MATHEMATICAL MODELING OF COAL LIQUID HYDROTREATMENT KINETICS

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PREFACE

This thesis work is an early portion of an effort to gain a comprehensive understanding of coal-derived liquid and other syn-fuel upgrading processes. Of the numerous individual processes taking place during this upgrading, or hydrotreatment, my attention was primarily focused on the removal of sulfur, nitrogen, and oxygen heteroatoms.

As a tool used to gain an understanding of the heteroatom removal processes I considered several types of both empirically and theoretically developed mathematical kinetic models. Using those models, I studied the reaction kinetics of the hydrotreatment of coal-derived liquids, which contain a complex mixture of reactants, and of reactant feeds containing a single model heterocompound.

Due to the theoretical nature of this study, the scarcity of applicable experimental data presented some difficulties. As a result, I limited the study of single heterocompound hydrotreatment to the hydrodesulfurization process.

I believe this work will be helpful to others in their continued effort to understand syn-fuel hydrotreatment. In as much, I know I have gained invaluable knowledge and experience through the completion of this work.

I would like to express my sincerest appreciation to my thesis advisor, Dr. Mayis Seapan, who, in addition to his instruction, has provided an unwavering source of friendly, patient support. Thanks also to Teresa Tackett for her skillful advice and production of this transcript. Finally, special thanks to Nichole and Wynona, who have patiently endured all and have provided a constant source of love and affection.

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LIST OF SYMBOLS

A	pre-exponential constant in temperature dependent reaction rate and adsorption equilibrium constants, variable units
Ci	concentration of species i in liquid phase (mole% or wt%)
D	free-liquid diffusivity of heterocompound (cm2/sec)
D_{eff}	effective diffusivity of heterocompound in catalyst pore (cm2/sec)
E	reaction activation energy or heat of adsorption, variable units
k	reaction rate constant, variable units
k_{obs}	observed reaction rate constant (hr^{-1})
Ki	adsorption equilibrium constant of species i (1/mole% or 1/wt%)
LHSV	liquid hourly space velocity (hr^{-1})
MW_L	molecular weight of solvent (g/gmole)
Pi	partial pressure of species i (psi or MPa)
Pc	critical pressure of solvent (atm)
r	reaction rate, variable units
r_{obs}	observed reaction rate (mole%/hr or wt%/hr)
R	gas constant, variable units
Rc	average catalyst particle radius (cm)
Rm	size of heterocompound molecule (angstroms)
Rp	average pore radius (angstroms)
S	solubility of hydrogen in solvent (g hydrogen/g solvent)
T	temperature (K or R)
Tc	critical temperature of solvent (K)

Tr	reduced temperature, unitless
V	reactor volume (cc)
V_L	molar volume of solvent at its normal boiling point (cc/g mole)
V_R	molar volume of heterocompound at its normal boiling point (cc/g mole)
W	weight of catalyst (g)
ε	catalyst void fraction, unitless
η	catalyst effectiveness factor, unitless
μ	viscosity of solvent (centipoise)
ρ	density of liquid (g/cc)
τ	catalyst tortuosity factor, unitless
ω	acentric factor, unitless

Superscripts

a,b,d,e,m,n	exponential power
', "	first and second reference condition

Subscripts

A, B, D,	denotes any species A, B, D
H	denotes hydrogen
P	denotes reaction product
R	denotes reaction reactant
1, 2	denotes first or second group when used in first sublevel, denotes inlet and outlet conditions when used in second sublevel

CHAPTER I

INTRODUCTION

Upgraded coal-derived liquids can be used as petroleum liquid substitutes in such applications as power generation fuels in combustion turbines and boilers, and as refinery feedstocks. Of the raw liquid products of coal liquefaction processes, most of the distillate liquids and essentially all the residual liquids are not directly suitable for use as petroleum-derived fuel substitutes. Upgrading is achieved through a hydrotreatment process in which the concentrations of sulfur, nitrogen, oxygen, and trace metal heteroatoms are reduced. Other consequential effects of hydrotreatment are hydrogenation, hydrocracking, increased storage stability, and reduction of viscosity, aromaticity and carcinogenicity.

Hydrotreatment, as it pertains to upgrading, is a process in which the major reactions, hydrogenation and hydrogenolysis of the hydrocarbon liquid, are promoted over a catalyst bed. Commercial hydrotreatment processes incorporate mostly fixed bed continuous flow reactors operating at high temperatures and pressures. The most common systems utilize the gravity induced trickle flow of the liquid feed with cocurrent hydrogen gas flow.

The reaction kinetics of hydrocarbon liquid hydrotreatment have been the subject of a number of studies and reports published since the 1960's. These works have covered a broad range of objectives, analysis procedures, proposed kinetic rate expressions, feed compositions, and operating and reactor conditions. However, a consensus opinion concerning hydrotreatment kinetics, especially in the case of coal-derived liquids, has not been formed and in many instances conflicting reports have been published (31).

Objectives

The objectives of this study of hydrotreatment kinetic modeling were threefold:

The first objective was to learn the reasons for the many differing and often contradictory reports concerning coal-derived liquid (CDL) hydrotreatment kinetics. Especially in question were inconsistent reports of the reaction orders and the temperature dependent Arrhenius constants.

The second objective of this work was to perform an evaluation of the kinetic rate expressions used to describe hydrotreatment processes. Specifically, these evaluations were to determine: What the various rate expressions are able to tell us through interpretation of their data fit results; determine the rate expression best suited for use in the modeling of CDL hydrotreatment kinetics; and determine the factors which have the greatest influence on the ability of a rate equation to describe hydrotreatment.

The third objective was to develop a mathematical kinetic model of the CDL hydrotreatment process. This kinetic model would use the rate expression which would allow the most accurate description of kinetic hydrotreatment data.

As a result of this work, the power-function or global models used by numerous authors to describe kinetic hydrotreatment data were found to yield calculated parameter values which were dependent on such factors as operating conditions and data fitting procedures. These dependencies are a possible reason for some of the inconsistent kinetic reports published over the years. A hyperbolic or intrinsic expression assuming two different types of reactant adsorption sites was found to be the superior type of rate expression for use in the description of catalytic hydrotreatmet kinetics. And, although the complexity of the CDL hydrotreatment process prevented the development of a mathematical kinetic model of that process, an accurate model was developed for the hydrodesulfurization of a model CDL compound, dibenzothiophene.

CHAPTER II

LITERATURE SURVEY AND PROCESS DESCRIPTION

Coal Liquids

An extensive literature survey was conducted in which information was reviewed concerning hydrocarbon liquid hydrotreatment and related subjects. Particular attention was focused on coal-derived liquids and heteroatom removal.

Coal-derived liquids are the products from any of more than twenty coal liquefaction processes. Three of the most popular processes are the Solvent Refined Coal (SRC), H-Coal, and Exxon Donor Solvent (EDS), all of which have been investigated on the pilot plant scale. Coal liquids are a complex mixture of aromatic and aliphatic hydrocarbons with sulfur, nitrogen, oxygen, and metallic compounds. Compared to petroleum liquids, they typically contain higher levels of nitrogen, oxygen and metallic heteroatoms, have a lower hydrogen content, and tend to be more viscous. Coal liquid heteroatoms are usually found in five and six member heterocycles. Sulfur is most abundant in the form of thiophene and its benzo- and dibenzo-derivatives, nitrogen in indoles, quinolines and carbazoles, and oxygen in phenols, fused ring furans, and carboxylic acids (23).

Hydrotreatment

Effects

The effects of primary concern in the hydrotreatment upgrading of hydrocarbon liquids are the removal of sulfur, nitrogen, oxygen, and metallic heteroatoms. These four heteroatom removal processes are referred to as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), and hydrodemetallation (HDM). Removal of these atoms is important for a number of reasons including: sensitivity and poisoning of reformer, hydrocracker, and other hydrotreatment catalysts; air pollution control standards governing combustion and catalyst regeneration gas emissions; and storage, handling, and corrosion problems. Depending upon the required specifications of the upgraded liquid, improvements in hydrogen content, storage stability, and viscosity may be of importance and can be accomplished to variable extents in the hydrotreatment process.

Reactor Systems

Several different types of batch and continuous flow reactors are used for hydrotreatment processing. Most batch reactors are used for laboratory reaction kinetic studies due to their ability to reduce flow, mass transfer, and temperature nonidealities. Conversely, nearly all commercial hydrotreatment processes incorporate continuous flow packed bed reactors, and most utilize the downward trickle flow of the liquid feed with cocurrent hydrogen gas flow.

Trickle-flow reactors have become most popular for several reasons. First, substantial savings may be realized by reduction of expensive hydrogen gas requirements needed for the vapor phase reactions once thought necessary to achieve high heteroatom conversion and limit catalyst coking (42). Also, the liquid phase reactant mixture suppresses excessive temperatures and hot spots caused by the exothermic hydrotreatment reactions. Such high temperatures can reduce catalyst life and cause unwanted hydrocracking.

Reactor conditions in commercial hydrotreatment processes cover a broad range of operating conditions, depending primarily upon the characteristics of the feedstock. Temperatures usually fall within a range of 300 to 450 C (550-850 F), pressure from 25 to 200 atm (350-3000 psi), and liquid hourly space velocities (LHSV) from 0.5 to 15 hr-1. Hydrogen consumption is highly dependent on feedstock properties and may range from less than 10 m^3 H_2/m^3 oil (56 std.cu.ft./bbl) for light distillate liquids to more than 1000 m^2 H_2/m^3 oil (5600 std.cu.ft./bbl) for heavy residual liquids (12, 25).

The use of Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalysts in the hydrotreatment process is almost universally accepted. The cobalt molybdate catalyst is a mixture of cobalt and molybdenum oxides dispersed in most cases over an aluminum oxide support. According to Richardson (22), the active component is a structurally unidentified cobalt-promoted MoO_3 complex, which assumes its true activated state after it sulfides. As a result of the dependence of catalyst's activity on its sulfided state, some minimal sulfur concentration must be present in the reactor at all times during the hydrotreatment process (24). This may require some hydrogen sulfide recirculation. Also,as a result of his catalyst study, Richardson reports that a Co:Mo ratio of 0.2 is desired for maximum activity. These catalyst particles are produced in the forms of spheres, tablets, pellets, and extrudates ranging from .08 to .32 cm (1/32 to 1/8 inch) in diameter (25). Other typical catalyst characteristics, as reported by Schuit (29), are bulk density (.15-1.0 g/cc), average pore volume (.2 - .8 cc/g), specific surface area (150 - 400 m2/g), and average pore diameter (6 - 20 nm).

Hydrotreatment catalyst deactivation is principally caused by coking and poisoning. Coking causes deactivation by deposition of carbonaceous material (coke) on catalysts and plugging their pores. The catalyst may be regenerated by burning off the coke, but the extent to which this may be accomplished may be limited due to the catalyst pores being plugged to the point where they inhibit the required diffusion of oxygen (24). Irreversible catalyst poisoning occurs through deposition of metals on the catalyst surface and adsorption of nitrogenous compounds on the acidic reaction adsorption sites.

Reaction Kinetics

Global Rate Equations.

The observed or global rate model is one of two common types used to describe hydrotreatment reaction kinetics. The global rate model is a power-function equation which has the general form:

$$r = kC_A^a \qquad [1]$$

The rate constant, k, follows the Arrhenius temperature dependency described by the following equation:

$$k = A\exp(-E/RT) \qquad [2]$$

Additional terms are sometimes included for dependence on hydrogen partial pressure and concentration of species other than the reactant. Such a rate expression could be written as follows:

$$r = k\, C_A^a\, C_B^b\, C_D^d\, P_H^e \qquad [3]$$

These global equations represent the reactor contents as a single homogeneous group.

As shown in a review by Seapan and Crynes (31), global rate equations have been used by several authors to represent multicomponent hydrocarbon hydrotreatment data from continuous flow reactors. The global rate expressions used by these authors can be separated into two groups.

The first group consists of simple first or second order expressions as described by Equation [1]. A host of authors have published works in which multicomponent hydrotreatment data was fitted by one of these simple power law expressions (1, 6, 11, 12, 14, 37, 38, 41, 44). The study by White (44) was the only member of this group in which an acceptable data fit was not reported. In that publication, a break in the linear Arrhenius plot was reported near 400 C (750 F), above and below which the data could be described by two separate straight lines.

