARQ 594
      IF(METHD.GE.0) GO TO 890                                           MARQ 595
      FNGN=FNGN/FCUT                                                     MARQ 596
      GO TO 900                                                          MARQ 597
  890 IF(METHD.EQ.1) FLAMB=FLAMB*FTWO                                    MARQ 598
  900 DO 910 JX=1,NV                                                     MARQ 599
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```
  910   H(JX)=(X(JX)-XSAVE(JX))/FCUT                                    MARQ 600
      FCUT=FCUT*FACCL                                                   MARQ 601
      IF(NTRAC.GE.1) WRITE(KW,920)JSUB,COSIN,STFAC                      MARQ 602
  920 FORMAT(/18H **** SUBITERATION,I3,4X,16H TAKE CUT STEPS.,4X,       MARQ 603
     *   13H COS(GAMMA) =,E12.5,8X,17H CUTSTEP FACTOR =,E12.5)          MARQ 604
C                                                                       MARQ 605
C                                     GO BACK AND TRY A SMALLER CUTSTEP. MARQ 606
      GO TO 600                                                         MARQ 607
C                                                                       MARQ 608
C  THE VALUE OF PHI HAS DECREASED.  TRY A HALF STEP.                    MARQ 609
C                                                                       MARQ 610
  930 IF(METHD.EQ.0 .OR. METHD.EQ.2) GO TO 1050                         MARQ 611
      DO 940 JX=1,NV                                                    MARQ 612
         XTEMP(JX)=X(JX)                                                MARQ 613
         IF(MASK(JX).NE.0) GO TO 940                                    MARQ 614
         X(JX)=XSAVE(JX)+(X(JX)-XSAVE(JX))/RTWO                         MARQ 615
         X(JX)=AMAX1(XMIN(JX),AMIN1(XMAX(JX),X(JX)))                    MARQ 616
  940    CONTINUE                                                       MARQ 617
      DO 950 JPT=1,NPTS                                                 MARQ 618
  950    FITSV(JPT)=FIT(JPT)                                            MARQ 619
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHALF)                            MARQ 620
      NF=NF+1                                                           MARQ 621
C                                                                       MARQ 622
C  USE QUADRATIC INTERPOLATION, IN ORDER TO TRY TO REFINE THE           MARQ 623
C  POSITION OF THE MINIMUM OF PHI.                                      MARQ 624
C                                                                       MARQ 625
      RLFAC=RUNIT                                                       MARQ 626
      DENOM=RTWO*((PHNEW-PHALF)-(PHALF-PHI))                            MARQ 627
      STFAC=RZERO                                                       MARQ 628
      IF(DENOM.LE.RZERO) GO TO 960                                      MARQ 629
      STFAC=(PHI-PHNEW)/DENOM                                           MARQ 630
      RSFAC=(RUNIT+STFAC)/RTWO                                          MARQ 631
C                                                                       MARQ 632
C                                      DO NOT EXTRAPOLATE.              MARQ 633
      IF(STFAC.GE.RUNIT) STFAC=RZERO                                    MARQ 634
  960 DO 970 JX=1,NV                                                    MARQ 635
         H(JX)=X(JX)
  970    X(JX)=X(JX)+(XTEMP(JX)-X(JX))*STFAC                            MARQ 637
      IF(PHALF.GE.PHNEW) GO TO 1010                                     MARQ 638
      RLFAC=RUNIT/RTWO                                                  MARQ 639
      JSUB=JSUB+1                                                       MARQ 640
      DO 980 JX=1,NV                                                    MARQ 641
  980 XTEMP(JX)=H(JX)
      DO 990 JPT=1,NPTS                                                 MARQ 643
  990    FITSV(JPT)=FIT(JPT)                                            MARQ 644
      IF(NTRAC.GE.1) WRITE(KW,1000)PHNEW,PHALF                          MARQ 645
 1000 FORMAT(/21H HALF STEP SUCCEEDED.,15X,8H PHNEW =,E15.8,18X,        MARQ 646
     *   8H PHALF =,E15.8)                                              MARQ 647
      PHNEW=PHALF                                                       MARQ 648
 1010 IF(STFAC.EQ.RZERO) GO TO 1020                                     MARQ 649
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                              MARQ 650
      NF=NF+1                                                           MARQ 651
      IF(PHI.LT.PHNEW) GO TO 1060                                       MARQ 652
 1020 DO 1030 JX=1,NV                                                   MARQ 653
 1030    X(JX)=XTEMP(JX)                                                MARQ 654
      DO 1040 JPT=1,NPTS                                                MARQ 655
 1040    FIT(JPT)=FITSV(JPT)                                            MARQ 656
      IF(STFAC.EQ.RZERO) GO TO 1060                                     MARQ 657
      IF(NTRAC.LT.1) GO TO 1080                                         MARQ 658
      WRITE(KW,1050)RSFAC,PHI                                           MARQ 659
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 1050 FORMAT(/25H QUADRATIC INTERPOLATION..22X.8H RSFAC =.E12.5.12X.     MARQ 660
     *    6H PHI =.E15.8)                                                MARQ 661
      GO TO 1080                                                         MARQ 662
 1060 RLFAC=RSFAC                                                        MARQ 663
      PHNEW=PHI                                                          MARQ 664
      IF(NTRAC.GE.1) WRITE(KW.1070)RLFAC.PHI                             MARQ 665
 1070 FORMAT(/35H QUADRATIC INTERPOLATION SUCCEEDED..12X.8H RLFAC =.     MARQ 666
     *    E12.5.12X.6H PHI =.E15.8)                                      MARQ 667
 1080 IF(RLFAC.LE.RZERO) GO TO 1090                                      MARQ 668
      FLAMB=FLAMB/RLFAC                                                  MARQ 669
      IF(METHD.LT.0) FMGN=FMGN*RLFAC                                     MARQ 670
C                                                                        MARQ 671
C  THE STEP IS ACCEPTED.  TEST FOR CONVERGENCE IF NO CONSTRAINT          MARQ 672
C  BECAME ACTIVE DURING THIS ITERATION.                                  MARQ 673
C                                                                        MARQ 674
 1090 CONTINUE                                                           MARQ 675
      IF(NTRAC.GE.1) WRITE(KW.1100)ITER.PHNEW                            MARQ 676
 1100 FORMAT(/16H END   ITERATION.I5.58X.6H PHI =.E15.8)                 MARQ 677
      PHI=PHNEW                                                          MARQ 678
      IF(JXLIM.GT.0) GO TO 1130                                          MARQ 679
      DO 1110 JX=1.NV                                                    MARQ 680
        IF(MASK(JX).NE.0) GO TO 1110                                     MARQ 681
        IF(DABS(X(JX)-XSAVE(JX)).GT.DELMN(JX)) GO TO 1130                MARQ 682
 1110   CONTINUE                                                         MARQ 683
      KFLAG=1                                                            MARQ 684
      IF(NTRAC.LT.-1) GO TO 1200                                         MARQ 685
      WRITE(KW.1120)                                                     MARQ 686
 1120 FORMAT(//38H CONVERGED WHEN THE STEP BECAME SMALL.)                MARQ 687
      GO TO 1200                                                         MARQ 688
C                                                                        MARQ 689
C  THE ITERATION HAS NOT YET CONVERGED.                                  MARQ 690
C                                                                        MARQ 691
 1130 IF(ITER.LT.MAXIT) GO TO 1150                                       MARQ 692
      KFLAG=-6                                                           MARQ 693
      WRITE(KW.1140)MAXIT                                                MARQ 694
 1140 FORMAT(//46H MAXIMUM NUMBER OF ITERATIONS REACHED IN MARQ..5X.     MARQ 695
     *    8H MAXIT =.I5)                                                 MARQ 696
      GO TO 1200                                                         MARQ 697
C                                                                        MARQ 698
C  IF SUBITERATIONS WERE NOT PERFORMED THIS ITERATION. DECREASE LAMBDA.  MARQ 699
C                                                                        MARQ 700
 1150 IF(NF.GE.NFMAX) GO TO 1180                                         MARQ 701
      IF(JSUB.GT.0) GO TO 1160                                           MARQ 702
      FMGN=DMIN1(FMGN*RTWO.RUNIT)                                        MARQ 703
      SCALJ=RUNIT+FLAMB                                                  MARQ 704
      IF(SCALJ.GT.RUNIT) FLAMB=FLAMB/DOWNU                               MARQ 705
      UPNU=DOWNU                                                         MARQ 706
      DOWNU=DMIN1(DOWNU*RTWO.FNU)                                        MARQ 707
      GO TO 1170                                                         MARQ 708
 1160 IF(METHD.NE.1) GO TO 1170                                          MARQ 709
      UPNU=FNULM                                                         MARQ 710
      DOWNU=FNULM                                                        MARQ 711
 1170 CONTINUE                                                           MARQ 712
C                                   GO BACK AND DO ANOTHER ITERATION.    MARQ 713
      GO TO 170                                                          MARQ 714
 1180 KFLAG=-7                                                           MARQ 715
      WRITE(KW.1190)NFMAX                                                MARQ 716
 1190 FORMAT(//23H NF HAS REACHED NFMAX =.I7.9H IN MARQ.)                MARQ 717
C                                                                        MARQ 718
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *  MARQ 719
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                                                                        MARQ 720
C                                                                       MARQ 721
C  THE ITERATION HAS TERMINATED.                                        MARQ 722
C  PRINT OUT THE DATA, FITTED VALUES, AND RESIDUALS.                    MARQ 723
C  COMPUTE AND PRINT THE STANDARD DEVIATION OF THE DATA FROM THE FIT.   MARQ 724
C                                                                       MARQ 725
 1200 CONTINUE                                                          MARQ 726
      SC=QSQRT(SC)                                                      MARQ 727
      IF(NTRAC.LT.-1) GO TO 1290                                        MARQ 728
      WRITE(KW,1210)ITER,NF,PHI,FMGN,FLAMB,SC                           MARQ 729
 1210 FORMAT(/1X,I4,11H ITERATIONS,7X,5H NF =,I5,9X,6H PHI =,E15.8,10X, MARQ 730
     *   7H FMGN =,E12.5,7X,9H LAMBDA =,E12.5//9X,15H NORM OF SCALED,   MARQ 731
     *    18H GRADIENT VECTOR =,E12.5)                                  MARQ 732
      WRITE(KW,760)(X(JX),JX=1,NV)                                      MARQ 733
      IF(NTRAC.GE.0) WRITE(KW,1220)                                     MARQ 734
 1220 FORMAT(///14X,1HJ,9X,5H Y(J),14X,7H FIT(J),10X,                   MARQ 735
     *   12H Y(J)-FIT(J),7X,8H YSIG(J),11X,13H (Y-FIT)/YSIG/1H )        MARQ 736
      SIG=YSIG(1)                                                       MARQ 737
      RMSDV=RZERO                                                       MARQ 738
      SDVMX=RZERO                                                       MARQ 739
      DO 1240 JPT=1,NPTS                                                MARQ 740
         IF(LEQL.EQ.0) SIG=YSIG(JPT)                                    MARQ 741
         YY=Y(JPT)                                                      MARQ 742
         PTERM=YY-FIT(JPT)                                              MARQ 743
         RTERM=PTERM/SIG                                                MARQ 744
         IF(NTRAC.GE.0) WRITE(KW,1230)JPT,YY,FIT(JPT),PTERM,SIG,RTERM   MARQ 745
 1230    FORMAT(5X,I10,5X,E15.8,5X,E15.8,5X,E12.5,5X,E12.5,10X,E12.5)   MARQ 746
         RMSDV=RMSDV+RTERM**2                                           MARQ 747
 1240    SDVMX=QMAX1(SDVMX,QABS(RTERM))                                 MARQ 748
      DENOM=NPTS-NACTV                                                  MARQ 749
      WRITE(KW,1250)DENOM                                               MARQ 750
 1250 FORMAT(//32H NUMBER OF DEGREES OF FREEDOM =,E12.5)                MARQ 751
      IF(DENOM.LE.RZERO) GO TO 1270                                     MARQ 752
      RMSDV=QSQRT(RMSDV/DENOM)                                          MARQ 753
      WRITE(KW,1260)RMSDV                                               MARQ 754
 1260 FORMAT(/43H R.M.S. SCALED DEVIATION OF DATA FROM FIT =,E12.5)     MARQ 755
 1270 CONTINUE                                                          MARQ 756
      WRITE(KW,1280)SDVMX                                               MARQ 757
 1280 FORMAT(/27H MAXIMUM SCALED DEVIATION =,E12.5)                     MARQ 758
C                                                                       MARQ 759
C  CALL FUNC TO SET THE FINAL VALUES.                                   MARQ 760
C                                                                       MARQ 761
 1290 CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                              MARQ 762
      FOBJ=PHI                                                          MARQ 763
C                                                                       MARQ 764
C  CALL MCERR TO PRINT THE PARAMETER ERRORS AND CORRELATIONS.           MARQ 765
C  A DUMMY ROUTINE MAY BE SUBSTITUTED FOR MCERR IF THESE ARE NOT NEEDED.MARQ 766
C                                                                       MARQ 767
      IF(MATRX.EQ.0) RETURN                                             MARQ 768
      CALL MCERR (NACTV,NPTS)                                           MARQ 769
C                                                                       MARQ 770
 1300 RETURN                                                            MARQ 771
C  END MARQ.                                                            MARQ 772
      END

      SUBROUTINE FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                        FUNC    1
C                                                                       FUNC    2
C   UPDATED BY J. CHANDLER, CSU DEPARTMENT OF COMPUTING AND             FUNC    2
C   INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES, MAY 1981        FUNC    2
C                                                                       FUNC    2
C  FUNC CALLS FUNK OR FOFX TO COMPUTE THE ARRAY OF FITTED VALUES FIT.   FUNC    3
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      C                                                                 FUNC   4
            DOUBLE PRECISION Y,YSIG,XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,     FUNC   5
           *     FLAMB,FNU,RELDF,RELMN                                  FUNC   6
            DOUBLE PRECISION X,FIT,F,PHI,SIG                            FUNC   7
      C                                                                 FUNC   8
            DIMENSION Y(1),YSIG(1),FIT(1)                               FUNC   9
      C                                                                 FUNC  10
            COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20), FUNC  11
           *     ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),               FUNC  12
           *     NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW           FUNC  13
            COMMON /NLLSQ/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDF,MAXIT, FUNC  14
           *     LEQU,MXSUB,MXUPD                                       FUNC  15
      C                                                                 FUNC  16
            RZERO=0.                                                    FUNC  17
            IF(KALCP.NE.0) GO TO 10                                     FUNC  18
      C                                                                 FUNC  19
            CALL FUNK (FIT)                                             FUNC  20
            GO TO 30                                                    FUNC  21
      C                                                                 FUNC  22
         10 DO 20 JPT=1,NPTS                                            FUNC  23
              CALL FCFX(JPT,NV,X,F)                                     FUNC  24
         20   FIT(JPT)=F                                                FUNC  25
      C                                                                 FUNC  26
         30 PHI=RZERO                                                   FUNC  27
            SIG=YSIG(1)                                                 FUNC  28
            DO 50 JPT=1,NPTS                                            FUNC  29
              IF(LEQU.EQ.0) SIG=YSIG(JPT)                               FUNC  30
      C                                                                 FUNC  31
      C                              CHECK FOR AN ILLEGAL VALUE OF SIG. FUNC  32
              IF(SIG.GT.RZERO) GO TO 50                                 FUNC  33
              WRITE(KW,40)LEQU,JPT,SIG                                  FUNC  34
         40   FORMAT(/28H ERROR IN NARQ....   LEQU = ,I1,5X,6H JPT =,I5,5X, FUNC  35
           *    7H YSIG =,E13.5,14H IS .LE. ZERO.)                      FUNC  36
              STOP                                                      FUNC  37
      C                                                                 FUNC  38
         50   PHI=PHI+((FIT(JPT)-Y(JPT))/SIG)**2                        FUNC  39
      C                                                                 FUNC  40
            RETURN                                                      FUNC  41
      C  END FUNC.                                                      FUNC  42
            END                                                         FUNC  43