The second group is represented by first or second order expressions which have been modified in some manner. Curtin (5), Shih (32), and Angevine (2) report acceptable fits to coal liquid and shale oil hydrotreatment data by global rate expressions which include time dependent catalyst deactivation constants. Sivasubrumanian (35, 36) and Mehta (17) reported that global equations incorporating a factor for incomplete catalyst wetting were able to fit hydrotreatment data acceptably well. Garg (9), Gary (10), Satchell (28), and Sooter (40) report good data fits by separating the feed mixture into separately reacting groups, each behaving according to a simple first order kinetic expression.

A common trend concerning these global kinetic expressions was apparent to this author. Those studies using data from liquids having a boiling range less than approximately 150 C (300 F) were able to fit the data with a simple first order model. At wider boiling ranges some studies report a break in the Arrhenius temperature plot for the simple first order model, while others proposed a higher order or modified version of the global rate model. As a rule, the liquids having a wide boiling range (greater than 150 C) could not be fitted by a simple first order global rate model. This phenomena is also discussed in a theoretical work in which Weekman (43) shows that a mixture of first order reactions follows an overall observed order greater than one. In contrast to the multicomponent hydrotreatment reports, most single component studies report first order dependencies on reactant concentration.

Intrinsic Rate Equations. Intrinsic or catalyst site rate models are also commonly used to describe hydrotreatment kinetics. The Langmuir-Hinshelwood adsorption model is the most widely used and accepted type of intrinsic rate model. A set of assumptions frequently made in hydrotreatment reaction studies is:

1. Reversible adsorption of heterocompound and hydrogen reactants.

2. Irreversible reaction of adjacently adsorbed heterocompound and hydrogen molecules.

3. Reversible desorption of hydrogenated product.

The Langmuir-Hinshelwood type intrinsic rate equation resulting from these assumptions is:

$$r = \frac{kC_AC_B}{(1 + K_AC_A + K_BC_B + K_PC_P)^2} \qquad [4]$$

where the reaction rate constant, k, and the adsorption equilibrium constants, K , follow the Arrhenius temperature dependencies described below:

$$k = A\ \exp(-E/RT) \qquad [5]$$

$$K_i = A_i \exp(+E_i/RT) \qquad [6]$$

The derivation of Equation [4] from the three assumptions listed above is shown in Appendix A. This type of intrinsic rate equation has many variable forms, each being individually derived from a specific set of adsorption and reaction assumptions.

A large number of hydrotreatment kinetic studies have been published in the past fifteen years, particularly of model compound hydrodesulfurization. After it became apparent to this author that a single rate equation derived from present adsorption-reaction theory would not be capable of describing the removal of all types of heteroatoms, attention was focused upon hydrodesulfurization, considered to be the most important of the heteroatom removal processes (7, 24, 30). It was thought an extensive understanding of this process would be a sound basis for the future development of an expanded model capable of describing the removal of a mixture of heteroatoms such as those found in coal derived liquids.

A number of model compound hydrodesulfurization studies were reviewed in this work. Among the most informative were reports about thiophene HDS published by Chakraborty (4), Massoth (16), and Satterfield (26, 27). In addition, several benzothiophene, dibenzothiophene, and other model compound HDS studies were reviewed (3, 7, 18, 33, 34). Most of these authors proposed intrinsic rate models that were specific forms of the generalized equation shown below:

$$r = \frac{kC_A C_B^{\ a}}{(1 + K_A C_A + K_B C_B + K_P C_P)^b} \qquad [7]$$

where A, B, and P represent heterocompound, hydrogen, and hydrogen sulfide, respectively. Reaction rate resistance due to competitive adsorption of hydrocarbons free of heteroatoms was normally assumed to be negligible or possibly not occurring at all. Broderick (3) and Massoth (16) studied several specific forms of Equation [7] but found the model described by Equation [8] to be superior,

$$r = \frac{kC_A C_B}{(1 + K_A C_A + K_P C_P)(1 + K_B C_B)} \qquad [8]$$

where A, B, and P again respectively represent heterocompound, hydrogen, and hydrogen sulfide. This observation was corroborated by Espino (7) and Singhal (34) in their studies of dibenzothiophene hydrodesulfurization kinetics. This model assumes the sulfur-containing molecules compete for one type of adsorption site while hydrogen molecules adsorb on a second type of site.

Several authors have suggested a two group theory could be used to describe the hydrodesulfurization of the sulfur-containing heterocompounds found in a wide boiling range liquid (9, 10, 29, 33, 40, 42). This concept involves the simultaneous first order reaction of two reactant groups, with each reaction proceeding at a rate proportional to the concentration of its group. Such an intrinsic rate expression could be written as shown in Equation [9],

$$r = \frac{\alpha k_1 C_A C_B}{(1 + K_A C_A + K_P C_P)(1 + K_H C_H)} + \frac{\beta k_2 C_B C_H}{(1 + K_B C_B + K_P C_P)(1 + K_H C_H)} \quad [9]$$

where α and β are the mixture fractions, and A and B represent the two reactant groups.

Process Models

For the purpose of use in this work, a process model was defined as an integrated plug flow design equation. The use of the ideal plug flow model implies the assumptions listed below (25):

1. No axial or radial dispersion.
2. No mass or heat transfer resistances in or between the gas, liquid and catalyst particle.
3. Catalyst particles are completely wetted.
4. Reaction occurs only at the solid-liquid interface.
5. No vaporization or condensation occurs.

Satterfield (24, 25) has indicated the nonidealities listed above do occur to varying extents, but the gas and liquid mass and heat transfer resistances are typically negligible, and, in the case of heteroatom removal, assumption of an irreversible first order reaction occurring at the solid-liquid interface is justified. Many authors have indicated significant pore diffusion resistance under some conditions. Another nonideality commonly assumed to significantly affect reactor performance is incomplete catalyst wetting. It should be noted that no multicomponent hydrotreatment process model was discovered in the literature search conducted in this work, except those which assumed global reaction kinetics and few or no reactor nonidealities.

CHAPTER III

PROCEDURE

Evaluation of Kinetic Rate Equations

In this work the abilities of several kinetic rate expressions were investigated through the performance and subsequent evaluation of HDS, HDN, and HDO data fit calculations. Evaluations began with the simplest forms of rate expressions and proceeded according to increasing model complexity.

Heck and Stein (12) published a paper containing experimental data from the hydrotreatment of two coal-derived liquids, an SRC recycle solvent and an H-coal distillate. These HDS, HDN, and HDO data were collected from each of 60 experimental runs, using both NiMo/Al_2O_3 and CoMo/Al_2O_3 commercial catalysts. Their system, using a trickle flow reactor, was typical in most respects of commercial hydrotreatment systems. The major deviations from large scale processes were lower liquid and gas velocities inside the reactor. This is a common characteristic of experimental reactors operating at space velocities similar to those used in commercial processes due to significant differences in the reactor length to diameter ratio. Because they contained an extensive set of experimental data collected from a system typifying commercial hydrotreatment, Heck and Stein's data were utilized in the data fit calculations of the model evaluations. In their work, Heck and Stein proposed the second order pressure dependent global rate model described in Equation [10].

$$r = A \exp(-E/RT)\ C_R^2\ P^m \qquad [10]$$

They reported the values of the model parameters which allowed the best fit to each of three data sets. Each set contained experimentally observed data for HDS, HDN, and HDO. As the first step taken to determine the reasons for the inconsistent global kinetic reports mentioned earlier, an attempt was made in this work to verify Heck and Stein's reported values of the second order model parameters. In addition, first and n-th order global models were tested and the calculated fits compared to those of the second order model. The comparative results of these three global rate models were used to determine the validity of using such simplified models to describe the intricate coal liquid heteroatom removal processes.

All the data fits in this work were calculated using a version of the Marquardt nonlinear data fit technique. This particular version was one modified by Professor John P. Chandler, of the Department of Computing and Information Sciences at Oklahoma State University. Chandler's version of the Marquardt computer program is listed in Appendix D. Output from this program includes several measures of the goodness of fit. These are: the residual mean square (rms) and minimized sum of squares (PHI), both measures of the deviation of the fitted from observed values; a correlation matrix indicating the degree of parameter interdependence; and the rescaled parameter errors, values equal to one standard deviation in the normalized distribution curve.

Evaluations similar to those of the global rate models were also made of several Langmuir-Hinshelwood type intrinsic models. A list of the intrinsic models considered in this work appears in Table I. The hydrocarbon reactant concentration appearing as a resistance term in the denominators of Equations I-a through I-c, C'_A represented three different concentrations in three separate evaluations of each rate equation. These three groups were:

1. All sulfur-containing hydrocarbons.

2. All sulfur, nitrogen, and oxygen-containing hydrocarbons.

3. All sulfur, nitrogen, and oxygen-containing hydrocarbons plus their heteroatom-free hydrocarbon products.

The concentration of the third group was assumed to be constant and equal to the sum of the initial heterocompound concentrations. Equations I-a and I-b assume all species compete for one type of adsorption site, while equations I-c and I-d assume competition between reactant and product for one type of adsorption site and noncompetitive adsorption of hydrogen on a different type of site. Equation I-a assumes no rate resistance due to hydrogen adsorption. Equation I-d assumes two sulfur compound groups that react at different rates but by the same physical processes. The results of the data fit calculations and subsequent analyses of these intrinsic rate equations are discussed in the next chapter.

Process Model Development

An ideal process model would be one that would accurately predict the performance of a hydrotreatment reactor under all ranges of operating conditions. Noting the complexity of such an ideal process model, this work focused on the development of a simplified version

TABLE I

INTRINSIC RATE MODELS FOR HYDRODESULFURIZATION KINETICS

$$r = \frac{kC_A C_H}{(1 + K_A C'_A + K_P C_P)^2} \qquad \text{I-a}$$

$$r = \frac{kC_A C_H}{(1 + K_A C'_A + K_H C_H + K_P C_P)^2} \qquad \text{I-b}$$

$$r = \frac{kC_A C_H}{(1 + K_A C'_A + K_P C_P)(1 + K_H C_H)} \qquad \text{I-c}$$

$$r = \frac{\alpha k_1 C_A C_B}{(1 + K_A C_A + K_P C_P)(1 + K_H C_H)} + \frac{\beta k_2 C_B C_H}{(1 + K_B C_B + K_P C_P)(1 + K_H C_H)} \qquad \text{I-d}$$

A, B - hydrocarbon reactants, P - reaction product, H - hydrogen

C'_A can represent the concentration of a species the same as or different than C_A.

Reactant group concentrations $\alpha + \beta = 1$.

which would be useful in the later elaboration of a more robust form. Therefore, a mathematical process model was developed for simulation of the hydrodesulfurization of a model sulfur compound dispersed in a liquid solvent. Attempts were made to simulate the conditions common to commercial scale upgrading of coal-derived liquids.

Although many studies have been published and much is known about the HDS of thiophene, dibenzothiophene was chosen as the model compound because it is more representative of the sulfur-containing heterocompounds found in coal-derived liquids (3). Tetralin was the choice as the model solvent for three reasons. First, tetralin is a molecule which typifies the size and cyclic structure of hydrocarbon molecules commonly found in coal-derived liquids. Second, it remains in the liquid phase, as does the largest fraction of a coal-derived liquid under the normal range of reactor operating conditions. The third reason for the selection of tetralin as a model solvent was that it, along with the dibenzothiophene reactant, describes the feed to a trickle flow reactor used by Espino (7) to collect HDS data. This description allowed Espino's experimental data to be used for a better evaluation of the model developed in this work.

This process, or reactor performance model,is yielded by the integration of the following rate equation:

$$r = \frac{k\eta C_R C_H}{(1 + K_R \eta C_R + K_P C_P)(1 + K_H C_H)} \qquad [11]$$

where R, H, and P represent dibenzothiophene, hydrogen, and hydrogen sulfide respectively. As mentioned earlier, several authors found Equation [11] to be the superior Langmuir-Hinshelwood form used to describe the HDS adsorption reaction processes. The catalyst effectiveness factor, η, has been incorporated to account for the potentially strong resistance to dibenzothiophene pore diffusion. The derivation of Equation [11] follows a set of steps very similar to those taken in the derivation shown in Appendix A. The differences are those which result from the assumption of two types of adsorption sites, rather than a single type of site. The integrated form of the plug flow design equation incorporating Equation [11] is shown below:

$$C_{R2} = C_{R1} + \frac{(1 + K_P(C_{R1} + C_{P1}))}{(k_R\eta - K_P)} \ln \frac{C_{R1}}{C_{R2}} - \frac{K(\eta)(C_H)(W)(100)}{(1 + K_HC_H)(K_R\eta - K_P)(LHSV)(V)(\rho)} \qquad [12]$$

where the subscripts 1 and 2 denote inlet and outlet conditions, and W, V, and ρ are catalyst weight, reactor volume, and liquid density respectively. The formal integration producing Equation [12] is presented in Appendix B.