            SUBROUTINE CALCD (JPT,F,LPDMA,LPDMB)                        CALCDUM1
      C                                                                 CALCDUM2
      C  UPDATE BY J. CHANDLER, MAY 1981, OSU COMPUTER SCIENCE          CALCDUM2
      C  DEPARTMENT--J. HANSON, UCC USER SERVICES                        CALCDUM2
      C                                                                 CALCDUM2
      C  THIS IS A DUMMY VERSION OF SUBROUTINE CALCD.                   CALCDUM3
      C  A NON-DUMMY VERSION OF CALCD MAY BE USED (OPTIONALLY) TO SUPPLY CALCDUM4
      C  TO NARQ ANALYTIC VALUES OF THE ELEMENTS OF THE JACOBIAN MATRIX, CALCDUM5
      C  INSTEAD OF APPROXIMATING THEM BY FINITE DIFFERENCES.           CALCDUM6
      C  HOWEVER, MOST USERS PREFER TO USE FINITE DIFFERENCES.          CALCDUM7
      C                                                                 CALCDUM8
            DOUBLE PRECISION P                                          CALCDUM9
            DIMENSION P(LPDMA,LPDMB)                                    CALCDU10
            RETURN                                                      CALCDU11
            END                                                         CALCDU12

            SUBROUTINE DERIV (JPT,FUNK,NPTS,FIT,FITSV,P,LPDMA,LPDMB)    DERIV  1
      C                                                                 DERIV  2
      C  UPDATED BY J. CHANDLER, OSU DEPARTMENT OF COMPUTING AND        DERIV  2
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C     INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES
C
C     DERIV 4.1          A.N.S.I. STANDARD FORTRAN          MAY 1981
C
C     DERIV COMPUTES THE JACOBIAN MATRIX P USING FINITE DIFFERENCES.
C
C     P(J,K) IS THE PARTIAL DERIVATIVE OF FIT(J) WITH RESPECT TO X(K).
C      IF KORDF.EQ.1, DERIV USES A NONCENTRAL DIFFERENCE FORMULA.
C     IF KORDF.EQ.2, DERIV USES A CENTRAL DIFFERENCE FORMULA.
C     KORDF.EQ.1 IS ABOUT TWICE AS FAST AS KORDF.EQ.2, BUT LESS ACCURATE.
C
      DOUBLE PRECISION P,XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,
     *     FLAMB,FNU,RELDF,RELMN,RZERO
      DOUBLE PRECISION X,FIT,FITSV,DEL,TWODL,XSAVE,FX0,FX1
C
      DIMENSION FIT(1),FITSV(1),P(LPDMA,LPDMB)
C
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20),
     *     ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),
     *     NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW
      COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDF,MAXIT,
     *     LEQU,MXSUB,MXUPD
C
      RZERO=0.
      JVARY=0
C
C     SAVE FIT IF KALCP.GE.0 .
C
      IF(KALCP.LT.0) GO TO 20
      DO 10 J=1,NPTS
   10   FITSV(J)=FIT(J)
C
C     LOOP OVER THE ACTIVE PARAMETERS X(JX).
C
   20 KX=0
      DO 150 JX=1,NV
        IF(MASK(JX).NE.0) GO TO 150
        KX=KX+1
        DEL=RELDF*X(JX)
        IF(DEL.EQ.RZERO) DEL=RELDF
        XSAVE=X(JX)
        X(JX)=XSAVE+DEL
        TWODL=DEL+DEL
        IF(KALCP)110,30,80
C
C     KALCP.EQ.0 .  COMPUTE P, ONE COLUMN AT A TIME.
C
   30   CALL FUNK (FIT)
        IF(KORDF.EQ.2) GO TO 50
        DO 40 J=1,NPTS
   40     P(J,KX)=(FIT(J)-FITSV(J))/DEL
        GO TO 140
C
C     KALCP.EQ.0 AND KORDF.EQ.2 .  IN THIS CASE, THE INPUT VALUES OF
C     FIT(J) WILL BE DESTROYED.
C
   50   X(JX)=XSAVE-DEL
        DO 60 J=1,NPTS
   60     FITSV(J)=FIT(J)
        JVARY=JX
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C     OUTPUT QUANTITIES....   ERR(*,*)                                  MQERR 15
C                                                                       MQERR 16
      DOUBLE PRECISION H,SCALE,XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,          MQERR 17
     *     QSQRT,ARG,RZERO,RUNIT,HUGE,PIVOT,Q,VIFMX,ER,TEMP,            MQERR 18
     *     DENOM,SCFAC,RESCL          ,X                                MQERR 19
C                                                                       MQERR 20
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20),       MQERR 21
     *     ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),                     MQERR 22
     *     NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW                 MQERR 23
C                                                                       MQERR 24
      QSQRT(ARG)=DSQRT(ARG)                                             MQERR 25
C                                                                       MQERR 26
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * MQERR 27
C                                                                       MQERR 28
      RZERO=0.                                                          MQERR 29
      RUNIT=1.                                                          MQERR 30
      HUGE=1.E30                                                        MQERR 31
C                                    PRINT QSAV.                        MQERR 32
      IF(NTRAC.LT.-1) GO TO 40                                          MQERR 33
      WRITE(KW,10)                                                      MQERR 34
   10 FORMAT(///18H SUBROUTINE MQERR.//26H QSAV (PT*P, SCALED, WHERE,   MQERR 35
     *  23H P IS THE JACOBIAN)....)                                     MQERR 36
      DO 30 JX=1,NACTV                                                  MQERR 37
        WRITE(KW,20)JX,(ERR(JX,KX),KX=1,JX)                             MQERR 38
   20   FORMAT(/1X,I3,2X,6E15.7/(6X,6E15.7))                            MQERR 39
   30   CONTINUE                                                        MQERR 40
C                                                                       MQERR 41
C     COMPUTE THE SCALED ERROR MATRIX, WHICH IS THE INVERSE OF QSAV.    MQERR 42
C     INVERT QSAV USING THE GAUSS-JORDAN METHOD WITHOUT PIVOTING.       MQERR 43
C     F. L. BAUER AND C. REINSCH, P. 45 IN -LINEAR ALGEBRA-             MQERR 44
C     BY J. H. WILKINSON AND C. REINSCH (SPRINGER-VERLAG, 1971)         MQERR 45
C     ERR(*,NV+1) IS USED AS A SCRATCH VECTOR.                          MQERR 46
C                                                                       MQERR 47
   40 NVPLU=NV+1                                                        MQERR 48
      NSMAL=0                                                           MQERR 49
      DO 130 LINV=1,NACTV                                               MQERR 50
        L=(NACTV+1)-LINV                                                MQERR 51
        PIVOT=ERR(1,1)                                                  MQERR 52
        IF(PIVOT.LE.RZERO) NSMAL=NSMAL+1                                MQERR 53
        IF(NACTV.LT.2) GO TO 90                                         MQERR 54
        DO 80 K=2,NACTV                                                 MQERR 55
          Q=ERR(K,1)                                                    MQERR 56
          IF(PIVOT.NE.RZERO) GO TO 50                                   MQERR 57
          ERR(K,NVPLU)=RZERO                                            MQERR 58
          GO TO 70                                                      MQERR 59
   50     IF(K.GT.L) GO TO 60                                           MQERR 60
          ERR(K,NVPLU)=-Q/PIVOT                                         MQERR 61
          GO TO 70                                                      MQERR 62
   60     ERR(K,NVPLU)=Q/PIVOT                                          MQERR 63
   70     DO 80 M=2,K                                                   MQERR 64
   80       ERR(K-1,M-1)=ERR(K,M)+Q*ERR(M,NVPLU)                        MQERR 65
   90   IF(PIVOT.NE.RZERO) GO TO 100                                    MQERR 66
        ERR(NACTV,NACTV)=RZERO                                          MQERR 67
        GO TO 110                                                       MQERR 68
  100   ERR(NACTV,NACTV)=RUNIT/PIVOT                                    MQERR 69
  110   IF(NACTV.LT.2) GO TO 130                                        MQERR 70
        DO 120 K=2,NACTV                                                MQERR 71
  120     ERR(NACTV,K-1)=ERR(K,NVPLU)                                   MQERR 72
  130   CONTINUE                                                        MQERR 73
C                                                                       MQERR 74
```

```
            CALL FUNK (FIT)                                             DERIV 61
            JVARY=0                                                     DERIV 62
            DO 70 J=1,NPTS                                              DERIV 63
   70         P(J,KX)=(FITSV(J)-FIT(J))/TWODL                           DERIV 64
            GO TO 140                                                   DERIV 65
C                                                                       DERIV 66
C    KALCP.GT.0 .  COMPUTE P, ONE ELEMENT AT A TIME.                    DERIV 67
C                                                                       DERIV 68
   80       DO 100 J=1,NPTS                                             DERIV 69
              CALL FOFX (J,NV,X,FX1)                                    DERIV 70
              IF(KORDF.EQ.2) GO TO 90                                   DERIV 71
              P(J,KX)=(FX1-FITSV(J))/DEL                                DERIV 72
              GO TO 100                                                 DERIV 73
   90         X(JX)=XSAVE-DEL                                           DERIV 74
              CALL FOFX (J,NV,X,FX0)                                    DERIV 75
              P(J,KX)=(FX1-FX0)/TWODL                                   DERIV 76
              X(JX)=XSAVE+DEL                                           DERIV 77
  100         CONTINUE                                                  DERIV 78
            GO TO 140                                                   DERIV 79
C                                                                       DERIV 80
C    KALCP.LT.0 .  COMPUTE ONE ROW OF P, ONE ELEMENT AT A TIME.         DERIV 81
C                                                                       DERIV 82
  110       FITSV(1)=FIT(JPT)                                           DERIV 83
            CALL FOFX (JPT,NV,X,FX1)                                    DERIV 84
            IF(KORDF.EQ.2) GO TO 120                                    DERIV 85
            P(1,KX)=(FX1-FITSV(1))/DEL                                  DERIV 86
            GO TO 130                                                   DERIV 87
  120       X(JX)=XSAVE-DEL                                             DERIV 88
            CALL FOFX (JPT,NV,X,FX0)                                    DERIV 89
            P(1,KX)=(FX1-FX0)/TWODL                                     DERIV 90
  130       FIT(JPT)=FITSV(1)                                           DERIV 91
C                                        RESTORE X(JX).                 DERIV 92
  140       X(JX)=XSAVE                                                 DERIV 93
  150       CONTINUE                                                    DERIV 94
C                                                                       DERIV 95
          IF(KALCP.LT.0) RETURN                                         DERIV 96
          DO 160 J=1,NPTS                                               DERIV 97
  160       FIT(J)=FITSV(J)                                             DERIV 98
C                                                                       DERIV 99
          RETURN                                                        DERIV100
C   END DERIV.                                                          DERIV101
          END                                                           DERIV102

          SUBROUTINE MQERR (NACTV,NPTS)                                 MQERR  1
C                                                                       MQERR  2
C    UPDATED BY J. CHANDLER, OSU DEPARTMENT OF COMPUTING AND            MQERR  2
C    INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES                 MQERR  2
C                                                                       MQERR  2
C    MQERR 3.0          A.N.S.I. STANDARD FORTRAN         MAY 1981      MQERR  3
C                                                                       MQERR  4
C    MQERR IS CALLED BY MARQ TO COMPUTE AND PRINT APPROXIMATE VALUES OF MQERR  5
C    THE PARAMETER ERRORS AND CORRELATIONS.                             MQERR  6
C                                                                       MQERR  7
C    FOR THE MEANING OF THE -MAXIMUM VARIANCE INFLATION FACTOR- BELOW,  MQERR  8
C    SEE...      D. W. MARQUARDT AND R. C. SNEE,                        MQERR  9
C                RIDGE REGRESSION IN PRACTICE,                          MQERR 10
C                THE AMERICAN STATISTICIAN 29 (1975) 3-20               MQERR 11
C                                                                       MQERR 12
C    INPUT QUANTITIES.....  KW,ERR(*,*),NACTV,DELTX(*),NPTS,NV,NTRAC,   MQERR 13
C                           MASK(*),FOBJ                                MQERR 14
```

```
      NRANK=NACTV-NSMAL                                                 MQERR 75
      IF(NRANK.LT.NACTV) WRITE(KW,140)NRANK,NACTV                       MQERR 76
  140 FORMAT(//51H THE SECOND DERIVATIVE MATRIX IS SINGULAR IN MQERR.,  MQERR 77
     *   5X,7H RANK =,I3,7X,8H ORDER =,I3//24H THEREFORE ALL PARAMETER, MQERR 78
     *   21H ERRORS ARE INFINITE.)                                      MQERR 79
C                                                                       MQERR 80
C                                  UNPACK THE ERROR MATRIX INTO THE UPPER MQERR 81
C                                   TRIANGLE OF ERR(*,*), DE-SCALING IT. MQERR 82
      JV=0                                                              MQERR 83
      VIFMX=RZERO                                                       MQERR 84
      DO 190 JX=1,NV                                                    MQERR 85
        IF(MASK(JX).EQ.0) JV=JV+1                                       MQERR 86
        KV=0                                                            MQERR 87
        DO 180 KX=1,JX                                                  MQERR 88
          ER=RZERO                                                      MQERR 89
          IF(MASK(JX).NE.0 .OR. MASK(KX).NE.0) GO TO 180                MQERR 90
          KV=KV+1                                                       MQERR 91
          TEMP=RZERO                                                    MQERR 92
          DENOM=DELTX(JV)*DELTX(KV)                                     MQERR 93
          IF(DENOM.EQ.RZERO) GO TO 150                                  MQERR 94
          TEMP=ERR(JV,KV)                                               MQERR 95
          ER=TEMP/DENOM                                                 MQERR 96
  150     IF(JX.NE.KX) GO TO 180                                        MQERR 97
          IF(TEMP.GT.RZERO) GO TO 170                                   MQERR 98
          IF(NTRAC.GE.-2) WRITE(KW,160)JX,KX,TEMP                       MQERR 99
  160     FORMAT(/6H THE (,I3,1H,,I3,23H) ELEMENT OF GSAV**-1 =,E12.5,  MQERR100
     *     5X,45H THEREFORE ALL PARAMETER ERRORS ARE INFINITE.)         MQERR101
          TEMP=-TEMP                                                    MQERR102
  170     IF(TEMP.GT.VIFMX) VIFMX=TEMP                                  MQERR103
  180     ERR(KX,JX+1)=ER                                               MQERR104
  190   CONTINUE                                                        MQERR105
C                                  COMPUTE AND PRINT THE STANDARD ERRORS. MQERR106
      NDF=NPTS-NACTV                                                    MQERR107
      SCFAC=HUGE                                                        MQERR108
      IF(NDF.LE.0) GO TO 200                                            MQERR109
      SCFAC=NDF                                                         MQERR110
      SCFAC=GSQRT(FOBJ/SCFAC)                                           MQERR111
  200 RESCL=NDF+NDF                                                     MQERR112
      IF(RESCL.GT.RZERO) RESCL=GSQRT(RESCL)                             MQERR113
      IF(NTRAC.LT.-1) GO TO 340                                         MQERR114
      WRITE(KW,210)NDF,NDF,RESCL,FOBJ,SCFAC                             MQERR115
  210 FORMAT(///41H NUMBER OF DEGREES OF FREEDOM (N.D.F.) = ,           MQERR116
     *   14H(NPTS-NACTV) =,I5//24H EXPECTED VALUE OF PHI = ,            MQERR117
     *   38H N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =,I5,                  MQERR118
     *   15H  PLUS OR MINUS,E12.5//22H ACTUAL VALUE OF PHI =,E12.5//    MQERR119
     *   38H RESCALING FACTOR = SQRT(PHI/N.D.F.) =,E12.5)               MQERR120
      WRITE(KW,220)VIFMX                                                MQERR121
  220 FORMAT(///36H MAXIMUM VARIANCE INFLATION FACTOR =,E12.5///        MQERR122
     *   32H APPROXIMATE STANDARD ERRORS..../8X,5H RESCALED/12X,1HJ,    MQERR123
     *   6X,7HMASK(J),5X,4HX(J),14X,5HERROR,12X,5HERROR)                MQERR124
      RESCL=HUGE                                                        MQERR125
      DO 270 JX=1,NV                                                    MQERR126
        SCALJ=RUNIT                                                     MQERR127
        ER=ERR(JX,JX+1)                                                 MQERR128
        IF(ER)230,250,240                                               MQERR129
  230   ER=-GSQRT(-ER)                                                  MQERR130
        SCALJ=-ER                                                       MQERR131
        GO TO 250                                                       MQERR132
  240   ER=GSQRT(ER)                                                    MQERR133
        SCALJ=ER                                                        MQERR134
```

```
688      250     IF(NCF.GT.0 .AND. NRANK.EQ.NACTV) RESCL=SCFAC*ER                MQERR135
689              DELTX(JX)=SCALJ                                                 MQERR136
690              WRITE(KW,260)JX,MASK(JX),X(JX),ER,RESCL                         MQERR137
691      260     FORMAT(/10X,I3,I10,6X,E16.8,4X,E13.5,4X,E13.5)                  MQERR138
692      270     CONTINUE                                                        MQERR139
       C                                  COMPUTE AND PRINT THE CORRELATIONS.    MQERR140
693             IF(NV.LT.2) GO TO 340                                            MQERR141
694             WRITE(KW,280)(K,K=1,NV)                                          MQERR142
695       280 FORMAT(///45H LOWER TRIANGLE OF THE CORRELATION MATRIX....//12X,   MQERR143
             *     7H K .....,I5,7I13/(11X,8I13))                                MQERR144
696             WRITE(KW,290)(MASK(K),K=1,NV)                                    MQERR145
697       290 FORMAT(/7X,12H MASK(K).....,I5,7I13/(11X,8I13))                    MQERR146
698             WRITE(KW,300)                                                    MQERR147
699       300 FORMAT(/3X,1HJ,4X,7HMASK(J) )                                      MQERR148
700           DO 330 JX=1,NV                                                     MQERR149
701              DO 310 KX=1,JX                                                  MQERR150
702       310      ERR(KX,1)=ERR(KX,JX+1)/(DELTX(JX)*DELTX(KX))                  MQERR151
703              WRITE(KW,320)JX,MASK(JX),(ERR(KX,1),KX=1,JX)                    MQERR152
704       320    FORMAT(/1X,I3,I8,8X,8E13.5/(17X,8E13.5))                        MQERR153
705       330    CONTINUE                                                        MQERR154
       C                                  RESCALE ERR AND SYMMETRIZE IT.         MQERR155
706       340 SCFAC=SCFAC**2                                                     MQERR156
707             IF(SCFAC.LT.RUNIT) SCFAC=RUNIT                                   MQERR157
708             DO 350 JX=1,NV                                                   MQERR158
709              DO 350 KX=1,JX                                                  MQERR159
710                ERR(JX,KX)=ERR(KX,JX+1)*SCFAC                                 MQERR160
711       350       ERR(KX,JX)=ERR(JX,KX)                                        MQERR161
       C                                                                         MQERR162
712             RETURN                                                           MQERR163
       C   END MQERR.                                                            MQERR164
713             END                                                              MQERR165

714             SUBROUTINE FOFX (JPT,NV,X,F)                                     FOFXDUM1
        C                                                                        FOFXDUM2
        C  UPDATED BY J. CHANDLER, MAY 1981, OSU COMPUTER SCIENCE                FOFXDUM2
        C  DEPARTMENT--J. HANSON, UCC USER SERVICES                              FOFXDUM2
        C                                                                        FOFXDUM2
        C  THIS IS A DUMMY VERSION OF SUBROUTINE FOFX.                           FOFXDUM3
        C  A NON-DUMMY VERSION OF FOFX MAY BE USED (OPTIONALLY) TO SUPPLY        FOFXDUM4
        C  TO MARQ VALUES OF THE FUNCTION BEING FITTED, INSTEAD OF USING A      FOFXDUM5
        C  -FUNK- SUBROUTINE TO DO THIS.  THE USE OF FOFX REQUIRES              FOFXDUM6
        C  SUBSTANTIALLY MORE OVERHEAD TIME DURING EXECUTION, BUT SAVES         FOFXDUM7
        C  CONSIDERABLE STORAGE BY NOT REQUIRING THAT THE JACOBIAN MATRIX, F,   FOFXDUM8
        C  BE STORED.                                                            FOFXDUM9
        C                                                                        FOFXDU10
715             DOUBLE PRECISION X,F                                             FOFXDU11
716             DIMENSION X(20)                                                  FOFXDU12
717             RETURN                                                           FOFXDU13
718             END                                                              FOFXDU14
***ERROR***  SUBPROGRAM DELMN  USED IN LINE      1 IS MISSING
***ERROR***  SUBPROGRAM GAUS   USED IN LINE      3 IS MISSING
***ERROR***  SUBPROGRAM FUNK   USED IN LINE      4 IS MISSING

STATEMENTS EXECUTED=        0

CORE USAGE        OBJECT CODE=   39960 BYTES,ARRAY AREA=   62688 BYTES,TOTAL AREA AVAILABLE=  129024  BYTE

DIAGNOSTICS         NUMBER OF ERRORS=        3, NUMBER OF WARNINGS=        2, NUMBER OF EXTENSIONS=        9

COMPILE TIME=     0.37 SEC,EXECUTION TIME=     0.00 SEC,       17.16.07     THURSDAY       3 MAR 83     WATFIV
```

APPENDIX E

LISTING OF GLOBAL MODEL DATA FIT PROGRAM

```
$JOB
C          ***************
C          HECK/STEIN DATA
C             (H-COAL)
C          USE MARQ TO FIT
C          HECK/STEIN MODEL
C          TO HOS DATA,
C          W/ PARAM. ESTIMATES
C          ***************
C
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL EXPIT
C
C          COMMON FOR STSET AND STEPT(AND MARQ)
C
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),
     * DELMN(20),ERR(20,21),FOBJ,NV,NTRAC,MATRX,
     * MASK(20),NFMAX,NFLAT,JVARY,NXTRA,KFLAG,
     *  NOREP,KERFL,KW
      COMMON /MLLSQ/ FLAMB,FNU,RELDF,RELMN,
     *  METHD,KALCP,KORDF,MAXIT,LEQL,NXSLB,NXUPD
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
C
C          COMMON FOR FUNK (BY EXPIT)
C
      COMMON /CSTOR/ T(25),P(25),ALHSV(25),C1(25)
C
      DIMENSION ADIF(50)
      ALL2=0.0
      KR=5
C
C          INITIATE MODEL FIT BY GIVING VALUES TO
C          MARQ VARIABLES . . .
C
      CALL STSET
      MAXIT=200
      NV=4
      XMIN(1)=XMIN(2)=0.0
      X(4)=1.2
      MASK(4)=1
C
C          READ AND WRITE THE INPUT DATA . . .
C
      WRITE (KW,50)
   50 FORMAT (15X,'TEMP',9X,'PRESSURE',6X,'LHSV',
     *   9X,'IN. CONC.',6X,'FIN. CONC.')
      READ (KR,100) NPTS
  100 FORMAT (I5)
      READ, (T(IA),IA=1,NPTS)
      READ, (P(IB),IB=1,NPTS)
      READ, (ALHSV(IC),IC=1,NPTS)
      READ, (C1(ID),ID=1,NPTS)
      READ, (Y(IG),IG=1,NPTS)
      DO 110 K=1,NPTS
      YSIG(K)=1.0
      T(K)=T(K)+460.0
  110 CONTINUE
      WRITE (KW,125) NPTS,(K,T(K),P(K),ALHSV(K),C1(K),
     *   Y(K),K=1,NPTS)
  125 FORMAT (//1X,I5//(1X,I5,5E15.5))
C
C          CALL THE FITTING ROUTINE . . .
C
      CALL STEPT(EXPIT)
C
      WRITE (KW,130)
  130 FORMAT (1H1,14X,'**************'/18X,'*  RESULTS  *'/18X,
     *   '**************')
      WRITE (KW,140) NPTS,X(1),X(2),X(3),X(4)
  140 FORMAT (////15X,'FOR',I2,2X,'DATA POINTS THE FITTED ',
     *   'PARAMETERS OF THE MODEL ARE - -'//15X,
     *   'RATE CONSTANT (K) =',E13.5//15X,
     *   'ACTIVATION ENERGY (E) =',E13.5//15X,
     *   'EXPONENT ON PRESSURE (A) =',E13.5//15X,
     *   'EXPONENT ON CONC. (N) =',E13.5//)
      WRITE (KW,145)
  145 FORMAT (15X,'CONC. OUT (DATA)',7X,'CONC. OUT (FIT)'//)
C
C          COMPUTE MEAN DEVIATION AND OTHER QUANTITIES . . .
C
  150 DO 200 K=1,NPTS
      ADIF(K)=DABS(Y(K)-FIT(K))
      ALL2=ADIF(K)+ALL2
      WRITE (KW,180) K,Y(K),FIT(K)
  180 FORMAT (7X,I2,11X,F8.5,11X,F8.5)
  200 CONTINUE
      ADEV=ALL2/NPTS
      WRITE (KW,220) ADEV
  220 FORMAT (//10X,'MEAN DEV. (WT. %) = ',F10.5////)
      STOP
      END

      SUBROUTINE EXPIT (FITM)
C
C          THIS SUBROUTINE IS REFERRED TO BY
C          MARQ AS FUNK(FIT).
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION FITM(1)
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),
     *  DELMN(20),ERR(20,21),FOBJ,NV,NTRAC,MATRX,
     *  MASK(20),NFMAX,NFLAT,JVARY,NXTRA,KFLAG,
     *  NOREP,KERFL,KW
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
      COMMON /CSTOR/ T(25),P(25),ALHSV(25),C1(25)
      R=1.987
      DO 200 J=1,NPTS
C
C          FF1,FF2, & FF COMPRISE THE "N"TH ORDER MODEL.
C
      FF1=X(1)*(DEXP(-X(2)/(R*T(J))))*(P(J)**X(3))/ALHSV(J)
      FF2=C1(J)**(1-X(4))
      FF=(FF2-(1.-X(4))*FF1)**(1./(1.-X(4)))
C     FF1=X(1)*(DEXP(-X(2)/(R*T(J))))*(P(J)**X(3))
C     FF2=1/C1(J)+FF1/ALHSV(J)
C     FF=1/FF2
      FITM(J)=FF
  200 CONTINUE
      RETURN
      END
```

```
MARQ....  BEGIN NONLINEAR LEAST SQUARES SOLUTION
MASK    =        0            0            0            1
X       =   0.00000D 00  0.00000D 00  0.00000D 00  0.12000D 01
XMAX    =   0.10000D 31  0.10000D 31  0.10000D 31  0.10000D 31
XMIN    =   0.00000D 00  0.00000D 00 -0.10000D 31 -0.10000D 31
DE_MN   =   0.10000D-07  0.10000D-07  0.10000D-07  0.00000D 00

NV =   4       NPTS =   21      LPDMA =   300      LPDMB =  20      NTRAC = 0      METHD =  1      KALCP =  0
KORDF = 1      NFLAT = 1       NFMAX =  32767     MAXIT =  200     MXSUB =  25
CRIT = 0.70711D 00      RELDF = 0.10000D-07      RELMN = 0.10000D-07

PHI (THE SUM OF SQUARES) = 0.19200000D 00                                                      LAMBDA = 0.10000D 01

*********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV( 2,  2) =  0.00000000D 00          ITERATION  1
*********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV( 3,  3) =  0.00000000D 00          ITERATION  1
RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.           RANK =   1         ORDER OF MATRIX =   3          ITERATION  1
FIX  X(  2) =  0.00000D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                           ITERATION  2

CONVERGENCE ACHIEVED UNDER THE NFLAT OPTION.
   73 ITERATIONS         NF =  418          PHI = 0.15219204D-02          FMGN = 0.10000D 01          LAMBDA = 0.37287D 02
          NORM OF SCALED GRADIENT VECTOR = 0.54376D-09
                    X =   0.1150984D 05  0.2330765D 05  0.3958883D 00  0.1200000D 01

              J          Y(J)               FIT(J)             Y(J)-FIT(J)         YSIG(J)            (Y-FIT)/YSIG
              1     0.99999970E-02     0.55824036D-02       0.44176D-02        0.10000D 01          0.44176D-02
              2     0.19999990E-01     0.14231724D-01       0.57683D-02        0.10000D 01          0.57683D-02
              3     0.99999970E-02     0.20818360D-02       0.79182D-02        0.10000D 01          0.79182D-02
              4     0.99999970E-02     0.12586734D-04       0.99874D-02        0.10000D 01          0.99874D-02
              5     0.99999970E-02     0.23521598D-03       0.97648D-02        0.10000D 01          0.97648D-02
              6     0.99999970E-02     0.73038545D-04       0.99270D-02        0.10000D 01          0.99270D-02
              7     0.99999970E-02     0.17896053D-01      -0.78961D-02        0.10000D 01         -0.78961D-02
              8     0.19999990E-01     0.33678932D-01      -0.13679D-01        0.10000D 01         -0.13679D-01
              9     0.99999970E-02     0.80447103D-02       0.19553D-02        0.10000D 01          0.19553D-02
             10     0.99999970E-02     0.16345962D-01      -0.63460D-02        0.10000D 01         -0.63460D-02
             11     0.29999990E-01     0.27015249D-01       0.29847D-02        0.10000D 01          0.29847D-02
             12     0.39999990E-01     0.45873645D-01      -0.58736D-02        0.10000D 01         -0.58736D-02
             13     0.19999990E-01     0.60242599D-02       0.13976D-01        0.10000D 01          0.13976D-01
             14     0.99999970E-02     0.19072672D-02       0.80927D-02        0.10000D 01          0.80927D-02
             15     0.99999970E-02     0.60568414D-03       0.93943D-02        0.10000D 01          0.93943D-02
             16     0.99999970E-02     0.57317775D-04       0.99427D-02        0.10000D 01          0.99427D-02
             17     0.99999970E-02     0.16871303D-03       0.98313D-02        0.10000D 01          0.98313D-02
```

```
          C $OPTIONS          .LIST
 **WARNING** MIS-FUNCHED JOB OPTION. .LIST   IS INVALID
          $ENTRY
              TEMP           PRESSURE      LHSV          IN. CONC.      FIN. CONC.