Assumption of the set of sequential steps outlined below provided the basis for development of the process model expressed by Equation [12].

1. Diffusion of hydrogen (H_2) from the bulk gas to the gas-liquid interface surrounding the catalyst pellets.

2. Dissolution of H_2 in the bulk liquid.

3. Diffusion of H_2 and dibenzothiophene (DBT) from the bulk liquid to the catalyst surface.

4. Diffusion of H_2 and DBT inward through the catalyst pores.

5. Adsorption of DBT and H_2S (a reaction product) on one type of

catalyst adsorption site.

6. Adsorption of H_2 on a second type of catalyst adsorption site.

7. Reaction of DBT and H_2 adsorbed on adjacent sites.

8. Desorption of the reaction products.[1]

9. Diffusion of reaction products outward through the catalyst pores.

10. Diffusion of the reaction products into the bulk liquid.

11. Diffusion of H_2S from the liquid-gas interface into the bulk gas.

As mentioned in Chapter II, there are five assumptions implied with the use of the ideal plug flow design equation. Four of those assumptions were retained in the development of the process model described by Equation [12]. The catalyst effectiveness factor was included to account for reactant pore diffusion resistance. The effects of this lone nonideality were incorporated in the process model for two reasons. First, pore diffusion resistance was found in the literature survey to be the nonideality most frequently observed and commonly reported to have significant effects on the reaction process. Second, it was believed by this author that reactor nonidealities would be better studied and modeled singularly, rather than as a group where the model factors representing them may be interdependent and simultaneously changing.

Hydrogen concentration in the liquid phase was calculated using a correlation developed in Prather (20) for the solubility of hydrogen in

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[1] In addition to the HDS products hydrogen sulfide, biphenyl, and cyclohexylbenzene, the hydrogenated but undesulfurized products tetrahydrodibenzothiophene and hexahydrodibenzothiophene appear to lesser extents (3).

a Solvent Refined Coal recycle solvent at high temperatures and hydrogen partial pressures. This correlation was developed assuming a linear equation for relating solubility to hydrogen partial pressure and by expressing the logarithm of the slopes of those lines as a linear function of the reciprocal absolute temperature. Hydrogen solubility was then calculated using the following equation:

$$S = \exp\ (-S1\ -S2/T)\ P_{H} \qquad [13]$$

where S1 and S2 are empirically evaluated constants. In lieu of specific values of S1 and S2 for the model system solvent, the values published by Prather for the SRC recycle solvent were used. The hydrogen solubility dependence on temperature and pressure, although not exactly accurate when using these values, was presumed to be satisfactorily representative for use in the process model.

The DBT effectiveness factor, η, was calculated using the following equations suggested by Froment (8) for heavy petroleum feedstocks. The values of the constants used in Equations [14-24] are listed in Table II.

$$\eta = \frac{3}{H^2}\ (H\ \coth(H)\ -1) \qquad [14]$$

$$H = Rc(k_{obs}/D_{eff})^{1/2} \qquad [15]$$

$$r_{obs} \simeq k_{obs} C_R \qquad [16]$$

$$D_{eff} = \frac{\varepsilon D}{\tau}\ (1 - \frac{R_m}{R_p})^4 \qquad [17]$$

The free liquid diffusivity, D, was calculated using Scheibel's correlation (21).

TABLE II

PHYSICAL CONSTANTS USED IN THE DBT PROCESS MODEL

MW_L - tetralin molecular weight (1.32.g/mole)

P_C - tetralin critical pressure (34.7 atm)

R_C - average catalyst particle radius (0.0105 cm)

R_M - DBT molecule size (10.0 angstroms)

T_C - tetralin critical temperature (719 K)

V_L - tetralin molar volume at normal boiling point (147.0 cc/gmole)

V_R - DBT molar volume at normal boiling point (182.0 cc/gmole)

ε - catalyst void fraction (0.5)

τ - catalyst tortuosity factor (2.5)

ω - tetralin acentric factor (0.303)

$$D = \frac{KT}{\mu V_R^{1/3}} \quad [18]$$

where:

$$K = Z(1 + (\frac{3V_L}{V_R})^{2/3}) \quad [19]$$

and:

$$Z = 25.2\text{ E-8 for } V_L/V_R < 1 \quad [20]$$

$$Z = 17.5\text{ E-8 for } 1 < V_L/V_R < 2.5 \quad [21]$$

$$Z = 8.2\text{ E-8 for } 2.5 < V_L/V_R \quad [22]$$

The solvent viscosity, μ, was calculated using Letsou and Steil's correlation for high temperature liquids (21).

$$\mu\xi = [(\mu\xi)' + \omega(\mu\xi)''] \quad [23]$$

$$(\mu\xi)' = 0.015174 - 0.02135\, T_r + 0.0075\, T_r^2 \quad [24]$$

$$(\mu\xi)'' = 0.042552 - 0.07674\, T_r + 0.0340\, T_r^2 \quad [25]$$

$$\xi = \frac{T_c^{1/6}}{MW_L^{1/2} P_c^{1/2}} \quad [26]$$

Except for the catalyst particle and pore radii, the sensitivity of the effectiveness factor to the physical constants listed in Table II was not explored. The values of R_c and R_p, 0.0105 cm (60-80 mesh) and 14 angstroms, respectively, were adopted because they resulted in the prediction of particle size effects that most closely resembled those reported by Espino (7). A more detailed study of these physical constant effects might allow the average pore radius to fall into a more representative range (25-50 angstroms).

The liquid density, ρ, was assumed to be negligibly affected by dissolved hydrogen and dibenzothiophene and calculated as that of the pure liquid solvent. Density values were determined by conversion of the values calculated using Gunn and Yamada's correlation for molar volume (21).

$$\frac{V_L'}{V_L''} = \frac{V_r(T_r')\,[1 - \omega\Gamma(T_r')]}{V_r(T_r'')\,[1 - \omega\Gamma(T_r'')]} \qquad [27]$$

$$Vr(Tr) = 0.33593 - 0.33953Tr + 1.51941Tr^2 - 2.02512Tr^3 + 1.11422Tr^4 \qquad [28]$$

$$\Gamma(Tr) = 0.29607 - 0.09045Tr - 0.04842Tr^2 \qquad [29]$$

where ' and " denote first and second reference conditions, respectively.

Experimental Data Fit

From the model described by Equation [12], the kinetic rate constant, k, and adsorption equilibrium constants K_H, K_R, K_P were calculated which best describe the set of dibenzothiophene HDS data published by Espino (7). This particular article was the only source uncovered in the literature survey which included the temperature, pressure, and space velocity ranges desired for such an evaluation of the process model. These data are tabulated in Appendix I. The specific values of these data points have been back calculated from a figure in the Espino paper. Other conditions desired for this model analysis and met by these data were trickle flow operation and liquid phase reaction in the catalyst. In addition, this paper included some information used to calculate hydrogen concentration, solvent density, effectiveness factor, catalyst weight, and reactor volume. These calculations, as described earlier, were performed in the first sections of the computer programs shown in Appendices F, G, and H.

The form of the process model described by Equation [12] proved to be very awkward in the data fit calculations. The four kinetic constants k, K_H, K_R, and K_P were very difficult to handle under nonisothermal conditions due to the interdependencies of their pre-exponential and exponential constants. This necessitated the calculations be performed using isothermal data with subsequent extraction of the exponential constants from the Arrhenius plots. After many trial and error attempts, the following form of Equation [12] was found to be most suitable for use in the data fit calculations:

$$\frac{1}{x}\ln\left(\frac{1}{1-x}\right) = \frac{C_H \eta W(100) X(1)}{xLHSV\ C_{R_1} V\rho (C_{P_1}/C_{R_1}+1)(1+X(2)C_H)} + \frac{(1 - X(3)\eta)}{(C_{P_1}/C_{R_1})} \qquad [30]$$

where x is the fractional reactant conversion.

The fitted parameters are:

$X(1) = kK_H K_R/K_P$ [31]

$X(2) = K_H$ [32]

$X(3) = K_R/K_P$ [33]

from which three separate constants k, K_H, and K_R/K_P may be calculated.

After the pre-exponential and exponential constants were calculated from a linear regression fit of the three Arrhenius plots, the resulting six constants were included in the model equation Equation [12] and the fit over the entire set of data calculated. The n-th order global model Equation [10] was also used to fit this same set of data points and the resulting parameter values and goodness of fit compared with the intrinsic model results. These fits are discussed in the next chapter.

Parameter Sensitivity Study

In an attempt to determine the influence of operating conditions on the observed global model parameters and to determine the relationships between the global and intrinsic kinetics, a parameter sensitivity study was conducted. The process model, Equation [12], with the intrinsic kinetic parameters fixed at the values obtained from the data fit described above, was used to generate a hypothetical dibenzothiophene HDS data set which was in turn used to calculate the n-th order global model parameters (Equation [10]). This procedure, depicted by Figure 1, allowed the global model parameters to be plotted as functions of temperature, hydrogen pressure, and space velocity for a HDS system following the behavior described by Equation [12].

The ranges of the operating parameters, T, P, and LHSV, used in the generation of the data set were expanded from those of the DBT HDS data used in the intrinsic process model evaluation. The limits on these ranges were extended until the corresponding conversions calculated from the DBT process model became extremely high and low. The values used throughout these parameter sensitivity calculations are listed in Table III.

Individual data fit calculations yielding values of the four global model parameters, A, E, m, and n, were performed at constant values of the operating parameter comprising the abscissas of the parameter sensitivity plots and the twenty five combinations of the two remaining operating parameters. Calculations were performed at various values of the operating parameter plotted along the abscissa for the entire range from which meaningful values of the global model parameters could be obtained. The end points of these curves were

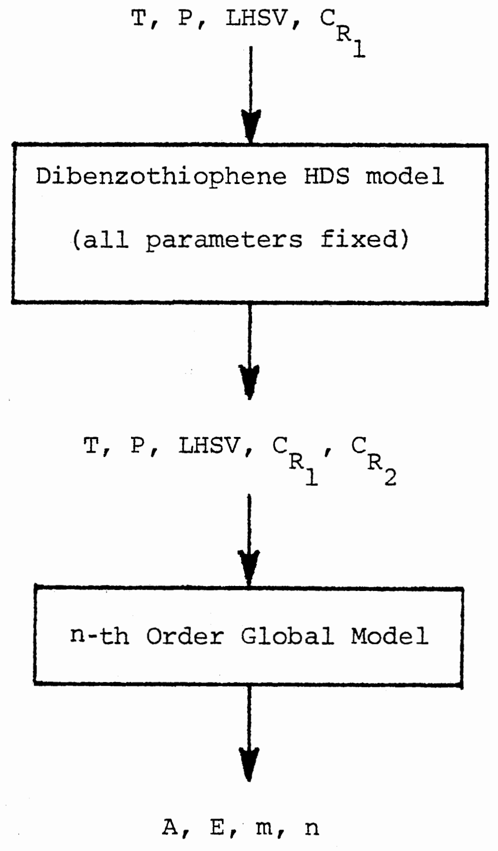

Figure 1. Parameter Sensitivity Calculation Flow Diagram

TABLE III

VALUES OF OPERATING PARAMETERS USED IN PARAMETER SENSITIVITY CALCULATIONS

T F	P psi H_2	LHSV (hr^{-1})
450	200	1
500	400	3
550	600	6
600	800	9
650	1000	12

usually those at which the corresponding DBT conversion was extremely high or low. The operating parameter held constant in these calculations was not confined to the ranges indicated in Table III.