      21

       1   0.118500 04    0.250000 04    0.202000 01    0.110000 00    0.100000-01
       2   0.113200 C4    0.250C00 C4    C.205C00 C1    0.110000 00    0.200000-01
       3   0.123500 04    0.250000 04    0.203000 01    0.110000 00    0.100000-01
       4   0.123000 04    0.250000 04    0.460000 00    0.110000 00    0.100000-01
       5   0.113500 C4    0.250000 04    C.440C00 C0    0.110000 00    0.100000-01
       6   0.118600 04    0.250C00 04    0.500000 00    0.110000 00    0.100000-01
       7   0.119000 C4    0.250000 04    0.392000 01    0.110000 00    0.100000-01
       8   0.113400 04    0.250000 04    0.395000 01    0.110000 00    0.200000-01
       9   0.124600 C4    0.250000 04    0.389000 C1    0.110000 00    0.100000-01
      10   0.123200 04    0.120000 C4    C.387C00 C1    0.110000 00    0.100000-01
      11   0.118600 04    0.120000 04    0.383000 01    0.110000 00    0.300000-01
      12   0.113300 04    0.120000 04    0.409000 01    0.110000 00    0.400C00-01
      13   0.113600 C4    0.120000 C4    0.102C00 C1    0.110000 00    0.200000-01
      14   0.118800 04    0.120000 04    0.101000 C1    0.110000 00    0.100000-01
      15   0.123700 C4    0.120000 04    0.102000 01    0.110000 00    0.100000-01
      16   0.123500 C4    0.120000 04    0.520000 C0    0.110000 00    0.100000-01
      17   0.118400 04    0.120000 04    0.460000 00    0.110000 00    0.100000-01
      18   0.118300 C4    0.800000 03    0.510C00 C0    0.110000 00    0.100000-01
      19   0.123300 04    0.800000 03    0.490000 00    0.110000 00    0.100000-01
      20   0.123400 C4    0.250000 04    0.203000 01    0.110000 00    0.100C00-01
      21   0.113700 C4    0.250000 04    0.206C00 C1    0.110000 00    0.300000-01
```

```
        18      0.99999970E-02      0.43620602D-03      0.95638D-02      0.10000D 01          0.95638D-02
        19      0.99999970E-02      0.89723027D-04      0.99103D-02      0.10000D 01          0.99103D-02
        20      0.99999970E-02      0.21261642D-02      0.78739D-02      0.10000D 01          0.78739D-02
        21      0.29999990E-01      0.13279612D-01      0.16720D-01      0.10000D 01          0.16720D-01

 NUMBER OF DEGREES OF FREEDOM =  0.18000D 02

 R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.10061D-01

 MAXIMUM SCALED DEVIATION = 0.16720D-01


 SUBROUTINE MOERR.

 QSAV (PT*P, SCALED, WHERE P IS THE JACOBIAN)....

   1     0.1000000D 01

   2    -0.9994966D 00  0.1000000D 01

   3     0.9987959D 00 -0.9985631D 00  0.1000000D 01


 NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    18

 EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =    18  PLUS OR MINUS 0.60000D 01

 ACTUAL VALUE OF PHI = 0.18219D-02

 RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.10061D-01


 MAXIMUM VARIANCE INFLATION FACTOR = 0.12223D 04

 APPROXIMATE STANDARD ERRORS....
                                                                    RESCALED
              J       MASK(J)          X(J)              ERROR          ERROR

              1          0          0.11509842D 05     0.48372D 07     0.48666D 05

              2          0          0.23307648D 05     0.88820D 06     0.89420D 04

              3          0          0.39588831D 00     0.33264D 02     0.33466D 00

              4          1          0.11999958D 01     0.00000D 00     0.00000D 00


 LOWER TRIANGLE OF THE CORRELATION MATRIX....

                K ....     1           2           3           4

           MASK(K)....     0           0           0           1

     J     MASK(J)
```

```
1       0       0.10000D 01
2       0       0.81244D 00  0.100000D 01
3       0      -0.432600D 00  0.17245[illegible] 00  0.100000D 01
4       1       0.000000D 00  0.000000D 00  0.000000D 00  0.000000D 00
```

```
**************
*   RESULTS  *
**************

FOR   21  CATA POINTS THE FITTED PARAMETERS CF THE MODEL ARE :

          RATE CONSTANT (K) =  C.11510D 05

          ACTIVATION ENERGY (E) =  0.23308D 05

          EXPONENT ON PRESSURE (N) =  0.39585D 0C

          EXFCNENT ON CCNC. (M) =  0.12000D 01

          CONC. OUT (DATA)       CCNC. OUT (FIT)

     1          0.01000             0.00558
     2          0.020C0             0.01423
     3          0.01000             C.0C288
     4          0.01000             0.00001
     5          0.01000             0.00024
     6          0.01000             C.00007
     7          0.01000             0.01790
     8          0.02000             0.03368
     9          0.01000             C.CC804
    10          0.01000             0.01635
    11          0.03000             0.02702
    12          0.04000             0.04587
    13          0.02000             0.0CE02
    14          0.010C0             0.00191
    15          C.01000             0.00061
    16          0.01000             0.00006
    17          0.01000             0.00017
    18          0.010C0             0.00044
    19          0.01000             0.00009
    20          0.010C0             0.00213
    21          0.03000             0.01328

        MEAN DEV. (WT. %) = 0.0CEEE824

STATEMENTS EXECUTEC=  152710
CORE USAGE      OBJECT CODE=   43496 BYTES,ARRAY AREA=   63888 BYTES,TOTAL AREA AVAILABLE=  129024  BYTES
DIAGNOSTICS         NUMBER CF ERRORS=       0, NUMBER CF WARNINGS=       1, NUMBER OF EXTENSIONS=      11
COMPILE TIME=     C.29 SEC,EXECUTICN TIME=    2.29 SEC,    14.19.27   MCNDAY     23 MAY 83    WATFIV - MAR 1980 V2L0

        C$STOP
```

APPENDIX F

LISTING OF INTRINSIC MODEL DATA FIT PROGRAM

```
$JOB
C
C                 PROGRAM NAME: FITD.CNT_
C                 PROGRAM NUMBER: 010434.02
C
C            ********************************
C
C            THE OBJECT OF THIS PROGRAM IS TO
C            USE 'MARQ' TO FIT INTRINSIC MODEL
C            TO DATA OF ESPINO ET AL. (572 F).
C
C            INTRINSIC MODEL:
C              REACTION-          A+B=P; IRREV.
C              ADSORPTION SCHEME- SINGLE SITE ; A&B ONLY
C              CONTROLLING MECH.- SURFACE RXN.
C
C            ********************************
C            ********  ISOTHERMAL DATA  ********
C            ********************************
C
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL EXFIT
C
C            COMMON FOR STSET AND STEPT(AND MARQ)
C
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),
     *  DELMN(20),ERR(20,21),FOBJ,NV,NTRAC,MATRX,
     *  MASK(20),NFMAX,NFLAT,JVARY,NXTRA,KFLAG,
     *  NOREP,KERFL,KW
      COMMON /NLLSA/ FLAMB,FNU,RELDF,RELMN,
     *  METHD,KALCP,KORDF,MAXIT,LEQU,MXSUB,MXUP)
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
C
C            COMMON FOR FUNK (MY EXFIT)
C
      COMMON /CSTOR/ T(25),P(25),ALHSV(25),C1(25),
     *  DEFF(25),G(25),RHFRC(50),EFF(50),VSOL(50)
C
      DIMENSION ADIF(50),DEVV1(50),AT(50)
      DIMENSION TRA(50),TRSOL(50),Q1(50),Q2(50),Q(50),
     *  VISOL(50),GAMA(50),GAMSOL(50),VRA1(50),VRSOL1(50),
     *  DIFUS(50),VA(50)
C
C
      ALL2=DEVV2=DEVV3=0.0
      KR=5
C
C
C            INITIATE MODEL FIT BY GIVING VALUES TO
C            MARQ VARIABLES . . .
C
      CALL STSET
C
      MAXIT=200
      NV=4
      XMIN(1)=XMIN(2)=XMIN(3)=XMIN(4)=0.D0
      X(1)=1.74D0
      X(2)=0.05D0
      X(3)=0.D0
      X(4)=700.D0
      MASK(3)=1
C
C            READ AND WRITE THE INPUT DATA . . .
C
      READ (KR,100) NPTS
  100 FORMAT (I5)
      READ, (T(IA),IA=1,NPTS)
      READ, (P(IB),IB=1,NPTS)
      READ, (ALHSV(IC),IC=1,NPTS)
      READ, (C1(ID),ID=1,NPTS)
      READ, (Y(IZ),IZ=1,NPTS)
      WRITE(KW,85); WRITE(KW,86)
   85 FORMAT(1H1,5X,'OPERATING CONDITIONS:'//)
   86 FORMAT(15X,'TEMP.',8X,'PRESSURE',6X,'LHSV',9X,'IN. CONC.'/
     *  14X,'(DEG. F)',7X,'(PSIA)',5X,'(HR.**-1)',8X,'(WT. %)'//)
      WRITE(KW,125) (K,T(K),P(K),ALHSV(K),C1(K),K=1,NPTS)
  125 FORMAT(1X,I5,4E15.5)
C
      DO 110 K=1,NPTS
C
      YSIG(K)=1.D0
C
C            CONVERT TEMPERATURES TO ABSOLUTE . . .
C
      T(K)=T(K)+460.D0
C
C            CONVERT CONCENTRATIONS TO WT. FRACTION . . .
C
      Y(K)=Y(K)/100.D0
      C1(K)=C1(K)/100.D0
  110 CONTINUE
C
C     ******************************
C       THIS SECTION COMPUTES SOME
C       PHYSICAL PROPS. FOR DBT
C       AND TETRALINE AND THEN
C       ESTIMATES THE EFFECTIVE
C       DIFFUSIVITY AT EACH OPERATING
C       CONDITION.
C     ******************************
C
C            CRITICAL PROPS., ETC. USED IN COMPUTATIONS.
C            TEMPS. IN RANKINE; PRESSURES IN ATMOSPHERES . . .
C
      R=82.056D0
      ESUBS=0.5D0
      TORTF=3.5D0
      RADP=150.D0
C
C            PROPS. OF DBT . . .
C
      AA=21.D0
      TCA=1647.D0
      TBA=1091.4D0
      PCA=39.7D0
      RMBA=184.27D0
C
C            PROPS. OF SOLVENT . . .
C
      ASOL=18.D0
```

```
      TCSOL=1298.1D0
      TBSOL=865.3D0
      PCSOL=35.8D0
      RMWSOL=132.21D0
C
C          CONSTANTS, COEFFICIENTS, ETC. . . .
C
      REX1=1.D0/6.D0; RVAR=3.D0/7.D0; RLGN=2.302581D0
      RC1=0.015174D0; RC2=0.021350D0; RC3=0.0075D0
      TC1=0.042552D0; TC2=0.07674D0; TC3=0.034D0
      UC1=0.29607D0; UC2=0.09045D0; UC3=0.0484D0
      VC1=0.33593; VC2=0.33953; VC3=1.51941; VC4=2.02512; VC5=1.11422
      XC1=1.3D0; XC2=0.50879D0; XC3=0.91534D0
      YC1=0.292D0; YC2=0.0967D0
      BB1=8.2D-8; BB2=25.2D-8; BB3=17.5D-8
      REX2=2.D0/3.D0; REX3=1.D0/3.D0
C
C          BEGIN CALCULATIONS . . .
C
      EA=((TCA/1.8)/((RMWA**3)*(PCA**4)))**REX1
      ESOL=((TCSOL/1.8)/((RMWSOL**3)*(PCSOL**4)))**REX1
      WA=RVAR*((DLOG(PCA)/RLGN)/(TCA/TBA-1.))-1.
      WSOL=RVAR*((DLOG(PCSOL)/RLGN)/(TCSOL/TBSOL-1.))-1.
      VSCA=(R*(TCA/1.8)/PCA)*(YC1-YC2*WA)
      VSCSOL=(R*(TCSOL/1.8)/PCSOL)*(YC1-YC2*WSOL)
C
      DO 60 N=1,NPTS
C
      TRA(N)=T(N)/TCA
      TRSOL(N)=T(N)/TCSOL
C
C          CALCULATE SOLVENT VISCOSITY . . .
C
      Q1(N)=RC1-RC2*TRSOL(N)+RC3*(TRSOL(N)**2)
      Q2(N)=TC1-TC2*TRSOL(N)+TC3*(TRSOL(N)**2)
      Q(N)=Q1(N)+WSOL*Q2(N)
      VISOL(N)=Q(N)/ESOL
C
C          CALCULATE MOLAR VOLUMES . . .
C
      GAMA(N)=UC1-UC2*TRA(N)-UC3*(TRA(N)**2)
      IF(TRA(N).GE.0.20 .AND. TRA(N).LE.0.80) GO TO 51
      IF(TRA(N).GE.0.80 .AND. TRA(N).LE.1.0) GO TO 52
   51 VRA1(N)=VC1-VC2*TRA(N)+VC3*(TRA(N)**2)
     *        -VC4*(TRA(N)**3)+VC5*(TRA(N)**4)
      GO TO 55
   52 REDT=1.0-TRA(N)
      VRA1(N)=1.0+(XC1*(DSQRT(REDT)))*(DLOG(REDT)/RLGN)
     *        -XC2*REDT-XC3*(REDT**2)
   55 VA(N)=VSCA*VRA1(N)*(1.-WA*GAMA(N))
C
      GAMSOL(N)=UC1-UC2*TRSOL(N)-UC3*(TRSOL(N)**2)
      IF(TRSOL(N).GE.0.20 .AND. TRSOL(N).LE.0.80) GO TO 57
      IF(TRSOL(N).GE.0.80 .AND. TRSOL(N).LE.1.0) GO TO 58
   57 VRSOL1(N)=VC1-VC2*TRSOL(N)+VC3*(TRSOL(N)**2)
     *        -VC4*(TRSOL(N)**3)+VC5*(TRSOL(N)**4)
      GO TO 59
   58 REDT1=1.0-TRSOL(N)
      VRSOL1(N)=1.0+(XC1*(DSQRT(REDT1)))*(DLOG(REDT1)/RLGN)
     *        -XC2*REDT1-XC3*(REDT1**2)
   59 VSOL(N)=VSCSOL*VRSOL1(N)*(1.-WSOL*GAMSOL(N))
C
C          CALCULATE DIFFUSION COEFF. OF DBT
C          AND EFFECTIVE DIFFUSIVITY . . .
C
      IF(VA(N).GE.VSOL(N)) RKK=BB1*(1.0+(3.0*VSOL(N)/VA(N))**REX2)
      IF(VA(N).LE.VSOL(N)) RKK=BB2
      VVV=2.5*VSOL(N)
      IF(VA(N).LE.VVV) RKK=BB3
      DIFUS(N)=(RKK*T(N)/1.8)/(VISOL(N)*(VA(N)**REX3))
      DEFF(N)=(ESUBS*DIFUS(N)/TORTF)*(1.-AA/RADP)**4
C
C          CALCULATION OF H2 SOLUBILITY
C          WHERE G=H2 CONC. IN WT. FRACTION
C          AND AT=TEMPERATURE IN KELVIN . . .
C
      AT(N)=T(N)/1.80
      G(N)=P(N)*(DEXP(-(12.24+716.0/AT(N))))
C
   60 CONTINUE
C
C     **************************************
C
C          CALL THE FITTING ROUTINE . . .
C
C     **************************************
C
      CALL STEPIT(EXFIT)
C     CALL HIGHFIT)
C
C     **************************************
C
C          WRITE OUT THE RESULTS . . .
C
C     **************************************
C
      WRITE(KW,91) ; WRITE(KW,92)
   91 FORMAT(1H1,4X,'PHYSICAL PROPERTIES AND EFFECTIVENESS FACTORS'/
     *  5X,'FOR THE MODEL SYSTEM OF DBT IN TETRALINE:'//)
   92 FORMAT(7X,'DBT',5X,'SOLVENT',4X,'SOLVENT',7X,'DBT',7X,'SOLVENT
     *  5X,'EFFECTIVE',17X,'EFFECTIVENESS'/5X,'REDUCED',3X,'REDUCED'
     *  3X,'VISCOSITY',5X,'VOLUME',6X,'VOLUME',4X,'DIFFUSIVITY',5X,
     *  'THIELE',8X,'FACTOR'/6X,'TEMP.',5X,'TEMP.',6X,'(CP)',6X,
     *  2('(CC/GMOL)',3X),'(CM**2/SEC)',4X,'MODULUS',4X,
     *  '(DBT IN SOLVENT)'//)
      WRITE(KW,93) (II,TRA(II),TRSOL(II),VISOL(II),VA(II),VSOL(II),
     *  DEFF(II),RHFAC(II),EFF(II),II=1,NPTS)
   93 FORMAT(1X,I2,2X,F7.5,3X,F7.5,3X,F9.7,3X,F9.3,3X,F9.3,3X,
     *  E12.6,3X,F9.5,2X,F12.10)
C
      WRITE(KW,5)
    5 FORMAT(1H1,9X,'T(K)',10X,'P(PSIA)',10X,'H2 CONC. (WT. FRCN.)'/
      WRITE(KW,8) (I,AT(I),P(I),G(I),I=1,NPTS)
    8 FORMAT(I4,4X,F7.2,9X,F7.1,10X,F10.7)
C
      WRITE (KW,130)
  130 FORMAT (1H1,14X,'**************'/15X,'*  RESULTS  *'/15X,
     *  '**************')
      WRITE (KW,140) NPTS,X(1),X(2),X(3),X(4)
  140 FORMAT (////10X,'FOR',I5,2X,'DATA POINTS THE FITTED ',
```