The form of the n-th order global model used in these calculations is expressed by Equation [34].

$$C_{R_2} = \left[C_{R_1}^{1-X(4)} - \frac{X(1)\ \exp\ (x(2)/RT) P^{X(3)} (1 - X(4))}{LHSV}\right]^{1-X(4)} \qquad [34]$$

where:

$X(1) = A$ [35]

$X(2) = E$ [36]

$X(3) = m$ [37]

$X(4) = n$ [38]

CHAPTER IV

DISCUSSION OF RESULTS

Global Kinetic Models

The global kinetic model described by Equation [39]

$$r = A \exp(-E/RT)\ C^n\ P^m \qquad [39]$$

was analyzed by calculation of the model parameters, A, E, m, and n. The parameter calculations were performed utilizing Heck and Stein's (12) HDS, HDN, and HDO data. The Marquardt data fit program mentioned earlier was used to calculate the model parameters for the n-th order form of Equation [39] and the first and second order versions in which n is equal to 1 and 2 respectively.

The second order parameter values calculated in this work were compared to those published by Heck and Stein (see Table IV). The published values of the pre-exponential constants, activation energies, and order of hydrogen pressure dependence were duplicated with only limited precision. All of the published values were, however, within 95 percent confidence intervals of those values calculated in this work. The lack of precision may be explained by uncertainties in outlet concentration (minimum detectable limits reported at several different operational conditions) and in differences in the data fit techniques.

In addition to the comparison of the second order results, global parameters were evaluated for the first and n-th order models. These values are shown in Table V and Table VI, respectively. As expected,

TABLE IV

COMPARISON OF SECOND ORDER GLOBAL KINETIC MODEL PARAMETERS

Feed Catalyst	Heteroatom	A $(psi^{-m}/wt\%/hr)$		E Btu/mole		m		Mean Deviation wt%	
SRC Recycle Solvent HDS-9A	Sulfur	4.46E2	3.76E2	28,960	28,380	1.37	1.36	.005	.005
	Nitrogen	1.14E9	3.58E9	59,930	64,150	0.87	0.96	.023	.024
	Oxygen	3.22E9	2.46E9	64,600	65,840	0.74	0.85	.081	.086
SRC Recycle Solvent HDS-1441A	Sulfur	5.71E6	1.25E9	45,710	55,830	1.08	0.96	.005	.007
	Nitrogen	1.91E9	1.23E9	64,750	63,980	1.03	1.04	.027	.033
	Oxygen	2.45E11	2.63E10	66,820	68,550	0.29	0.71	.148	.091
H-Coal Distillate HDS-1441A	Sulfur	2.45E5	8.52E7	31,580	45,630	0.79	0.84	.005	.008
	Nitrogen	1.81E7	1.90E7	56,390	56,750	1.29	1.30	.015	.018
	Oxygen	2.24E8	6.00E7	65,720	64,030	1.41	1.49	.061	.074

Note: The values in the first columns are those calculated in this work, the values in the second columns are those published by Heck and Stein (12).

TABLE V

FIRST ORDER GLOBAL KINETIC MODEL PARAMETERS

Feed Catalyst	Heteroatom	A (psi^{-m}/hr)	E (Btu/lbmole)	m	Mean Deviation wt%
SRC Recycle Solvent HDS-9A	Sulfur	4.89E-2 ± 2.22E-1	9,650 ± 8,740	1.143 ± .349	.010
	Nitrogen	5.72E3 ± 2.83E4	35,820 ± 9,270	0.944 ± .357	.031
	Oxygen	7.92E4 ± 2.27E5	39,220 ± 5,280	0.776 ± .206	.114
SRC Recycle Solvent HDS-1441A	Sulfur	3.92E2 ± 3.26E3	26,030 ± 16,220	0.889 ± .374	.010
	Nitrogen	1.19E5 ± 4.74E5	44,710 ± 7,600	1.016 ± .282	.026
	Oxygen	1.79E7 ± 8.40E7	46,330 ± 8,400	0.467 ± .304	.160
H-Coal Distillate HDS-1441A	Sulfur	6.72E3 ± 5.43E4	21,450 ± 17,220	0.282 ± .651	.009
	Nitrogen	5.83E3 ± 2.38E4	40,290 ± 9,280	1.231 ± .301	.020
	Oxygen	5.87E6 ± 3.80E7	55,030 ± 16,530	1.223 ± .542	.086

Note: The indicated error regions are 95% confidence intervals.

TABLE VI

N-th ORDER GLOBAL KINETIC MODEL PARAMETERS

Feed Catalyst	Heteroatom	A $(psi^{-m}/wt\%^{n-1}/hr)$	E (Btu/lbmole)	m	n	Mean Deviation wt%
SRC Recycle Solvent HDS-9A	Sulfur	1.53E9 ± 3.07E10	61,650 ± 42,810	1.712 ± .852	3.111 ± 1.24	.003
	Nitrogen	3.73E7 ± 3.46E8	53,050 ± 18,660	0.885 ± .396	1.765 ± .543	.023
	Oxygen	4.20E6 ± 1.25E7	48,910 ± 6,330	0.766 ± .152	1.455 ± .193	.059
SRC Recycle Solvent HDS-1441A	Sulfur	8.38E9 ± 1.57E11	61,860 ± 39,260	1.278 ± .741	2.597 ± .920	.004
	Nitrogen	4.51E6 ± 2.55E7	52,040 ± 11,480	1.018 ± .301	1.445 ± .370	.023
	Oxygen	2.62E8 ± 1.69E9	52,190 ± 12,530	0.413 ± .340	1.375 ± .382	.129
H-Coal Distillate HDS-1441A	Sulfur	8.27E12 ± 1.68E14	68,330 ± 44,070	1.374 ± .995	3.687 ± 1.303	.003
	Nitrogen	1.35E6 ± 6.06E6	50,810 ± 10,310	1.251 ± .288	1.685 ± .345	.013
	Oxygen	3.88E8 ± 3.80E9	67,260 ± 25,280	1.430 ± .607	2.075 ± .672	.061

Note: The indicated error regions are 95% confidence intervals.

the additional degrees of freedom in the n-th order rate equation allow a better fit. The first order rate equation, which best describes the behavior of single reactant feeds, yields the poorest fit to the experimental data. This indicates the complexity of the reactant mixture. Equating global orders to true kinetic orders has been a common misinterpretation of data fit results. In all three global equations the hydrogen partial pressure dependencies are similar and show approximately a first order dependence with all values confined between zero and two.

Conclusions concerning activation energy were more difficult to make. The first and second order equations showed these values to increase from sulfur to nitrogen to oxygen containing compounds; whereas, the n-th order equation showed no consistent trend. Activation energies covered the broad range from 10,000 to 70,000 Btu/lbmole (75 -530 kJ/mol).

During the course of the data fit calculations it was found that in some cases the converged results were dependent upon the initial parameter guesses supplied to the program. This problem was overcome by repeating the calculations with improved guesses for the kinetic parameters until the best fit was obtained. In those calculations the best fit was obtained by minimizing the value of the following objective function:

$$\mathrm{FOBJ} = \sum (C_{\mathrm{fit}} - C_{\mathrm{calc}})^2 \qquad [40]$$

where C_{fit} and C_{dat} are the calculated and experimentally observed concentrations, respectively.

Another phenomena occasionally observed throughout the data fit calculations performed in this work was the ability of the model equations to yield only a slightly poorer fit to a data set with a strikingly different set of parameter values. For instance, if the order of reactant concentration, n, is fixed at an arbitrary value far from its "best fit" value, the remaining model parameters, A, E, and m, allow the model equation enough flexibility to fit the experimental data set with nearly the same accuracy. This fact is manifested in part by the large parameter confidence regions, especially in the cases of the pre-exponential constants, in which all the confidence regions are of greater magnitude than the parameter values. Also an important fact was the observed dependence of the converged parameter values on the variable forms of the fitted function, i.e., $C_{fit} = f(A, E, m, n)$ or $0 = f(A, E, m, n)$.

These observations indicated shallow parameter surface minima, which may have been caused by poorly conditioned data or model equation (data or model equation that does not allow a sharp definition of the model parameters), or both. Because these observations generally held for all nine experimental data sets, this author believed the global model equations were the cause for these parameter calculation problems, therein lying a likely explanation for some of the discrepant literature reports mentioned earlier.

The facts that reaction orders greater than one produced more accurate results and that the values of the global parameters were scattered and inconsistent both indicated the inability of the global rate equation. Although such global rate equations are capable of describing coal liquid heterocompound conversion with good accuracy, their empirical nature keeps from yielding accurate information concerning the actual kinetic processes taking place at the reaction sites. These observations indicated the global rate model is oversimplified for use as multicomponent hydrotreatment performance prediction tool.

Intrinsic Kinetic Models

Multicomponent Systems

An attempt was made in this work to fit the Heck and Stein (12) coal liquid hydrotreatment data with the single and two type site rate equations. An extensive effort was made to fit the data set with Equations I-a through I-c (Table I), and numerous theoretically justifiable variations of them. These rate expressions could not be used to describe coal liquid hydrotreatment satisfactorily. In most cases divergent results were obtained using a Marquardt nonlinear technique to fit these rate expressions to coal liquid data. When converged results were obtained, they were unacceptable in each case due either to physically meaningless values for the equilibrium constants, or excessively large confidence regions, or both. It was believed by this author that the complex nature of the multicomponent coal liquids did not allow them to be treated as a single group, therefore not allowing these types of single group intrinsic models to describe their kinetic data.

Several authors have suggested a two group theory could be used to describe the hydrotreatment of typical heavy petroleum and coal liquids (9, 29, 42). This concept involves the simultaneous first order reactions of two reactant groups, with each reaction proceeding at a rate proportional to the concentration of its group. Such a rate expression is described by Equation I-d in Table I. Although this two group expression may be used to fit multicomponent feedstock HDS data, the single compound performance model should be developed to adequately account for the many system variables before an expanded version is considered. The complexity of a multicomponent systems makes preliminary understanding of the complete single component system a practical necessity.

Process Model

The process model described by Equation [12] incorporates the intrinsic kinetic rate expression, Equation [11], found to be superior for description of HDS data. The kinetic rate constant k and adsorption equilibrium constants K_H, K_R, K_P were calculated such that the process model, in the form of Equation [30], best described each of five sets of isothermal HDS data. These data were collected in a study of the hydrodesulfurization of dibenzothiophene (7). The calculated values of the kinetic constants and the average percent errors of the corresponding fits to the five isothermal data sets are shown in Table VII. The program used to perform these calculations, along with the input data and the best fit values of the parameters, are listed for each case in Appendix F. In all five sets of isothermal calculations, the process model was able to describe the data set very well. In each case the average error of the fitted outlet concentration profile values was less than two percent.

The Arrhenius plots of the three intrinsic constants k, K_H, and K_R/K_P appear in Figures 2, 3 and 4, respectively. The exponential constants were calculated via linear regression fits for each of the

TABLE VII

DIBENZOTHIOPHENE HDS KINETIC MODEL CONSTANTS (ISOTHERMAL PARAMETER EVALUATIONS)

Temperature °C	Temperature °F	k wt%/hr	K_H wt%$^{-1}$	K_R/K_P	Avg. % Error
285	545	8.043 E-2	1.893 E1	3.495 E-1	0.714
300	572	1.563 E-1	1.135 E1	9.355 E-1	1.098
310	590	3.136 E-1	8.177 E0	1.397 E0	1.502
325	617	8.511 E-1	5.415 E0	1.535 E0	1.279
350	662	2.648 E0	2.606 E0	2.436 E0	0.748

k - reaction rate constant

K_H - hydrogen adsorption equilibrium constant

K_R - dibenzothiophene adsorption equilibrium constant

K_P - hydrogen sulfide adsorption equilibrium constant

$$\text{Avg. \% Error} = \sum \frac{\text{ABS}(C_{fit} - C_{dat})}{C_{dat}\,(\text{NPTS})} \times 100\%$$

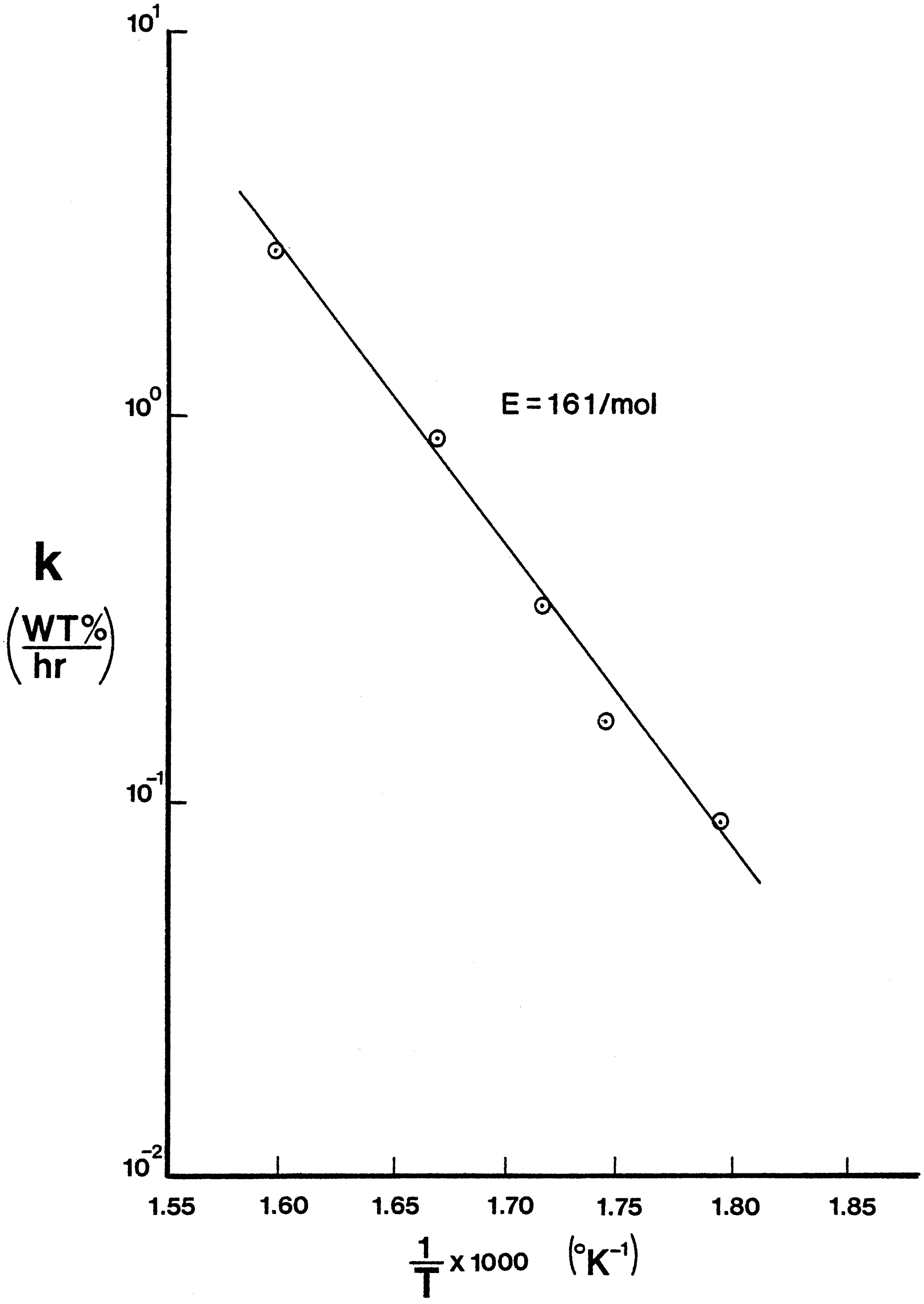

Figure 2. Arrhenius Plot of the Process Model Reaction Rate Constant

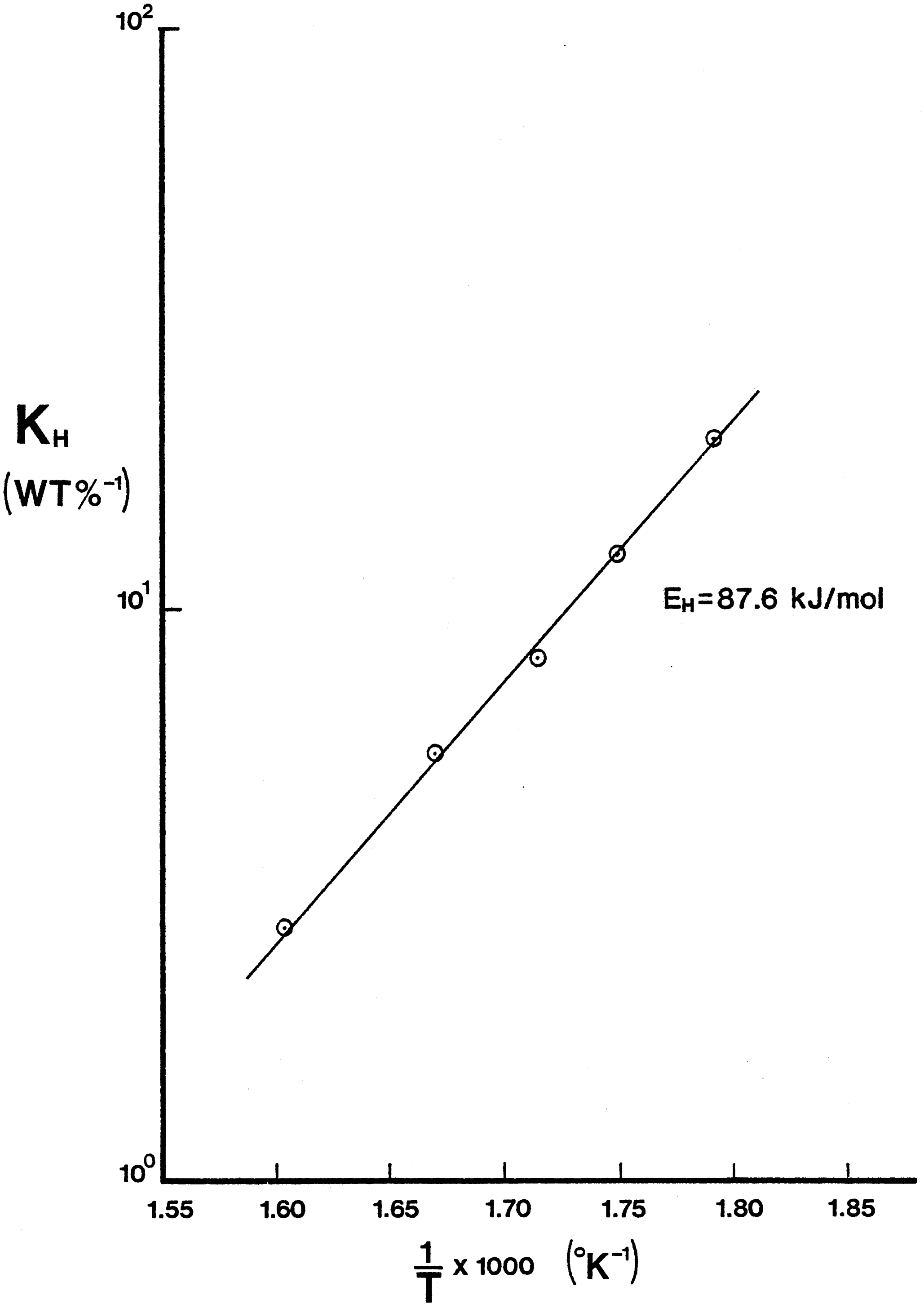

Figure 3. Arrhenius Plot of the Process Model Hydrogen Adsorption Equilibrium Constant

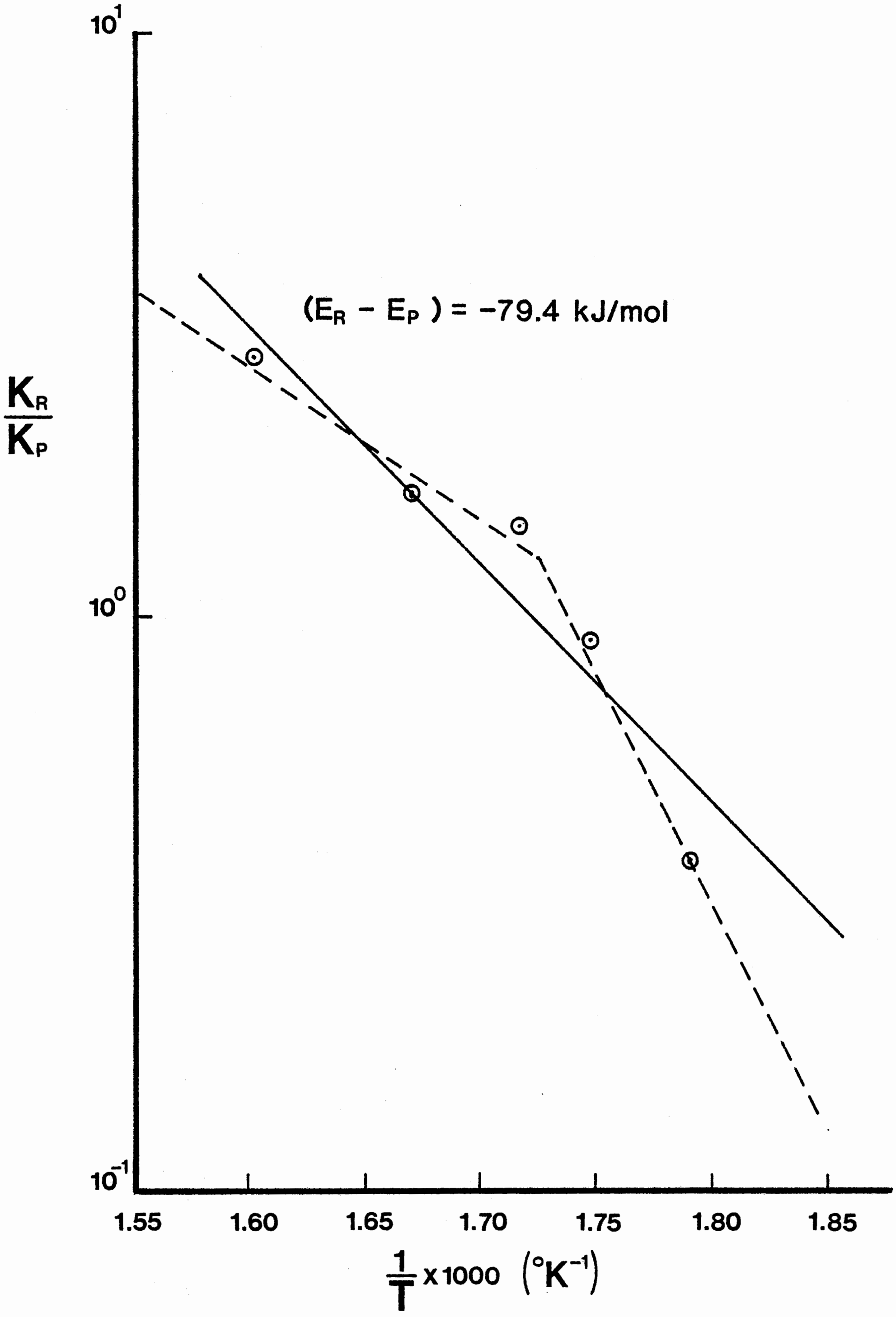

Figure 4. Arrhenius Plot of the Process Model DBT-H_2S Adsorption Equilibrium Constant Ratio

three plots. These constants are listed in Table VIII. Both the reaction rate constant and the hydrogen adsorption equilibrium constant adhered closely to the expected Arrhenius temperature dependency. The calculated reaction activation energy for the HDS of dibenzothiophene was 161 kJ/mol (21,333 BTU/lbmole), which closely compares with the values reported by Espino (7), 163 kJ/mol (21,667 BTU/lbmole), and Rollman (23), 151 kJ/mol (20,000 BTU/lbmole). The calculated heat of adsorption for hydrogen, 87 kJ/mol (11,611 BTU/lbmole), also falls within the range commonly reported in the literature (7). The ratio of dibenzothiophene to hydrogen sulfide adsorption equilibrium constants did not follow the Arrhenius temperature dependency well. The break in the Arrhenius plot (Figure 4) implies the difference in the heats of adsorption, $(E_R - E_P)$, shifts near 300 C (572 F). A likely cause for such a shift would be that, in addition to hydrogen sulfide, the other DBT HDS products, biphenyl and cyclohexylbenzene are in competition with dibenzothiophene for catalyst adsorption sites. Under these conditions, a shift in the quantity $(E_R - E_P)$ may occur with a shift in the product composition near the adsorption sites. Parallel hydrogenation-hydrogenolysis reactions of DBT which produce cyclohexylbenzene and biphenyl, respectively, have been supported in the literature (3, 7, 13). The two line segments in Figure 4 could represent these two temperature dependent DBT reactions, and thereby account for the break in the Arrhenius plot.