```
     *   'PARAMETERS OF THE MODEL ARE - -'//15X,
     *   'RATE CONSTANT (K) =',E13.5//15X,
     *   'ADSORPTION COEFF. OF "A" =',E13.5//15X,
     *   'ADSORPTION COEFF. OF "P" =',E13.5//15X,
     *   'ADSORPTION COEFF. OF "B" =',E13.5//)
      WRITE (KW,145)
  145 FORMAT (15X,'CONC. OUT (DATA)',7X,'CONC. OUT (FIT)',
     *   7X,'% ERROR ((Y-FIT)/Y)*100 '//)
C
C     ****************************************************************
C
C          COMPUTE MEAN DEVIATION AND AVRG. PERCENT ERROR . . .
C
C     ****************************************************************
C
  150 DO 200 K=1,NPTS
C
      ADIF(K)=DABS(Y(K)-FIT(K))
      ALL2=ADIF(K)+ALL2
C
      DEVV1(K)=((Y(K)-FIT(K))/Y(K))*100.0
      DEVV2=DABS(DEVV1(K))+DEVV2
C
      WRITE (KW,180) K,Y(K),FIT(K),DEVV1(K)
  180 FORMAT (7X,I3,11X,F8.5,11X,F8.5,8X,F12.8)
  200 CONTINUE
C
      ADEV=ALL2/NPTS
      DEVV3=DEVV2/NPTS
      WRITE (KW,220) ADEV
  220 FORMAT (//15X,'MEAN DEV. (WT. %) = ',F10.8)
      WRITE (KW,240) DEVV3
  240 FORMAT(//10X,'AVERAGE % ERROR =',F10.7///)
      STOP
      END
```

```
      SUBROUTINE EXFIT (FITM)
      SUBROUTINE HIGH(FITM)
C
C          THIS SUBROUTINE IS REFERRED TO BY
C          MARQ AS FUNK(FIT).
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION FITM(1)
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),
     *  DELMN(20),ERR(20,21),FOBJ,NV,NTRAC,MATRX,
     *  MASK(20),NPMAX,NFLAT,JVARY,NXTRA,KFLAG,
     *  NOREP,KERFL,KW
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
      COMMON /CSTOR/ T(25),P(25),ALMSV(25),C1(25),
     *  DEFF(25),G(25),RHFAC(50),EFF(50),VSOL(50)
      DIMENSION RATEK(50)
C
      RADC=0.01D0
      R=1.986D0
      ZNUM=1.D-7
C
      DO 200 J=1,NPTS
C
C          CALCULATE RXN. RATE COEFF., THE THIELE
C          MODULUS, AND EFFECTIVENESS FACTOR . . .
C
      RATEK(J)=X(1)
      RMWA1=184.27D0
      RPARM=X(1)*X(2)*X(4)*RMWA1*G(J)
      RHFAC(J)=RADC*(DSQRT(RPARM/DEFF(J)/3600.D0))/3.D0
      IF(RHFAC(J).LE.ZNUM) RHFAC(J)=ZNUM
      EFF(J)=DTANH(RHFAC(J))/RHFAC(J)
C
C
C          CALL THE ROUTINE ('BSCT' OR 'SECNT') TO FIND THE OUTLET
C          CONCENTRATION . . .
C
      CALL BSCT(C1(J),RATEK(J),X(2),X(3),X(4),G(J),P(J),
     *  ALMSV(J),EFF(J),VSOL(J),FITM(J))
C
C
  200 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SECNT(CIN.RATEX.XA.XP.XB.G1.RP.RLMSV.EFFEC.VOL.FITK)
C
C          THIS SUBROUTINE CONTAINS A NUMERICAL PROCEDURE.
C          THE SECANT METHOD. TO SOLVE FOR THE OUTLET
C          CONCENTRATION.
C
      IMPLICIT REAL*8 (A-H.O-Z)
      DIMENSION CA(50).EROR(50).FOFCA(50).DRVCA(50)
      ZZERO=1.D-6
      CPO=0.D0
C
C          INITIALIZE THE METHOD . . .
C
      CA(1)=CIN/4.D0
      CA(2)=CIN/2.D0
      DO 700 KK=1.2
      FOFCA(KK)=CONC(CIN.CPO.RATEX.XA.XP.XB.G1.RP.RLMSV.CA(KK).
     *  EFFEC.VOL)
  700 CONTINUE
C
      L=1
  710 L=L+1
      DRVCA(L)=(FOFCA(L)-FOFCA(L-1))/(CA(L)-CA(L-1))
      EROR(L)=DABS(CA(L)-CA(L-1))
      FRACX=ZZERO*DMAX1(DABS(CA(L)).DABS(CA(L-1)))
      IF(EROR(L).LE.FRACX) GO TO 750
      CA(L+1)=CA(L)-FOFCA(L)/DRVCA(L)
      FOFCA(L+1)=CONC(CIN.CPO.RATEX.XA.XP.XB.G1.RP.RLMSV.CA(L+1).
     *  EFFEC.VOL)
      GO TO 710
  750 FITK=CA(L)
C          WRITE(5.*) FOFCA1.FOFCA2.FOFCA3.FOFCA(L).CA(L)
      RETURN
      END
```

```
      SUBROUTINE BSCT(CIN.RATEX.XA.XP.XB.G1.RP.RLMSV.EFFEC.VOL.FITK
C
C          USE BISECTING METHOD TO COMPUTE OUTLET CONC.
C
      IMPLICIT REAL*8 (A-H.O-Z)
      ZZERO=1.D-10
      NUMB=0
      CPO=0.D0
      F1=CONC(CIN.CPO.RATEX.XA.XP.XB.G1.RP.RLMSV.CIN.EFFEC.VOL )
      IF(F1) 62.95.64
   62 IJ=1
      GO TO 70
   64 IJ=2
   70 F2=CONC(CIN.CPO.RATEX.XA.XP.XB.G1.RP.RLMSV.ZZERO.EFFEC.VOL )
      IF(F2) 72.95.74
   72 KL=1
      GO TO 76
   74 KL=2
   76 IF(IJ.EQ.KL) GO TO 96
      CA2=CIN
   80 CA1=CA2
      CA2=CA2/2.D0
   81 FC=CONC(CIN.CPO.RATEX.XA.XP.XB.G1.RP.RLMSV.CA2.EFFEC.VOL)
      NUMB=NUMB+1
C     IF(NUMB.GE.100) GO TO 95
      IF(DABS(FC).LE.ZZERO) GO TO 95
      IF(FC) 82.95.84
   82 MN=1
      GO TO 90
   84 MN=2
   90 IF(MN.EQ.IJ) GO TO 80
      CA2=(CA1+CA2)/2.D0
      GO TO 81
   95 FITK=CA2
      GO TO 98
   96 WRITE(6.97)
   97 FORMAT(////10X.'***  NO SOLUTION IN RANGE  ***'/////)
      FITK=CIN
   98 CONTINUE
C     WRITE(6.99) NUMB
C  99 FORMAT(10X.I3)
      RETURN
      END
```

```
 231          FUNCTION CONC(CAIN,CPIN,RATEC,XA1,XP1,XB1,G2,PRES,ZLMSV,COUT,
             *  EFFAC,VOLUM)
        C
        C           THIS ROUTINE COMPUTES THE FUNCTION FOR WHICH THE ROOT
        C           IS BEING DETERMINED IN ROUTINE 'SECNT' OR 'BSCT'.
        C
 232          IMPLICIT REAL*8 (A-H,O-Z)
        C
        C           MOLECULAR WTS. OF DBT AND SOLVENT . . .
        C
 233          RMWA2=184.27D0
 234          RMWB2=132.21D0
        C
        C           CALCULATE OIL DENSITY IN GRAMS/CM**3 . . .
        C
 235          DOIL=RMWB2/VOLUM
        C
        C           CALCULATE "CATALYST BED PARAMETER", W*RMWA2/DOIL/V,
        C           BASED UPON "W" = 1 GRAM OF CATALYST, AND
        C           "V" = 1 CM**3 OF CATALYST . . .
        C
 236          RBED=RMWA2/DOIL
        C
        C           FIND THE VALUE OF THE FUNCTION . . .
        C
 237          FOFCA1=((1.D0+XB1*G2)**2)*DLOG(CAIN/COUT)
 238          FOFCA2=2.D0*XA1*(1.D0+XB1*G2)*(CAIN-COUT)
 239          FOFCA3=0.5D0*(XA1**2)*(CAIN**2-COUT**2)
 240          FOFCA4=(RATEC*XA1*XB1*G2*RBED/ZLMSV)*EFFAC
        C
 241          CONC=FOFCA1+FOFCA2+FOFCA3-FOFCA4
        C
 242          RETURN
 243          END

        $ENTRY
```

```
OPERATING CONDITIONS:

                TEMP.          PRESSURE          LHSV          IN. CONC.
              (DEG. F)          (PSIA)        (HR.**-1)        (WT. %)

      1     0.572000D 03     0.250000D 03     0.100000D 01     0.243000D 01
      2     0.572000D 03     0.250000D 03     0.300000D 01     0.243000D 01
      3     0.572000D 03     0.250000D 03     0.600000D 01     0.243000D 01
      4     0.572000D 03     0.250000D 03     0.900000D 01     0.243000D 01
      5     0.572000D 03     0.350000D 03     0.100000D 01     0.243000D 01
      6     0.572000D 03     0.350000D 03     0.300000D 01     0.243000D 01
      7     0.572000D 03     0.350000D 03     0.600000D 01     0.243000D 01
      8     0.572000D 03     0.350000D 03     0.900000D 01     0.243000D 01
      9     0.572000D 03     0.350000D 03     0.120000D 02     0.243000D 01
     10     0.572000D 03     0.450000D 03     0.100000D 01     0.243000D 01
     11     0.572000D 03     0.450000D 03     0.300000D 01     0.243000D 01
     12     0.572000D 03     0.450000D 03     0.600000D 01     0.243000D 01
     13     0.572000D 03     0.450000D 03     0.900000D 01     0.243000D 01
     14     0.572000D 03     0.450000D 03     0.120000D 02     0.243000D 01
```

```
MARQ....  BEGIN NONLINEAR LEAST SQUARES SOLUTION

MASK    =        0            0            1            0

X       =   0.17440D 01  0.50000D-01  0.00000D 00  0.70000D 03

XMAX    =   0.10000D 31  0.10000D 31  0.10000D 31  0.10000D 31

XMIN    =   0.00000D 00  0.00000D 00  0.00000D 00  0.00000D 00

DELMN   =   0.17440D-07  0.50000D-09  0.00000D 00  0.70000D-05

NV =    4       NPTS =     14       LPDMA =   300       LPDMB =   20        NTRAC = 0       METHD =  1        KALCP =  0

KORDF = 1         NFLAT = 1        NFMAX = 32767        MAXIT =  200        MXSUB =  25

CRIT = 0.70711D 00        RELDF = 0.10000D-07        RELMN = 0.10000D-07

PHI (THE SUM OF SQUARES) = 0.78962175D-03                                                          LAMBDA = 0.10000D 01

********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.1000000D 01              ITERATION    1
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.9999963D 00              ITERATION    2
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.1000000D 01              ITERATION    3
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.9999262D 00              ITERATION    4
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.1000000D 01              ITERATION    5
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.1000000D 01              ITERATION    6
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.9999679D 00              ITERATION    7
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.9999931D 00              ITERATION    8
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.1000000D 01              ITERATION    9
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.1000000D 01              ITERATION   10
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(   2,   1) =  0.1000000D 01              ITERATION   11

CONVERGENCE ACHIEVED UNDER THE NFLAT OPTION.
 11 ITERATIONS         NF =    77          PHI = 0.34723847D-05             FNGN = 0.10000D 01          LAMBDA = 0.37750D 04
         NORM OF SCALED GRADIENT VECTOR = 0.18944D-04
               X =   0.1076149D 01  0.3048959D-01  0.0000000D 00  0.4446079D 03

     J          Y(J)               FIT(J)           Y(J)-FIT(J)      YSIG(J)           (Y-FIT)/YSIG

     1     0.90999970E-02     0.93265493D-02     -0.22655D-03     0.10000D 01       -0.22655D-03
     2     0.17399990E-01     0.17661016D-01     -0.26102D-03     0.10000D 01       -0.26102D-03
     3     0.20599990E-01     0.20716531D-01     -0.11653D-03     0.10000D 01       -0.11653D-03
     4     0.21699990E-01     0.21848161D-01     -0.14816D-03     0.10000D 01       -0.14816D-03
     5     0.70999970E-02     0.72589060D-02     -0.15891D-03     0.10000D 01       -0.15891D-03
     6     0.17999990E-01     0.16245994D-01      0.17540D-02     0.10000D 01        0.17540D-02
     7     0.19699990E-01     0.19869415D-01     -0.16942D-03     0.10000D 01       -0.16942D-03
     8     0.21099990E-01     0.21248467D-01     -0.14847D-03     0.10000D 01       -0.14847D-03
     9     0.21899990E-01     0.21973443D-01     -0.73444D-04     0.10000D 01       -0.73444D-04
    10     0.57999970E-02     0.59492415D-02     -0.14924D-03     0.10000D 01       -0.14924D-03
    11     0.14999990E-01     0.15203936D-01     -0.20384D-03     0.10000D 01       -0.20384D-03
    12     0.18999990E-01     0.19221652D-01     -0.22165D-03     0.10000D 01       -0.22165D-03
```

```
        13      0.20599990E-01     0.20784134D-01     -0.18414D-03     0.10000D 01          -0.18414D-03
        14      0.21499990E-01     0.21612329D-01     -0.11233D-03     0.10000D 01          -0.11233D-03

 NUMBER OF DEGREES OF FREEDOM =  0.11000D 02
 R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.56185D-03
 MAXIMUM SCALED DEVIATION = 0.17540D-02

 SUBROUTINE MQERR.
 QSAV (PT*P. SCALED, WHERE P IS THE JACOBIAN)....
   1     0.1000000D 01
   2     0.1000000D 01  0.1000000D 01
   3     0.9952360D 00  0.9952350D 00  0.1000000D 01

 THE SECOND DERIVATIVE MATRIX IS SINGULAR IN MQERR.          RANK =  2        ORDER =  3
 THEREFORE ALL PARAMETER ERRORS ARE INFINITE.
 THE ( 2, 2) ELEMENT OF QSAV**-1 =  0.00000D 00      THEREFORE ALL PARAMETER ERRORS ARE INFINITE.

 NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =   11
 EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =   11  PLUS OR MINUS 0.46904D 01
 ACTUAL VALUE OF PHI = 0.34724D-05
 RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.56185D-03

 MAXIMUM VARIANCE INFLATION FACTOR = 0.10520D 03

 APPROXIMATE STANDARD ERRORS....                                          RESCALED
          J       MASK(J)          X(J)               ERROR               ERROR
          1          0          0.10751490D 01       0.52887D 03         0.10000D 31
          2          0          0.30489586D-01       0.00000D 00         0.10000D 31
          3          1          0.00000000D 00       0.00000D 00         0.10000D 31
          4          0          0.44450792D 03       0.33823D 06         0.10000D 31

 LOWER TRIANGLE OF THE CORRELATION MATRIX....
```

```
             K ....    1            2            3            4
          MASK(K)....  0            0            1            0
J        MASK( J)
1         0        0.100000D 01
2         0        0.000000D 00  0.000000D 00
3         1        0.000000D 00  0.000000D 00  0.000000D 00
4         0       -0.99524D 00   0.000000D 00  0.000000D 00  0.100000D 01
```

```
PHYSICAL PROPERTIES AND EFFECTIVENESS FACTORS
FOR THE MODEL SYSTEM OF DBT IN TETRALINE:

       DBT       SOLVENT     SOLVENT         DBT        SOLVENT      EFFECTIVE                       EFFECTIVENESS
     REDUCED     REDUCED    VISCOSITY       VOLUME       VOLUME      DIFFUSIVITY         THIELE          FACTOR
      TEMP.       TEMP.       (CP)        (CC/GMOL)    (CC/GMOL)     (CM**2/SEC)         MODULUS     (DBT IN SOLVENT)

  1  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.01841     0.9998869835
  2  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.01841     0.9998869835
  3  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.01841     0.9998869835
  4  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.01841     0.9998869835
  5  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02179     0.9998417855
  6  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02179     0.9998417855
  7  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02179     0.9998417855
  8  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02179     0.9998417855
  9  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02179     0.9998417855
 10  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02471     0.9997965924
 11  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02471     0.9997965924
 12  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02471     0.9997965924
 13  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02471     0.9997965924
 14  0.62659     0.79740    0.1644723      177.640      181.166     0.848011D-05        0.02471     0.9997965924
```

```
             T(K)          P(PSIA)        H2 CONC. (WT. FRCN.)

   1       573.33          250.0          0.0003466
   2       573.33          250.0          0.0003466
   3       573.33          250.0          0.0003456
   4       573.33          250.0          0.0003466
   5       573.33          350.0          0.0004852
   6       573.33          350.0          0.0004852
   7       573.33          350.0          0.0004852
   8       573.33          350.0          0.0004852
   9       573.33          350.0          0.0004852
  10       573.33          450.0          0.0006239
  11       573.33          450.0          0.0006239
  12       573.33          450.0          0.0006239
  13       573.33          450.0          0.0006239
  14       573.33          450.0          0.0006239
```

```
              *************
              *  RESULTS  *
              *************

        FOR   14  DATA POINTS THE FITTED PARAMETERS OF THE MODEL ARE - -
              FATE CONSTANT (K) =  0.10761D 01
              ADSCRPTION COEFF. OF "A" =  0.30490D-01
              ADSORPTION COEFF. OF "P" =  0.00000D 00
              ADSORPTION COEFF. OF "B" =  0.44461D 03

              CONC. OUT (DATA)        CONC. OUT (FIT)       % ERROR: ((Y-FIT)/Y)*100

         1         0.00910              0.00933              -2.48955
         2         0.01740              0.01766              -1.50009
         3         0.02060              0.02072              -0.56568
         4         0.02170              0.02185              -0.68277
         5         0.00710              0.00726              -2.23811
         6         0.01800              0.01625               9.74448
         7         0.01970              0.01987              -0.85998
         8         0.02110              0.02125              -0.70364
         9         0.02190              0.02197              -0.33535
        10         0.00580              0.00595              -2.57313
        11         0.01500              0.01520              -1.35891
        12         0.01900              0.01922              -1.15659
        13         0.02060              0.02078              -0.89386
        14         0.02150              0.02161              -0.52246

        MEAN DEV. (WT. %) = 0.00028355

        AVERAGE % ERROR = 1.8310426

    STATEMENTS EXECUTED= 5528246
    CORE USAGE        OBJECT CODE=   55295 BYTES,ARRAY AREA=   73096 BYTES,TOTAL AREA AVAILABLE=  129024  BYTES
    DIAGNOSTICS        NUMBER OF ERRORS=       0, NUMBER OF WARNINGS=       0, NUMBER OF EXTENSIONS=      15
    COMPILE TIME=     0.38 SEC,EXECUTION TIME=    56.71 SEC,    14.39.27     WEDNESDAY     4 JAN 84     WATFIV - MAR 1980 V2L0

        C$STOP
```

APPENDIX G

LISTING OF PROGRAM USED IN PARAMETER SENSITIVITY STUDY

```
$JOB
C                   PROGRAM NAME: GENA.CNTL
C                   PROGRAM NUMBER: 012084.01
C
C          ***************************************
C
C          THE OBJECT OF THIS PROGRAM IS TO
C          USE 'MARQ' TO FIT GLOBAL, "N"TH ORDER
C          MODEL TO DATA GENERATED BY INTRINSIC
C          REACTION-BASED MODEL.
C
C          INTRINSIC MODEL:
C            REACTION-              A+B=P; IRREV.
C            ADSORPTION SCHEME-     DUAL SITE ; A&B/B
C            CONTROLLING MECH.-     SURFACE RXN.
C
C          MODEL COMPOUND SYSTEM:
C               A = DIBENZOTHIOPHENE (IN TETRALINE)
C               B = HYDROGEN
C               P = HYDRODESULFURIZATION PRODUCTS
C
C          ***************************************
C
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL EXFIT
C
C          COMMON FOR STSET AND STEPT(AND MARQ)
C
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),
     * DELMN(20),ERR(20,21),FOBJ,NV,NTRAC,MATRX,
     * MASK(20),NFMAX,NFLAT,JVARY,NXTRA,KFLAG,
     * NOREP,KERFL,KW
      COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,
     * METHD,KALCP,KORDF,MAXIT,LEQU,MXSUB,MXUPD
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
C
C          COMMON FOR FUNK (MY EXFIT)
C
      COMMON /CSTOR/ T(25),P(25),ALHSV(25),C1(25),
     * DEFF(25),G(25),RHPAC(50),EFF(50),VSOL(50)
C
      DIMENSION ADIF(50),DEVV1(50),AT(50)
      DIMENSION TRA(50),TRSOL(50),Q1(50),Q2(50),O(50),
     * VISOL(50),GAMA(50),GAMSOL(50),VRA1(50),VRSOL1(50),
     * DIFUS(50),VA(50)
      DIMENSION RATEK(50),RKA(50),RKB(50),PKP(50)
C
C
C          SELECT THE ROOT-FINDING PROCEDURE WHICH WILL
C          BE USED TO COMPUTE THE INTRINSIC MODEL-GENERATED
C          OUTLET CONCENTRATION.  IF "ICALL" = 1 , BISECTING
C          METHOD IS USED.  IF "ICALL" = 2 , SECANT METHOD
C          IS USED.
C
C
C*OPTIONS LIST
      ICALL=1
C
      ALL2=DEVV2=DEVV3=0.0
      KR=5
      KW=6
C          ***************************************
C
C          THIS SECTION GENERATES THE INTRINSIC
C          MODEL PARAMETERS AT EACH GIVEN
C          OPERATING CONDITION . . .
C
C          ***************************************
C
      ZZ3=0.D0
C
C          CONSTANTS USED IN THE CORRELATIONS FOR
C          THE PARAMETERS OF THE INTRINSIC MODEL . . .
C
      ZK1=0.21874720685399D5
       ZK2=-0.61253649011330D3
       ZK3=0.57582257626801D0
       ZK4=-0.18002839330295D-3
      ZKA1=-0.48121308445175D2
       ZKA2=0.13546470798660D0
       ZKA3=-0.12708249021518D-3
       ZKA4=0.39745524251675D-7
      ZKB1=0.72153248206598D7
       ZKB2=-0.20090035099312D5
       ZKB3=0.18636365886361D2
       ZKB4=-0.57596353811257D-2
      ZKP1=0.43535931897521D6
       ZKP2=-0.12140546687897D4
       ZKP3=0.11278595691641D1
       ZKP4=-0.34905879501636D-3
C
C          READ AND WRITE THE INPUT DATA . . .
C
      READ (KR,100) NPTS
  100 FORMAT (I5)
      READ, (T(IA),IA=1,NPTS)
      READ, (P(IB),IB=1,NPTS)
      READ, (ALHSV(IC),IC=1,NPTS)
      READ, (C1(ID),ID=1,NPTS)
      WRITE(KW,85); WRITE(KW,86)
   85 FORMAT(1H1,5X,'OPERATING CONDITIONS:'//)
   86 FORMAT(15X,'TEMP.',8X,'PRESSURE',6X,'LHSV',9X,'IN. CONC.'/
     * 14X,'(DEG. F)',7X,'(PSIA)',5X,'(HR.**-1)',8X,'(WT. %)'//)
      WRITE(KW,125) (K,T(K),P(K),ALHSV(K),C1(K),K=1,NPTS)
  125 FORMAT(1X,I5,4E15.5)
      WRITE(KW,28)
   28 FORMAT(1H1,4X,'INTRINSIC EQUATION PARAMETERS - -'///
     * 13X,'TEMP (K)',11X,'RATE CONSTANT',13X,'KA',18X,
     * 'KB',17X,'KP'//)
C
C
      DO 110 K=1,NPTS
C
      YSIG(K)=1.D0
C
C          CONVERT TEMPERATURES TO ABSOLUTE . . .
C
      T(K)=T(K)+460.D0
C
```

```
C             CONVERT CONCENTRATIONS TO WT. FRACTION . . .
C
        C1(K)=C1(K)/100.D0
C
C             ESTIMATE THE INTRINSIC MODEL PARAMETERS
C             AT EACH OPERATING CONDITION . . .
C
C             NOTE:     RATEK= RXN. RATE COEFFICIENT.
C                       RKA=ADSORPTION COEFF. OF "A".
C                       RKB=ADSORPTION COEFF. OF "B".
C                       RKP=ADSORPTION COEFF. OF "P".
C
        RATEK(K)=ZK1+ZK2*T(K)+ZK3*(T(K)**2)+ZK4*(T(K)**3)
        RKA(K)=ZKA1+ZKA2*T(K)+ZKA3*(T(K)**2)+ZKA4*(T(K)**3)
        RKB(K)=ZKB1+ZKB2*T(K)+ZKB3*(T(K)**2)+ZKB4*(T(K)**3)
        RKP(K)=ZKP1+ZKP2*T(K)+ZKP3*(T(K)**2)+ZKP4*(T(K)**3)
C
        IF(RATEK(K).LE.Z23) RATEK(K)=Z23
        IF(RKA(K).LE.Z23) RKA(K)=Z23
        IF(RKB(K).LE.Z23) RKB(K)=Z23
        IF(RKP(K).LE.Z23) RKP(K)=Z23
C
  110 CONTINUE
C*OPTIONS_LIST
C
C             IDENTIFY THE "CONSTANTS OF VARIANCE" FOR THE
C             INTRINSIC MODEL PARAMETERS . . .
C
        VARK=1.D0
        VARKA=1.D0
        VARKB=1.D0
        VARKP=1.D0
C
        DO 231 K=1,NPTS
C
C             INTERPOLATE FOR "RKP" . . .
C
C       IF(T(K).EQ.T(8)) RKP(K)=(2.D0*RKP(10)+5.D0*RKP(6))/7.D0
C       IF(T(K).EQ.T(8)) RKB(K)=(2.D0*RKB(10)+5.D0*RKB(6))/7.D0
C
C             APPLY THE "CONSTANTS OF VARIANCE" . . .
C
        RATEK(K)=RATEK(K)*VARK
        RKA(K)=RKA(K)*VARKA
        RKB(K)=RKB(K)*VARKB
        RKP(K)=RKP(K)*VARKP
C
        WRITE(KW,131) K,T(K),RATEK(K),RKA(K),RKB(K),RKP(K)
  131 FORMAT(5X,I3,5X,F6.1,6X,4E20.7)
C
  231 CONTINUE
C
C             *********************************
C             THIS SECTION COMPUTES SOME
C             PHYSICAL PROPS. FOR "DBT" AND
C             TETRALINE (SOLVENT) AND ESTIMATES
C             THE EFFECTIVE DIFFUSIVITY, THE
C             EFFECTIVENESS FACTOR, AND THE
C             HYDROGEN SOLUBILITY AT EACH
C             OPERATING CONDITION.
```