The ability of the dibenzothiophene HDS process model, as described by Equation [12], to fit the entire non-isothermal set of conversion data was also evaluated. The six kinetic constants, A, A_H, A_R/A_P, E, E_H, and $(E_R - E_P)$ were fixed at their respective values shown

TABLE VIII

INTRINSIC KINETIC CONSTANTS DETERMINED FROM THE ARRHENIUS PLOTS OF k, K_H, AND K_R/K_P

	Reaction Rate Constant		Adsorption Equilibrium Constant Hydrogen		Adsorption Equilibrium Constant DBT:H_2S	
	$k = A \exp(-E/RT)$		$K_H = A_H \exp(E_H/RT)$		$K_R/K_P = A_R/A_P \exp((E_R-E_P)/RT)$	
Slope = E/R	-19328	(K)	10535	(K)	-9547	(K)
Standard Error	6963	(K)	7007	(K)	6076	(K)
E	160700	(J/mol)	87592	(J/mol)	-79378	(J/mol)
Intercept = ln A	32.029		-15.949		16.394	
Standard Error	11.887		11.962		10.373	
A	8.128 E13	(wt%/hr)	1.185 E-7	(wt%$^{-1}$)	1.318 E7	(wt%$^{-1}$)
Coeff. of det.	0.9933		0.9996		0.8668	

in Table VIII. The fitted values of the DBT concentration profile are tabulated in Appendix H. Although this model was able to describe the isothermal data very well, the non-isothermal fit was very poor. The average deviation from the experimental outlet DBT concentrations was in excess of 400%, whereas the isothermal errors were all less than 2%. By comparison, the n-th order global fit to these data points resulted in an average error of about 7%, as shown in Appendix I. The corresponding global parameters were:

$A = 1.88\ E9\ (\text{wt}\ \%^{1-n}/\text{PSI}^{m}/\text{hr})$

$E = 5.27\ E4\ (\text{BTU/lbmole})$

$m = 0.82$

$n = 0.84$

Obviously, the process model described by Equation [12] is completely unsatisfactory for description of non-isothermal data. This inability is due to an inadequate description of the K_R/K_P ratio as a function of temperature. The model equation is however very accurate when the data are broken down into isothermal groups. The development of an accurate product formation model, allowing the proper description of the K_R/K_P ratio as a function of temperature, and refinement of the effectiveness factor and solubility calculations would result in a very accurate and useful single component HDS model. Such a model could serve as the basis for an expanded version, perhaps in the form of a summation of individual sections, to describe multicomponent hydrotreatment.

Parameter Sensitivity Study

Parameter sensitivity calculations were performed in the manner depicted by Figure 1. All the resulting parameter sensitivity plots include the individual points through which the curves were drawn. Although the curves are theoretical, the points were plotted to indicate the specific values of the operating parameter, T, P, or LHSV, at which the n-th order global parameters were calculated. These values of the global parameters, A, E, m, and n are tabulated in Appendix C.

The calculations performed at constant temperature and constant pressure required the following combination of parameters:

$K_t = A \exp(-E/RT)$ at constant temperature [41]

$K_p = AP^m$ at constant pressure [42]

The temperature and pressure related global parameters from Equations [41] and [42] were calculated from the slopes and intercepts of their respective Arrhenius and log K vs. log P plots. These plots are shown in Figures 5 and 6, and the calculated values of the corresponding global parameters, A, E, and m, tabulated in Appendix C (Tables XV and XVI).

In addition to the calculations utilizing the simple objective function equal to the sum of residual squares, Equation [40], a second set of calculations was made using the normalized objective function described by Equation [43].

$$\mathrm{FOBJ} = \sum\left(\frac{C_{\mathrm{fit}} - C_{\mathrm{dat}}}{C_{\mathrm{dat}}}\right)^2 \qquad [43]$$

This function, which allowed the lower outlet concentrations to be most heavily weighted during the data fit calculations, was used to determine the dependence of the global data fit results on the form of the minimized objective function. The two curves in each of the parameter sensitivity plots represent the global parameter values calculated using the two objective functions.

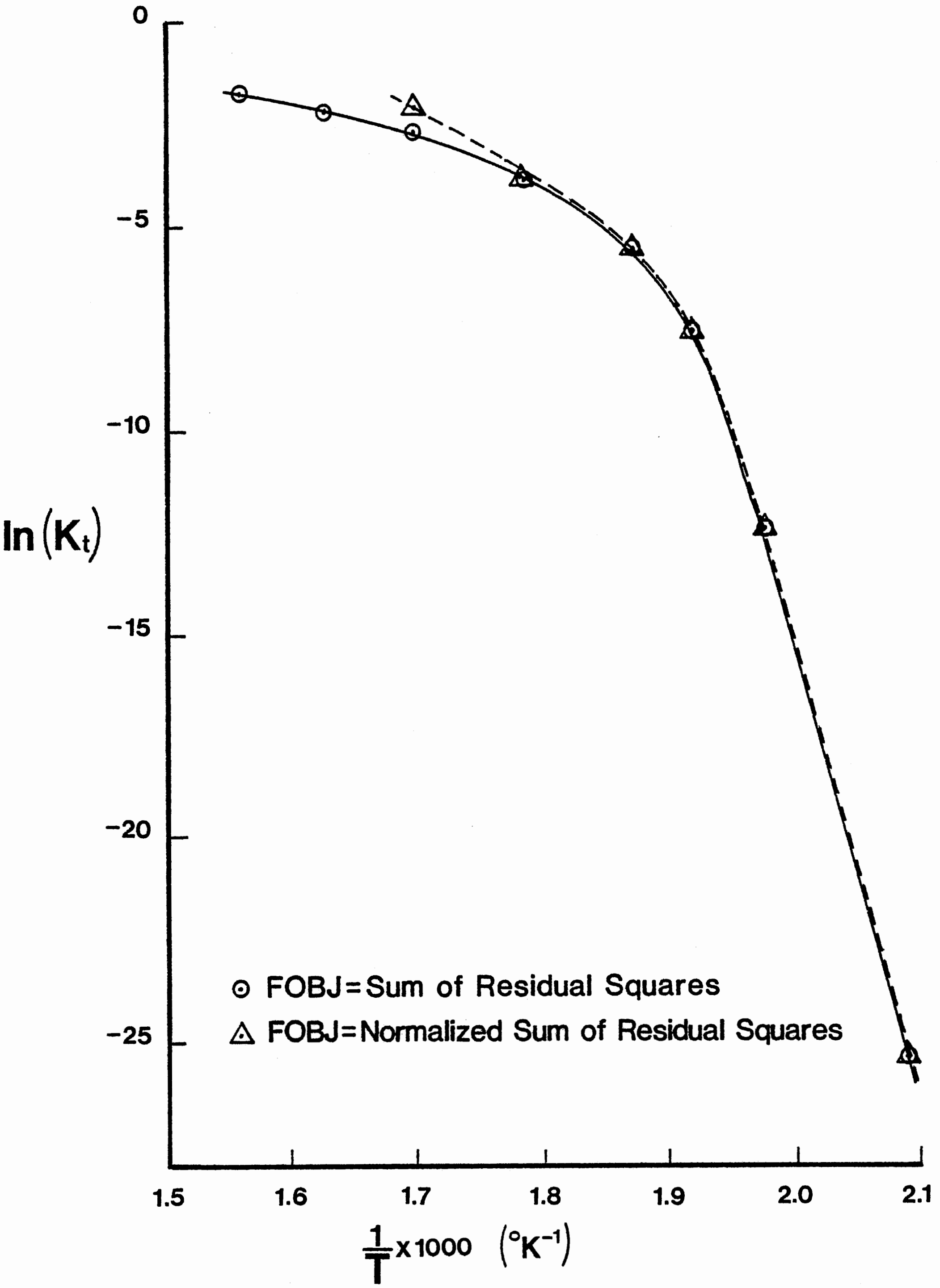

Figure 5. Arrhenius Plot of the Global Model Constant K_t

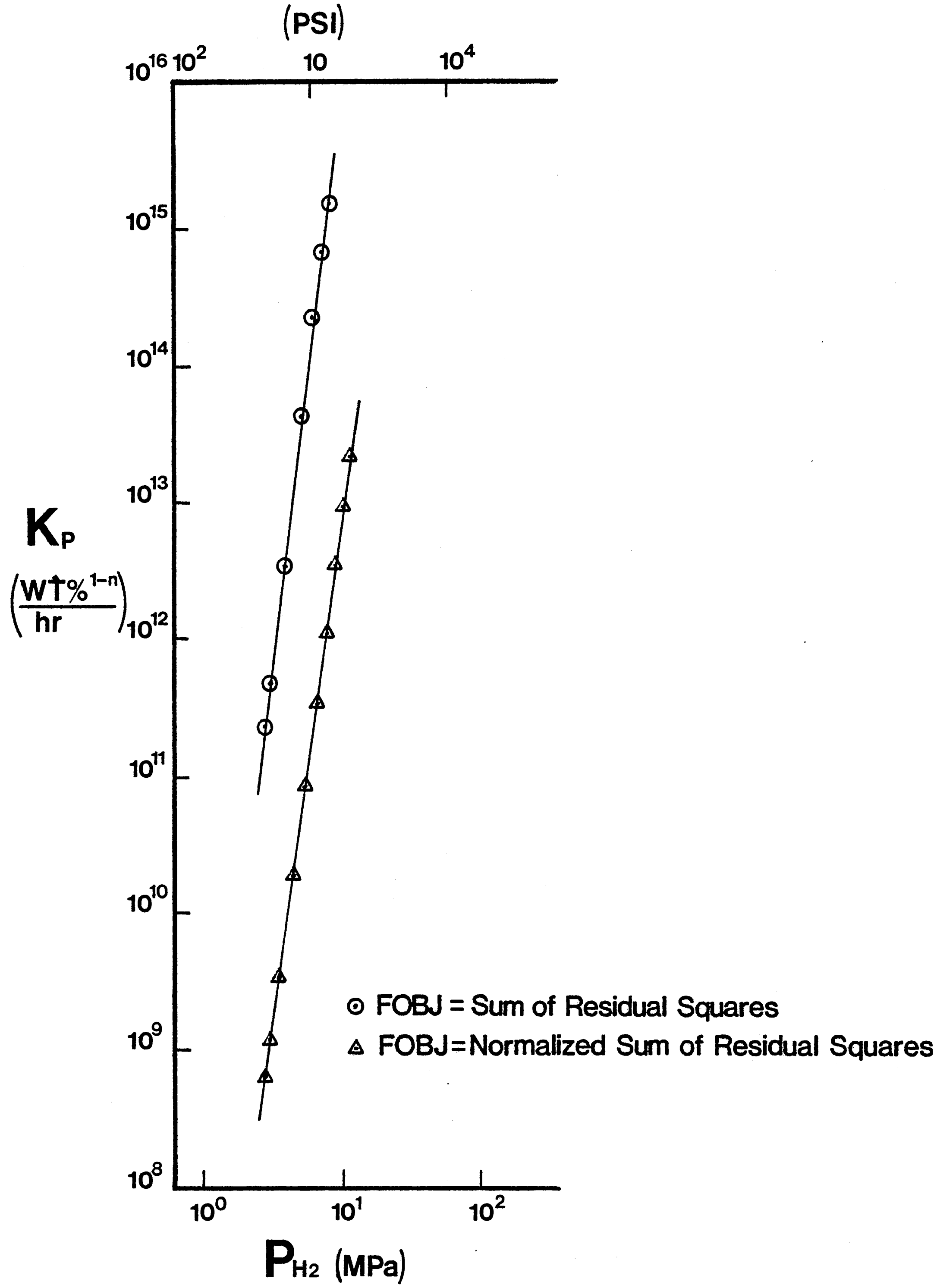

Figure 6. Global Model Constant K_p Dependence on Hydrogen Pressure

The general form of Equation [34] described below,

$$C_{R_2} = X^Y \qquad [44]$$

presented problems during the course of these calculations. In some regions of the three or four dimensional surface searched by the data fit routine, X may become negative. Because Y is not an integer value, this condition resulted in a fatal computer error which halted all calculations and prevented a converged solution. Two solutions to this dilemma were considered. First, Equation [44] could be rearranged into one of several versions of Equation [45].

$$C_{R_2}^{1/Y} = X \qquad [45]$$

This solution was rejected because it did not allow a direct fit to the outlet concentration profile. The second solution considered was the examination of X before the data fit program reached the exponential form (Equation [34]). In any case where X was negative it was set equal to zero, thereby eliminating the fatal program error. In a few cases where the outlet concentration was very low the data fit routine converged where X and therefore C_{R_2} remained equal to zero. These cases generally arose at or beyond the operating parameter limits discussed in Chapter III.