```
C             ********************************
C
C             CRITICAL PROPS., ETC. USED IN COMPUTATIONS.
C             TEMPS. IN RANKINE; PRESSURES IN ATMOSPHERES . . .
C
        R=82.0567D0
        ESUBS=0.5D0
        TORTF=3.5D0
        RACP=150.D0
        RADC=0.01D0
C
C             PROPS. OF DBT . . .
C
        AA=21.D0
        TCA=1647.D0
        TBA=1091.4D0
        PCA=39.7D0
        RMWA=184.27D0
C
C             PROPS. OF SOLVENT . . .
C
        ASOL=18.D0
        TCSOL=1294.2D0
        TBSOL=865.3D0
        PCSOL=35.8D0
        RMWSOL=132.21D0
C
C             CONSTANTS, COEFFICIENTS, ETC. . . .
C
        REX1=1.D0/6.D0; RVAR=3.D0/7.D0; RLGN=2.302581D0
        RC1=3.015174D0; RC2=0.02135D0; RC3=0.0075D0
        TC1=0.042552D0; TC2=0.07674D0; TC3=0.034D0
        UC1=0.29637D0; UC2=0.09045D0; UC3=0.0484D0
        VC1=0.33593; VC2=0.33953; VC3=1.51941; VC4=2.02512; VC5=1.11422
        XC1=1.3D0; XC2=0.50879D0; XC3=0.9534D0
        YC1=0.292D0; YC2=0.0957D0
        BB1=8.2D-6; BB2=25.2D-3; BB3=17.5D-8
        REX2=2.D0/3.D0; REX3=1.D0/3.D0
C
C             BEGIN CALCULATIONS . . .
C
        EA=((TCA/1.8)/((RMWA**3)*(PCA**4)))**REX1
        ESOL=((TCSOL/1.8)/((RMWSOL**3)*(PCSOL**4)))**REX1
        WA=RVAR*((DLOG(PCA)/RLGN)/(TCA/TBA-1.))-1.
        WSOL=RVAR*((DLOG(PCSOL)/RLGN)/(TCSOL/TBSOL-1.))-1.
        VSCA=(R*(TCA/1.8)/PCA)*(YC1-YC2*WA)
        VSCSOL=(R*(TCSOL/1.8)/PCSOL)*(YC1-YC2*WSOL)
C
        DO 60 N=1,NPTS
C
        TRA(N)=T(N)/TCA
        TRSOL(N)=T(N)/TCSOL
C
C             CALCULATE SOLVENT VISCOSITY . . .
C
        Q1(N)=RC1-RC2*TRSOL(N)+RC3*(TRSOL(N)**2)
        Q2(N)=TC1-TC2*TRSOL(N)+TC3*(TRSOL(N)**2)
        Q(N)=Q1(N)+WSOL*Q2(N)
        VISOL(N)=Q(N)/ESOL
C
```

```
C           CALCULATE MOLAR VOLUMES . . .
C
      GAMA(N)=UC1-UC2*TRA(N)-UC3*(TRA(N)**2)
      IF(TRA(N).GE.0.20 .AND. TRA(N).LE.0.80) GO TO 51
      IF(TRA(N).GE.0.80 .AND. TRA(N).LE.1.0) GO TO 52
   51 VRA1(N)=VC1-VC2*TRA(N)+VC3*(TRA(N)**2)
     *         -VC4*(TRA(N)**3)+VC5*(TRA(N)**4)
      GO TO 55
   52 REDT=1.0-TRA(N)
      VRA1(N)=1.0+(XC1*(DSQRT(REDT)))*(DLOG(REDT)/RLGN)
     *         -XC2*REDT-XC3*(REDT**2)
   55 VA(N)=VSCA*VRA1(N)*(1.-WA*GAMA(N))
C
      GAMSOL(N)=UC1-UC2*TRSOL(N)-UC3*(TRSOL(N)**2)
      IF(TRSOL(N).GE.0.20 .AND. TRSOL(N).LE.0.80) GO TO 57
      IF(TRSOL(N).GE.0.80 .AND. TRSOL(N).LE.1.0) GO TO 58
   57 VRSOL1(N)=VC1-VC2*TRSOL(N)+VC3*(TRSOL(N)**2)
     *         -VC4*(TRSOL(N)**3)+VC5*(TRSOL(N)**4)
      GO TO 59
   58 REDT1=1.0-TRSOL(N)
      VRSOL1(N)=1.0+(XC1*(DSQRT(REDT1)))*(DLOG(REDT1)/RLGN)
     *         -XC2*REDT1-XC3*(REDT1**2)
   59 VSOL(N)=VSCSOL*VRSOL1(N)*(1.-WSOL*GAMSOL(N))
C
C           CALCULATE DIFFUSION COEFF. OF DBT
C           AND EFFECTIVE DIFFUSIVITY . . .
C
      IF(VA(N).GE.VSOL(N)) RKK=BB1*(1.0+(3.0*VSOL(N)/VA(N)))**REX2
      IF(VA(N).LE.VSOL(N)) RKK=BB2
      VVV=2.5*VSOL(N)
      IF(VA(N).LE.VVV) RKK=BB3
      DIFUS(N)=(RKK*T(N)/1.8)/(VISOL(N)*(VA(N)**REX3))
      DEFF(N)=(ESJBS*DIFUS(N)/TORTF)*(1.-AA/RADP)**4
C
C           CALCULATION OF H2 SOLUBILITY
C           WHERE G=H2 CONC. IN WT. FRACTION
C           AND AT=TEMPERATURE IN KELVIN . . .
C
      AT(N)=T(N)/1.80
      G(N)=P(N)*(DEXP(-(12.28+715.0/AT(N))))
C*OPTIONS LIST
C
C           CALCULATE THE THIELE MODULUS AND THE
C           EFFECTIVENESS FACTOR (FOR DBT IN SOLVENT) . . .
C
      RPARM=RATEK(N)*RKA(N)*RKB(N)*RMWA*G(N)
      RHFAC(N)=RADC*(DSQRT(RPARM/DEFF(N)/3630.D0))/3.D0
      EFF(N)=DTANH(RHFAC(N))/RHFAC(N)
C
C     ****************************************************************
C
C           CALL THE ROUTINE ('SECNT' OR 'BSCT') TO FIND THE
C           INTRINSIC MODEL- GENERATED OUTLET CONCENTRATION . . .
C
C     ****************************************************************
C
      IF(ICALL.EQ.2) GO TO 21
      CALL BSCT(C1(N),RATEK(N),RKA(N),RKP(N),RKB(N),G(N),
     *  P(N),ALHSV(N),EFF(N),VSOL(N),Y(N))
      GO TO 60
   21 CALL SECNT(C1(N),RATEK(N),RKA(N),RKP(N),RKB(N),G(N),
     *  P(N),ALHSV(N),EFF(N),VSOL(N),Y(N))
   60 CONTINUE
C
C     *************************************
C
C           THIS SECTION FITS THE INTRINSIC
C           MODEL-GENERATED DATA TO THE
C           GLOBAL MODEL . . .
C
C     *************************************
C
C           INITIATE MODEL FIT BY GIVING VALUES TO
C           MARQ VARIABLES . . .
C
      CALL STSET
C
      MAXIT=200
      NV=4
      XMIN(1)=XMIN(2)=XMIN(3)=0.D0
      XMAX(4)=20.D0
      X(1)=5.943D6
      X(2)=0.4D5
      X(3)=0.4D0
      X(4)=0.5D0
C
C           CALL THE FITTING ROUTINE . . .
C
      CALL STEPT(EXFIT)
C     CALL HIGH(FIT)
C
C     *************************************
C
C           WRITE OUT THE RESULTS . . .
C
C     *************************************
C
      WRITE(KW,91) ; WRITE(KW,92)
   91 FORMAT(1H1,6X,'PHYSICAL PROPERTIES AND EFFECTIVENESS FACTORS'/
     *  8X,'FOR THE MODEL SYSTEM OF DBT IN TETRALINE:'//)
   92 FORMAT(7X,'DBT',5X,'SOLVENT',4X,'SOLVENT',7X,'DBT',7X,'SOLVENT',
     *  2X,'EFFECTIVE',17X,'EFFECTIVENESS'/5X,'REDUCED',3X,'REDUCED',
     *  3X,'VISCOSITY',5X,'VOLUME',6X,'VOLUME',4X,'DIFFUSIVITY',5X,
     *  'THIELE',8X,'FACTOR'/6X,'TEMP.',5X,'TEMP.',6X,'(CP)',6X,
     *  2('(CC/GMOL)',3X),'(CM**2/SEC)',4X,'MODULUS',4X,
     *  '(DBT IN SOLVENT)'//)
      WRITE(KW,93) (II,TRA(II),TRSOL(II),VISOL(II),VA(II),VSOL(II),
     *  DEFF(II),RHFAC(II),EFF(II),II=1,NPTS)
   93 FORMAT(1X,I2,2X,F7.5,3X,F7.5,3X,F9.7,3X,F9.3,3X,F9.3,3X,
     *  E12.6,2X,F10.7,2X,F12.10)
C
      WRITE(KW,4)
    4 FORMAT(/////5X,'HYDROGEN SOLUBILITY DATA:'///)
      WRITE(KW,5)
    5 FORMAT(10X,'T(K)',10X,'P(PSIA)',13X,'H2 CONC. (WT. FRCN.)'//)
      WRITE(KW,8) (I,AT(I),P(I),G(I),I=1,NPTS)
    8 FORMAT(I4,4X,F7.2,9X,F7.1,10X,F10.7)
C
      WRITE (KW,130)
  130 FORMAT (1H1,14X,'*************'/15X,'*  RESULTS  *'/15X,
```

```
     *  '**************')
      WRITE (KW,140) NPTS,X(1),X(2),X(3),X(4)
  140 FORMAT (////10X,'FOR',I5,2X,'DATA POINTS THE FITTED ',
     *  'PARAMETERS OF THE MODEL ARE - -'//15X,
     *  'PRE-EXPONENTIAL CONTANT =',E13.5//15X,
     *  'ACTIVATION ENERGY =',E13.5//15X,
     *  'PRESSURE EXPONENT =',E13.5//15X,
     *  'CONCENTRATION EXPONENT =',E13.5//)
      WRITE (KW,145)
  145 FORMAT (15X,'CONC. OUT (DATA)',7X,'CONC. OUT (FIT)',
     *  7X,'% ERROR: ((Y-FIT)/Y)*100 '//)
C
C     ***********************************************************
C
C        COMPUTE MEAN DEVIATION ("ADEV") AND
C        AVERAGE PERCENT ERROR ("DEVV3") . . .
C
C     ***********************************************************
C
  150 DO 200 K=1,NPTS
C
      ADIF(K)=DABS(Y(K)-FIT(K))
      ALL2=ADIF(K)+ALL2
C
      DEVV1(K)=((Y(K)-FIT(K))/Y(K))*100.0
      DEVV2=DABS(DEVV1(K))+DEVV2
C
      WRITE (KW,180) K,Y(K),FIT(K),DEVV1(K)
  180 FORMAT (7X,I3,8X,F11.9,8X,F11.9,8X,F12.8)
  200 CONTINUE
C
      ADEV=ALL2/NPTS
      DEVV3=DEVV2/NPTS
      WRITE (KW,220) ADEV
  220 FORMAT (//10X,'MEAN DEV. (WT. %) = ',F10.8)
      WRITE (KW,240) DEVV3
  240 FORMAT(//10X,'AVERAGE % ERROR =',F10.7///)
      STOP
      END
```

```
      SUBROUTINE EXFIT (FITM)
C     SUBROUTINE HIGH(FITM)
C
C        THIS SUBROUTINE IS REFERRED TO BY
C        MARQ AS FUNK(FIT).
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION FITM(1)
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),
     *  DELMN(20),ERR(20,21),FOBJ,NV,NTRAC,MATRX,
     *  MASK(20),NFMAX,NFLAT,JVARY,NXTRA,KFLAG,
     *  NOREP,KERFL,KW
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
      COMMON /CSTOR/ T(25),P(25),ALHSV(25),C1(25),
     *  DEFF(25),G(25),RMFAC(20),EFF(50),VSOL(50)
      R=1.986D0
      REXH=2.D0/3.D0
      XNUMB=1.001D0; XNUMS=0.9900
C     WRITE(KW,23) (X(JW),JW=1,NV)
C  23 FORMAT(//10X,'X VALUES:',5X,8E16.8)
C
      DO 200 J=1,NPTS
C
C        ZZ1 AND ZZ2 COMPRISE THE FIRST-ORDER MODEL.
C        AND FF GIVES THE GENERAL "NTH-ORDER MODEL.
C
C*OPTIONS LIST
      RHOLD=ALHSV(J)**REXH
C     RHOLD=ALHSV(J)
      IF (X(4).LE.XNUMB .AND. X(4).GE.XNUMS) GO TO 80
      FF1=X(1)*(DEXP(-X(2)/R/T(J)))*(P(J)**X(3))/RHOLD
      FF2=C1(J)**(1.D0-X(4))
      FF=(FF2-(1.D0-X(4))*FF1)**(1.D0/(1.D0-X(4)))
      FITM(J)=FF
      GO TO 200
   80 X(4)=1.D0
      ZZ1=X(1)*(DEXP(-X(2)/R/T(J)))*(P(J)**X(3))/RHOLD
      ZZ2=C1(J)*(DEXP(-ZZ1))
      FITM(J)=ZZ2
  200 CONTINUE
C
      RETURN
      END
```

```
      SUBROUTINE SECNT(CIN,RATEX,XA,XP,XB,G1,RP,RLHSV,EFFEC,VOL,FITK)
C
C         THIS SUBROUTINE CONTAINS A NUMERICAL PROCEDURE,
C         THE SECANT METHOD, TO SOLVE FOR THE OUTLET
C         CONCENTRATION.  THIS METHOD IS MUCH FASTER
C         THAN THE BISECTING METHOD, BUT IS MORE PRONE
C         TO GENERATE CONCENTRATION VALUES WHICH ARE
C         NOT COMPATIBLE WITH THE FUNCTION BEING USED
C         IN ROUTINE 'CONC'.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION CA(50),EROR(50),FOFCA(50),DRVCA(50)
      ZZERO=1.D-9
      CPO=0.D0
C
C         INITIALIZE THE METHOD . . .
C
      CA(1)=CIN/4.D0
      CA(2)=CIN/2.D0
      DC 700 KK=1,2
      FOFCA(KK)=CONC(CIN,CPO,RATEX,XA,XP,XB,G1,RP,RLHSV,CA(KK),
     *  EFFEC,VOL)
  700 CCATINUE
C
C         ITERATE TO FIND OUTLET CONCENTRATICN . . .
C
      L=1
  710 L=L+1
      DRVCA(L)=(FOFCA(L)-FOFCA(L-1))/(CA(L)-CA(L-1))
      EROR(L)=DABS(CA(L)-CA(L-1))
      FRACX=ZZERO*DMAX1(DABS(CA(L)),DABS(CA(L-1)))
      IF(EROR(L).LE.FRACX) GO TO 750
      CA(L+1)=CA(L)-FOFCA(L)/DRVCA(L)
      FOFCA(L+1)=CONC(CIN,CPO,RATEX,XA,XP,XB,G1,RP,RLHSV,CA(L+1),
     *  EFFEC,VOL)
      GO TO 710
  750 FITK=CA(L)
      RETURN
      END
```