Another procedure which proved very helpful in obtaining meaningful converged values of the global parameters was to set a minimum limit on the concentrations included in the hypothetical data set. This precluded some of the problems encountered with the exponential form of Equation [34].

From the parameter sensitivity curves the only cases in which the global parameter was observed as a constant function of the operating parameter were: pre-exponential constant, A, and order of hydrogen pressure dependence, m, versus hydrogen pressure. The values of these constants were calculated from the linear plots shown in Figure 6 and appear in Appendix J. The calculated orders of hydrogen pressure dependence, 7.0 and 8.0 for the two curves, are unexpected considering the first order dependence of the intrinsic process model used to generate the data set. No logical explanation for these values was apparent to this author.

In Figure 7 the two curves representing m as a function of space velocity were nearly mirror images of each other for most of the space velocity range. In both cases, however, all values of m fell within the range 0.6 to 1.0. The order of hydrogen pressure dependence was also a strong function of temperature, with both curves almost identically rising from about 0.15 at 230 C (446 F) to values approaching 1.0 as the temperature rose to 370 C (698 F) (see Figure 8). Sonnemans (39) reports that although no explanations for the effect of temperature on order of hydrogen pressure dependence were offered, several authors reported such effects.

The fluctuations of the value of m as a function of temperature and space velocity is probably not due to changes in the true order of the reaction, but to the attempt to describe the contribution of the following portion of the process model rate equation to the behavior of the hypothetical system:

$$\frac{C_H}{(1 + K_H C_H)} \qquad [46]$$

Although the intrinsic model assumes first order in hydrogen pressure

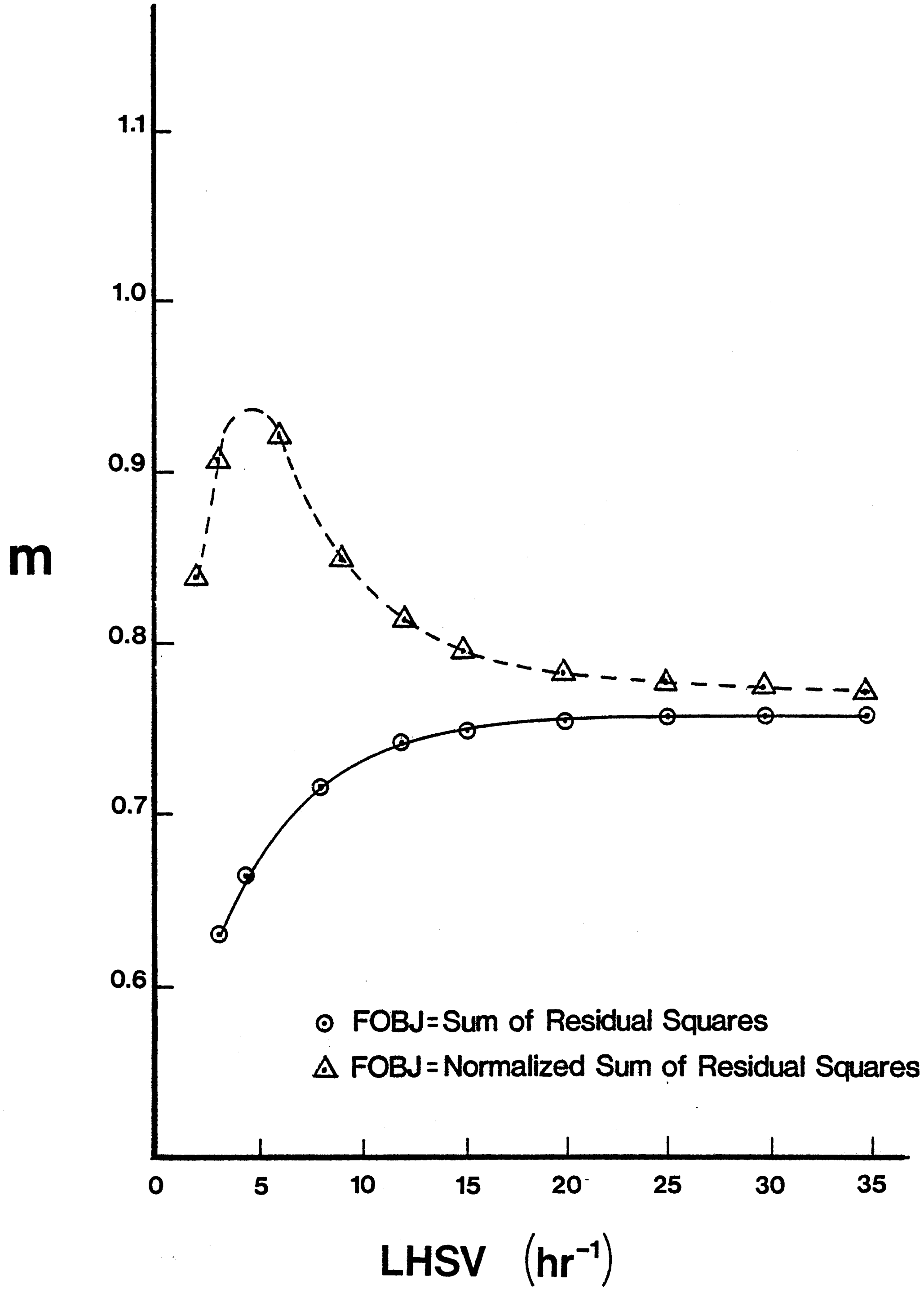

Figure 7. Global Model Order of Hydrogen Pressure Dependence on Space Velocity

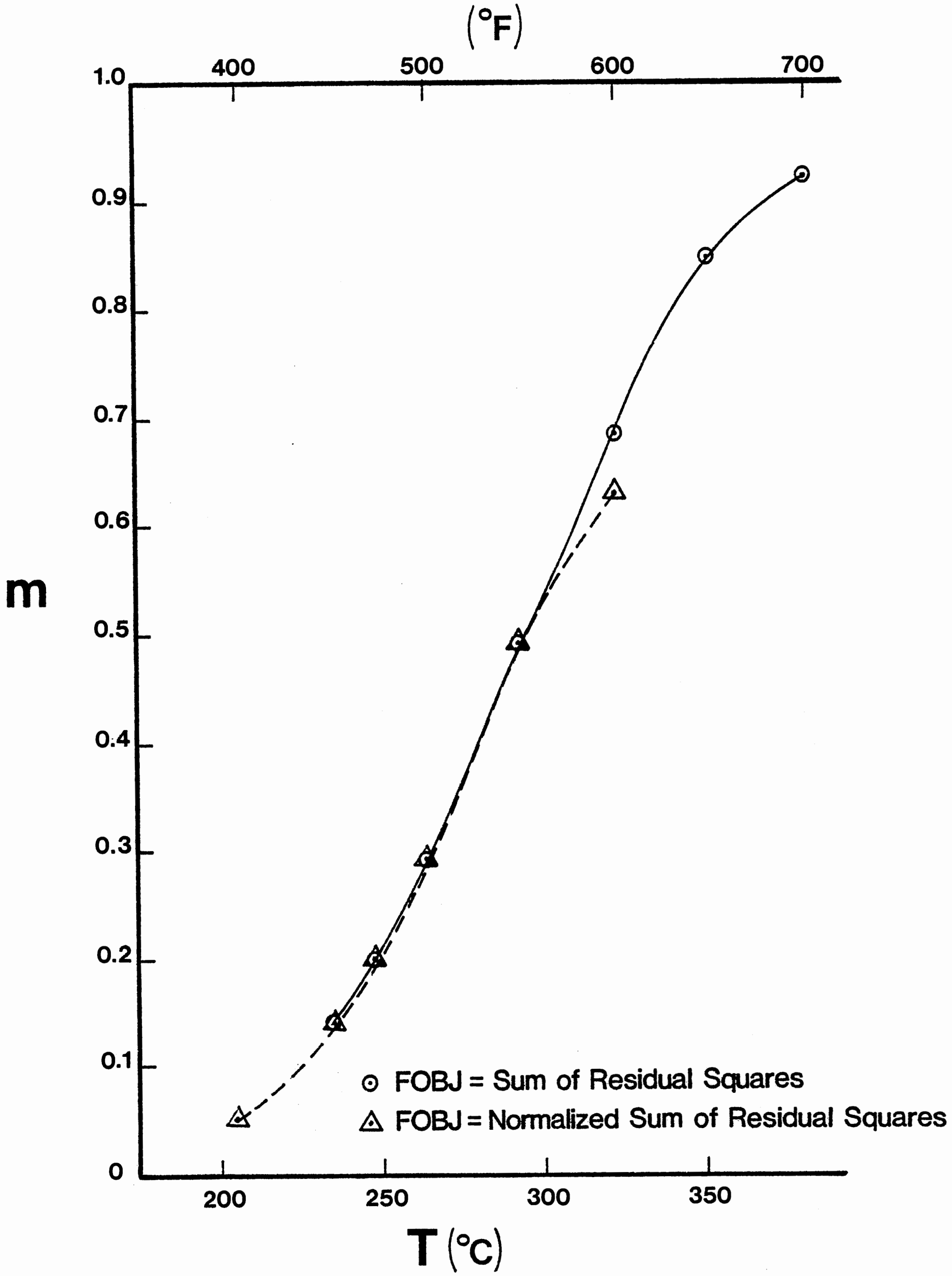

Figure 8. Global Model Order of Hydrogen Pressure Dependence on Temperature

dependence, one can see how the observed global order would vary with changes in the operating conditions, especially temperature due to its strong influence on the reaction rate and adsorption constants.

Not only the plots of m vs LHSV and m vs T, but all the parameter sensitivity curves showed how one could calculate different values for the global model parameters, depending on what objective function he choses to use. In this case for example, if the hypothetical data were real experimental data collected at a space velocity of 6 hr^{-1}, one would calculate orders of hydrogen partial pressure dependence equal to 0.695 and 0.910 for the two respective objective functions (see Figure 7).

The global order of DBT concentration dependence, n, varied as the operating temperature, hydrogen pressure, and space velocity changed. These dependencies are indicated by the curves in Figures 9, 10, and 11, respectively. Except at temperatures below 290 C (554 F), all values of n fell somewhere in the range between 0.5 and 1.5. As in the case of the order of hydrogen pressure dependence, the variations in n with changing T, P, and LHSV can be attributed to the attempted description of the DBT concentration terms in the intrinsic rate equation by the simplified global counterpart C_R^n.

The variations in these global parameters indicate another likely reason for discrepant literature reports. As an example, if experimental data following the same behavior as this hypothetical system were collected from isothermal runs at 225 C the observed order of DBT concentration dependence, n, would be near 12.5, while isothermal runs above 300 C would result in values near one.