```
      SUBROUTINE BSCT(CIN,RATEX,XA,XP,XB,G1,RP,RLHSV,EFFEC,VOL,FITK )
C
C         USE BISECTING METHOD TO COMPUTE OUTLET CONC.
C         THIS ROUTINE IS SLOWER THAN ROUTINE 'SECNT', BUT
C         MORE RELIABLE.  THE IMPROVED RELIABILITY IS DUE
C         TO THE FACT THAT THE ONLY SOLUTICNS PERMISSIBLE
C         IN 'BSCT' ARE THOSE THAT ARE COMPATIBLE WITH THE
C         FUNCION BEING USED IN ROUTINE 'CONC'.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      ZZERO=1.D-10
      CPO=0.D0
C
C          INITIALIZE THE METHOD . . .
C
      CA2=CIN
      F1=CONC(CIN,CPO,RATEX,XA,XP,XB,G1,RP,RLHSV,CA2,EFFEC,VOL )
      IF(F1) 62,95,64
   62 IJ=1
      GO TO 70
   64 IJ=2
   70 CA2=ZZERO
      F2=CONC(CIN,CPO,RATEX,XA,XP,XB,G1,RP,RLHSV,CA2,EFFEC,VOL )
      IF(F2) 72,95,74
   72 KL=1
      GC TO 78
   74 KL=2
   78 IF(IJ.EQ.KL) GO TO 95
      CA2=CIN
   80 CA1=CA2
      CA2=CA2/2.D0
C
C          ITERATE TO FIND THE OUTLET CONCENTRATION . . .
C
   81 FC=CONC(CIN,CPO,RATEX,XA,XP,XB,G1,RP,RLHSV,CA2,EFFEC,VOL)
      IF(DABS(FC).LE.ZZERO) GO TO 95
      IF(FC) 82,95,84
   82 MN=1
      GO TO 90
   84 MN=2
   90 IF(MN.EQ.IJ) GO TO 80
      CA2=(CA1+CA2)/2.D0
      GO TO 81
C
   95 FITK=CA2
      GO TO 98
   96 WRITE(6,97)
   97 FCRMAT(////10X,'***   NO SOLUTION IN RANGE   ***'////)
      FITK=CIN
   98 CCNTINUE
      RETURN
      END
```

```
 285          FUNCTION CONC(CAIN,CPIN,RATEC,XA1,XP1,XB1,G2,PRES,ZLHSV,COUT,
             *   EFFAC,VOLUM)
        C
        C          THIS ROUTINE COMPUTES THE FUNCTION FOR WHICH THE ROOT
        C          IS BEING DETERMINED IN ROUTINE 'SECNT' OR 'BSCT'.
        C
 286          IMPLICIT REAL*8 (A-H,O-Z)
        C
        C          MOLECULAR WTS. OF CBT AND SOLVENT . . .
        C
 287          RMWA2=184.27D0
 288          RMWB2=132.21D0
        C
        C          CALCULATE OIL DENSITY IN GRAMS/CM**3 . . .
        C
 289          DOIL=RMWB2/VOLUM
        C
        C          CALCULATE "CATALYST BED PARAMETER", W*RMWA2/DOIL/V,
        C          BASED UPON "W" = 1 GRAM OF CATALYST, AND
        C          "V" = 1 CM**3 OF CATALYST . . .
        C
 290          RBED=RMWA2/DOIL
        C$OPTIONS LIST
        C
        C          FIND THE VALUE OF THE FUNCTION . . .
        C
 291          FOFCA1=(XA1-XP1*0.85D0)*(CAIN-COUT)
 292          FOFCA2=(1.D0+XP1*CPIN+XP1*CAIN*0.85D0)*DLOG(CAIN/COUT)
 293          FOFCA3=(RATEC*XA1*XB1*G2*RBED/(1.D0+XB1*G2))/ZLHSV)*EFFAC
        C
 294          CONC=FOFCA1+FOFCA2-FOFCA3
        C
 295          RETURN
 296          END

        $ENTRY
```

```
OPERATING CONDITIONS:

               TEMP.         PRESSURE        LHSV          IN. CONC.
             (DEG. F)         (PSIA)      (HR.**-1)        (WT. %)

   1       0.545000D 03    0.250000D 03   0.100000D 01   0.243000D 01
   2       0.545000D 03    0.350000D 03   0.300000D 01   0.243000D 01
   3       0.545000D 03    0.450000D 03   0.600000D 01   0.243000D 01
   4       0.572000D 03    0.250000D 03   0.300000D 01   0.243000D 01
   5       0.572000D 03    0.350000D 03   0.600000D 01   0.243000D 01
   6       0.572000D 03    0.450000D 03   0.900000D 01   0.243000D 01
   7       0.617000D 03    0.250000D 03   0.900000D 01   0.243000D 01
   8       0.617000D 03    0.350000D 03   0.120000D 02   0.243000D 01
   9       0.617000D 03    0.450000D 03   0.150000D 02   0.243000D 01
  10       0.662000D 03    0.250000D 03   0.900000D 01   0.243000D 01
  11       0.662000D 03    0.350000D 03   0.120000D 02   0.243000D 01
  12       0.662000D 03    0.450000D 03   0.150000D 02   0.243000D 01
```

```
INTRINSIC EQUATION PARAMETERS - -

          TEMP (K)          RATE CONSTANT          KA                  KB                 KP

  1       1005.0          0.8897700D 00      0.8934000D-02      0.1572700D 04      0.7981900D 02
  2       1005.0          0.8897700D 00      0.8934000D-02      0.1572700D 04      0.7981900D 02
  3       1005.0          0.8897700D 00      0.8934000D-02      0.1572700D 04      0.7981900D 02
  4       1032.0          0.4348900D 01      0.1687400D-01      0.1431600D 03      0.2049400D 00
  5       1032.0          0.4348900D 01      0.1687400D-01      0.1431600D 03      0.2049400D 00
  6       1032.0          0.4348900D 01      0.1687400D-01      0.1431600D 03      0.2049400D 00
  7       1077.0          0.5940800D 02      0.1936700D-01      0.3138700D 02      0.1814624D-07
  8       1077.0          0.5940800D 02      0.1936700D-01      0.3138700D 02      0.1814624D-07
  9       1077.0          0.5940800D 02      0.1936700D-01      0.3138700D 02      0.1814624D-07
 10       1122.0          0.9077800D 02      0.2726800D-01      0.2890300D 02      0.1121953D-07
 11       1122.0          0.9077800D 02      0.2725800D-01      0.2890300D 02      0.1121953D-07
 12       1122.0          0.9077800D 02      0.2726800D-01      0.2890300D 02      0.1121953D-07
```

```
MARQ....  BEGIN NONLINEAR LEAST SQUARES SOLUTION
MASK    =       0            0            0            0
X       =   0.59430D 07  0.40000D 05  0.40000D 00  0.50000D 00
XMAX    =   0.10000D 31  0.10000D 31  0.10000D 31  0.20000D 02
XMIN    =   0.00000D 00  0.00000D 00 -0.10000D 31  0.00000D 00
DELMN   =   0.59430D-01  0.40000D-03  0.40000D-08  0.50000D-08

NV =    4        NPTS =    12      LPDMA =    300      LPDMB =  20      NTRAC = 0       METHD =  1       KALCP =  0
KORDF = 1        NFLAT = 1         NFMAX =  32767      MAXIT =  200     MXSUB =   25
CRIT = 0.70711D 00       RELDF = 0.10000D-07      RELMN = 0.10000D-07

PHI (THE SUM OF SQUARES) = 0.27320595D-03                                                     LAMBDA = 0.10000D 01


CONVERGENCE ACHIEVED UNDER THE NFLAT OPTION.
  74 ITERATIONS       NF =  497        PHI = 0.53766631D-05           FNGN = 0.10000D 01           LAMBDA = 0.30948D 03
        NORM OF SCALED GRADIENT VECTOR = 0.15444D-09
             X =   0.3253503D 06  0.3890606D 05  0.5829528D 00  0.3016772D 00

          J        Y(J)               FIT(J)            Y(J)-FIT(J)        YSIG(J)              (Y-FIT)/YSIG

          1    0.14725440E-01     0.15768245D-01     -0.10428D-02     0.10000D 01          -0.10428D-02
          2    0.19204100E-01     0.19174395D-01      0.29711D-04     0.10000D 01           0.29711D-04
          3    0.21060780E-01     0.20525247D-01      0.53554D-03     0.10000D 01           0.53554D-03
          4    0.18152200E-01     0.17379701D-01      0.77251D-03     0.10000D 01           0.77251D-03
          5    0.19885940E-01     0.18932560D-01      0.95438D-03     0.10000D 01           0.95438D-03
          6    0.20528610E-01     0.19536554D-01      0.99205D-03     0.10000D 01           0.99205D-03
          7    0.16563880E-01     0.16970145D-01     -0.40626D-03     0.10000D 01          -0.40626D-03
          8    0.16279640E-01     0.16939901D-01     -0.66025D-03     0.10000D 01          -0.66025D-03
          9    0.16124840E-01     0.16955530D-01     -0.83074D-03     0.10000D 01          -0.83074D-03
         10    0.10491350E-01     0.10056867D-01      0.43449D-03     0.10000D 01           0.43449D-03
         11    0.10100050E-01     0.10003325D-01      0.96730D-04     0.10000D 01           0.95730D-04
         12    0.98999900E-02     0.10031075D-01     -0.14109D-03     0.10000D 01          -0.14109D-03

NUMBER OF DEGREES OF FREEDOM =  0.80000D 01
R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.81976D-03
MAXIMUM SCALED DEVIATION = 0.10428D-02

SUBROUTINE MQERR.
```

```
QSAV (PT*P, SCALED, WHERE P IS THE JACOBIAN)....
  1     0.1000000D 01
  2    -0.9991242D 00  0.1000000D 01
  3     0.9991158D 00 -0.9979018D 00  0.1000000D 01
  4    -0.9995625D 00  0.9976060D 00 -0.9987613D 00  0.1000000D 01

NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =     8
EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =     8  PLUS OR MINUS 0.40000D 01
ACTUAL VALUE OF PHI = 0.53761D-05
RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.81976D-03

MAXIMUM VARIANCE INFLATION FACTOR = 0.16279D 05

APPROXIMATE STANDARD ERRORS....
                                                                  RESCALED
          J        MASK(J)          X(J)             ERROR          ERROR
          1           0          0.32535030D 06     0.14777D 10     0.12114D 07
          2           0          0.38905065D 05     0.39349D 07     0.32256D 04
          3           0          0.58295282D 00     0.15290D 03     0.12534D 00
          4           0          0.30167723D 00     0.63193D 03     0.51803D 00

LOWER TRIANGLE OF THE CORRELATION MATRIX....
              K ....      1             2            3            4
        MASK(K)....       0             0            0            0
   J    MASK(J)
   1      0       0.10000D 01
   2      0       0.94910D 00  0.10000D 01
   3      0      -0.43648D 00 -0.28814D 00  0.10000D 01
   4      0       0.95557D 00  0.87983D 00 -0.22467D 00  0.10000D 01
```

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PHYSICAL PROPERTIES AND EFFECTIVENESS FACTORS
FOR THE MODEL SYSTEM OF DBT IN TETRALINE:

       DBT      SOLVENT      SOLVENT        DBT        SOLVENT      EFFECTIVE        THIELE     EFFECTIVENESS
     REDUCED    REDUCED     VISCOSITY      VOLUME      VOLUME      DIFFUSIVITY       MODULUS        FACTOR
      TEMP.      TEMP.        (CP)       (CC/GMOL)   (CC/GMOL)    (CM**2/SEC)                  (DBT IN SOLVENT)

  1  0.61020    0.77654    0.1797284     175.476     177.104    0.758819D-05    0.0177211    0.9998953338
  2  0.61020    0.77654    0.1797284     175.476     177.104    0.758819D-05    0.0209679    0.9998534746
  3  0.61020    0.77654    0.1797284     175.476     177.104    0.758819D-05    0.0237754    0.9998116197
  4  0.62659    0.79740    0.1644723     177.640     181.166    0.848011D-05    0.0156268    0.9999186090
  5  0.62659    0.79740    0.1644723     177.640     181.166    0.848011D-05    0.0184899    0.9998860571
  6  0.62659    0.79740    0.1644723     177.640     181.166    0.848011D-05    0.0209655    0.9998535077
  7  0.65392    0.83217    0.1405938     181.446     189.946    0.102800D-04    0.0270099    0.9997568929
  8  0.65392    0.83217    0.1405938     181.446     189.946    0.102800D-04    0.0319585    0.9996596898
  9  0.65392    0.83217    0.1405938     181.446     189.946    0.102800D-04    0.0362376    0.9995625093
 10  0.68124    0.86694    0.1186505     185.543     200.241    0.125961D-04    0.0351790    0.9995876826
 11  0.68124    0.86694    0.1186505     185.543     200.241    0.125961D-04    0.0416244    0.9994228699
 12  0.68124    0.86694    0.1186505     185.543     200.241    0.125961D-04    0.0471976    0.9992581223


     HYDROGEN SOLUBILITY DATA:

            T(K)             P(PSIA)           H2 CONC. (WT. FRCN.)

  1        558.33             250.0            0.0003352
  2        558.33             350.0            0.0004692
  3        558.33             450.0            0.0006033
  4        573.33             250.0            0.0003455
  5        573.33             350.0            0.0004852
  6        573.33             450.0            0.0006239
  7        598.33             250.0            0.0003652
  8        598.33             350.0            0.0005112
  9        598.33             450.0            0.0006573
 10        623.33             250.0            0.0003831
 11        623.33             350.0            0.0005363
 12        623.33             450.0            0.0006896
```

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             *************
             *  RESULTS  *
             *************

   FOR    12  DATA POINTS THE FITTED PARAMETERS OF THE MODE_ ARE - -
             PRE-EXPONENTIAL CCNTANT =  0.32535D 06
             ACTIVATION ENERGY =  ).38936D 95
             FRESSJRE EXPJNENT =  0.58295D 00
             CCNCENTRATION EXFONENT =  0.30168D 00

             CONC. OUT (DATA)         CCNC. OUT (FIT)          % ERROR; ((Y-FIT)/Y)*100

     1          0.014725445            0.015768245               -7.08163
     2          0.019204108            ).019174395                0.15473
     3          0.021060790            0.020525247                2.54285
     4          0.)181522)9            ).017379701                4.25572
     5          0.019886944            0.018932560                4.79904
     6          0.020528622            0.019536564                4.83256
     7          0.016563891            0.016970145               -2.45265
     8          0.016279651            0.016939901               -4.05568
     9          0.016124843            0.016955580               -5.15191
    10          0.010491362            ).010056867                4.14146
    11          0.010100056            0.010003325                0.95773
    12          0.009889991            ).010031075               -1.42653

   MEAN DEV. (WT. %) = 0.00057471

   AVERAGE % ERROR = 3.4877067

 STATEMENTS EXECUTED=  203991
 CORE USAGE       CBJECT CODE=   58392 BYTES,ARRAY AREA=   74296 BYTES,TOTAL AREA AVAILABLE=  378880  BYTES
 DIAGNOSTICS       NUMBER OF ERRORS=      0, NUMBER OF WARNINGS=      0, NUMBEP OF EXTENSIONS=     14
 COMPILE TIME=     0.42 SEC,EXECUTION TIME=     2.68 SEC,     15.31.35    FRIDAY      20 JAN 84    WATFIV - MAR 1980 V2L0

          C$STOP
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VITA 2

Richard Lee Jones

Candidate for the Degree of

Master of Science

Thesis: PARAMETER SENSITIVITY STUDIES IN MODELLING OF HYDROTREATMENT KINETICS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Stigler, Oklahoma, September 10, 1959, the son of Mr. and Mrs. Allen L. Jones.

Education: Graduated from Stigler High School, Stigler, Oklahoma, in May, 1977; received Bachelor of Science degree in Engineering Physics from Northeastern Oklahoma State University in 1981; completed requirements for the Master of Science degree at Oklahoma State University in May, 1984.

Professional Experience: Associate Engineer, Conoco, Incorporated, 1981-82; graduate research assistant, Oklahoma State University, School of Chemical Engineering, 1982-83; graduate teaching assistant, Oklahoma State University, School of Chemical Engineering, 1983.