Likewise, the dependency of the pre-exponential constant, A, and

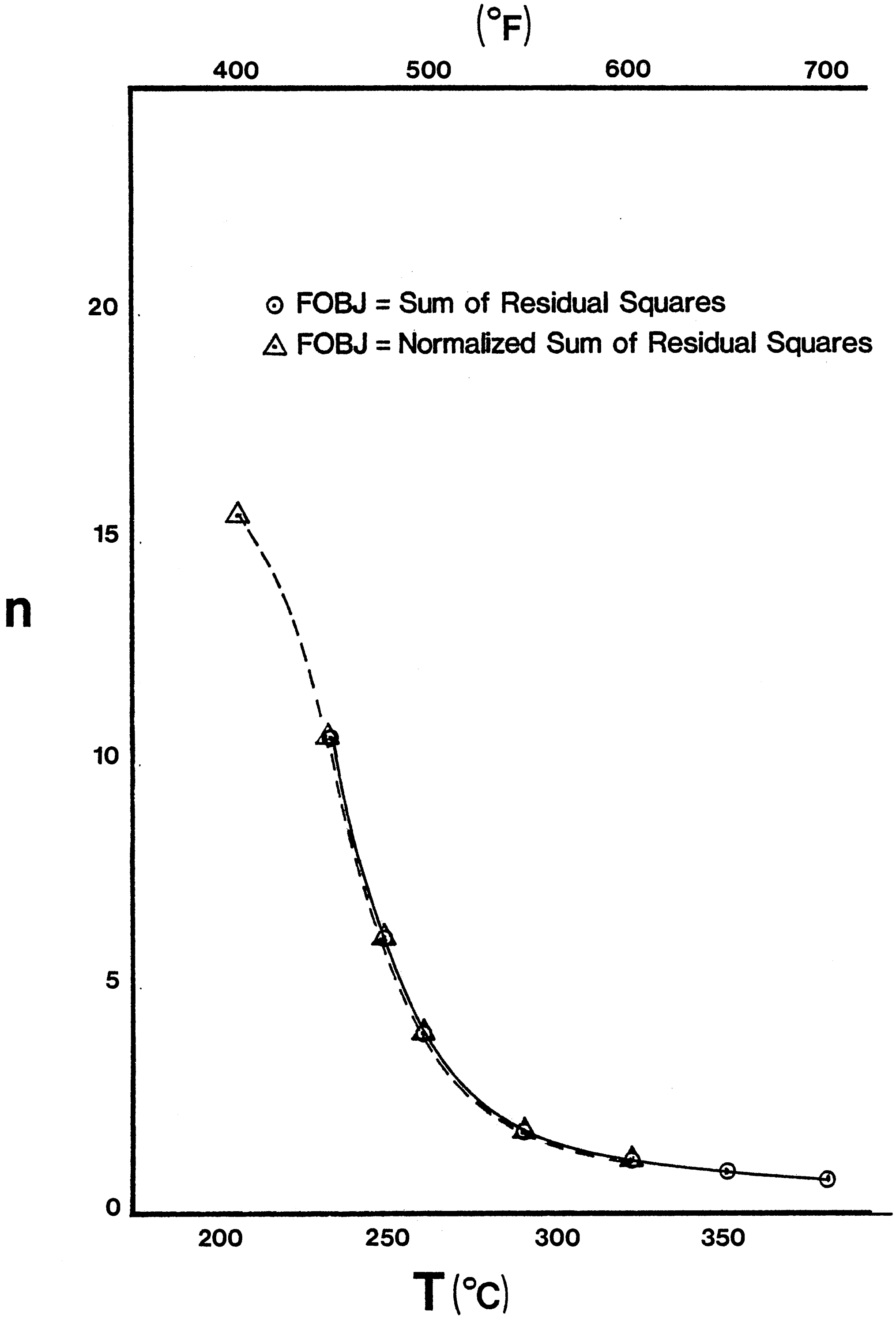

Figure 9. Global Model Order of DBT Concentration Dependence on Temperature

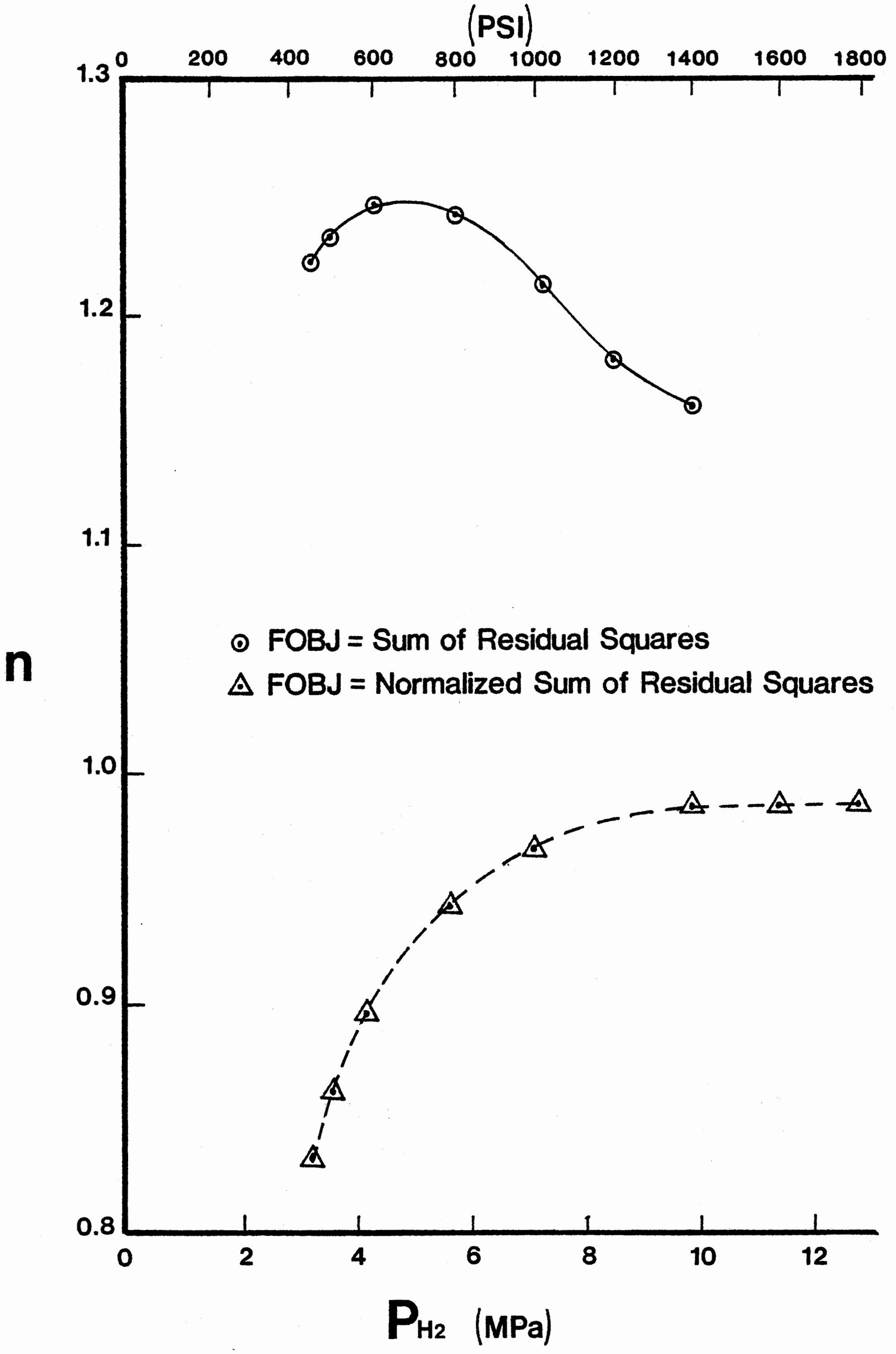

Figure 10. Global Model Order of DBT Concentration Dependence on Hydrogen Pressure

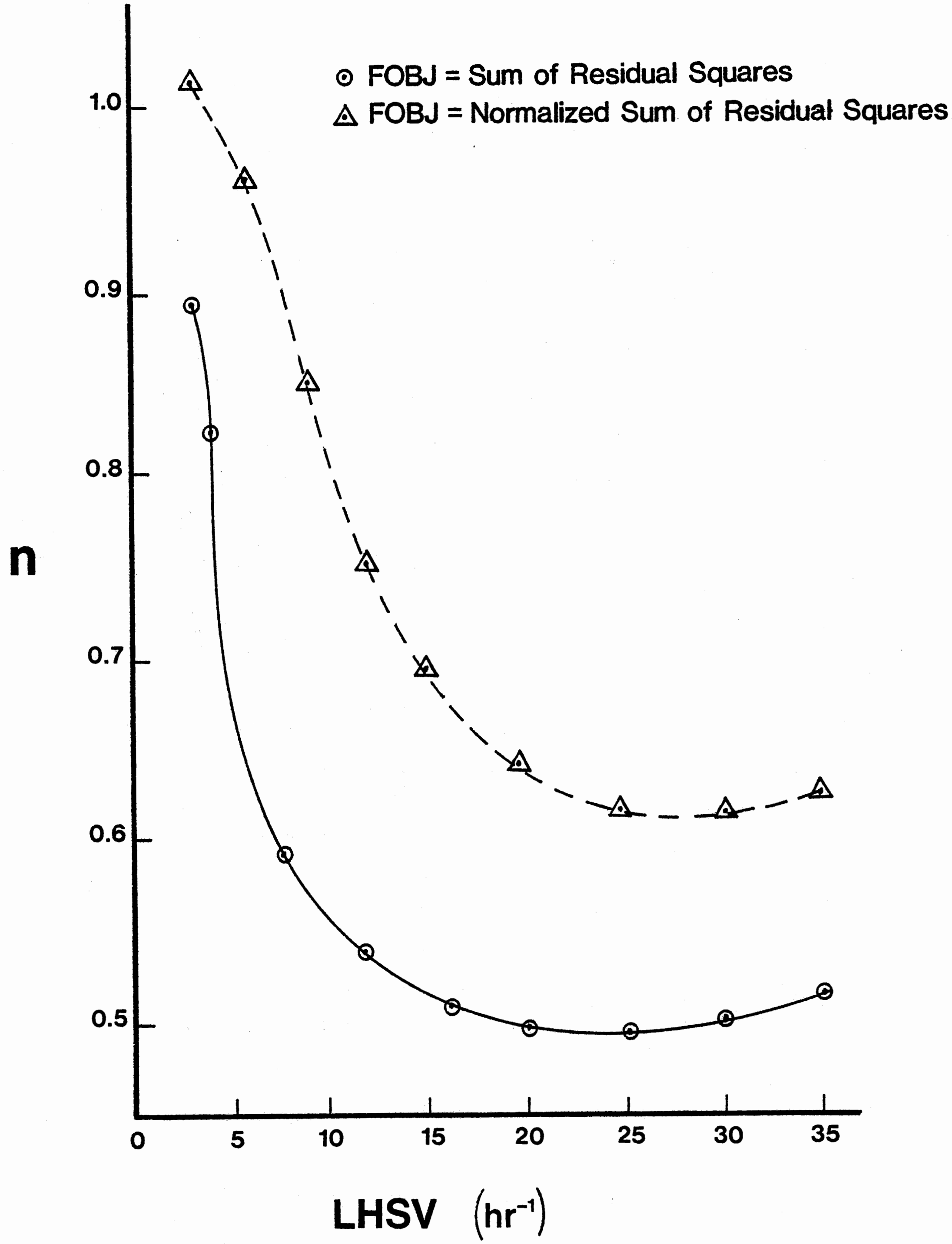

Figure 11. Global Model Order of DBT Concentration Dependence on Space Velocity

activation energy, E, on T, P, and LHSV could be attributed to the attempted description of the combined behavioral effects of the intrinsic constants k, K_H, K_R, and K_P. These plots are shown in Figures 12-16. As one would expect, temperature has a strong effect on these values while hydrogen pressure and space velocities have relatively small influences.

These operating parameter versus global parameter curves establish trends concerning their relationship to the intrinsic kinetics of the hypothetical system. A complete family of such curves, each generated under a specified set of values for the intrinsic parameters and other model constants, would allow some characteristics of the intrinsic kinetics to be recognized from such curves. Eventually, by following a similar procedure for a host of process models, developed under various assumptions concerning rate equations and the physical processes taking place inside the reactor, an analysis of appropriate global data fit calculations could provide information concerning the intrinsic kinetics of a real hydrotreatment system.

Two important observations are apparent from this parameter sensitivity study. First, due to the shallow surface minima, the calculated global parameters have large confidence regions associated with them, and are sensitive to differences in: the data set operating conditions; minimized ojbective functions; forms of the fitted rate equation; and data fit routines. These characteristics of the global kinetic model are a probable cause for the inconsistent values of the model parameters reported in the literature. Second, due to the empirical nature of the global models, the values of their parameters have no directly corresponding relationship to the true reaction

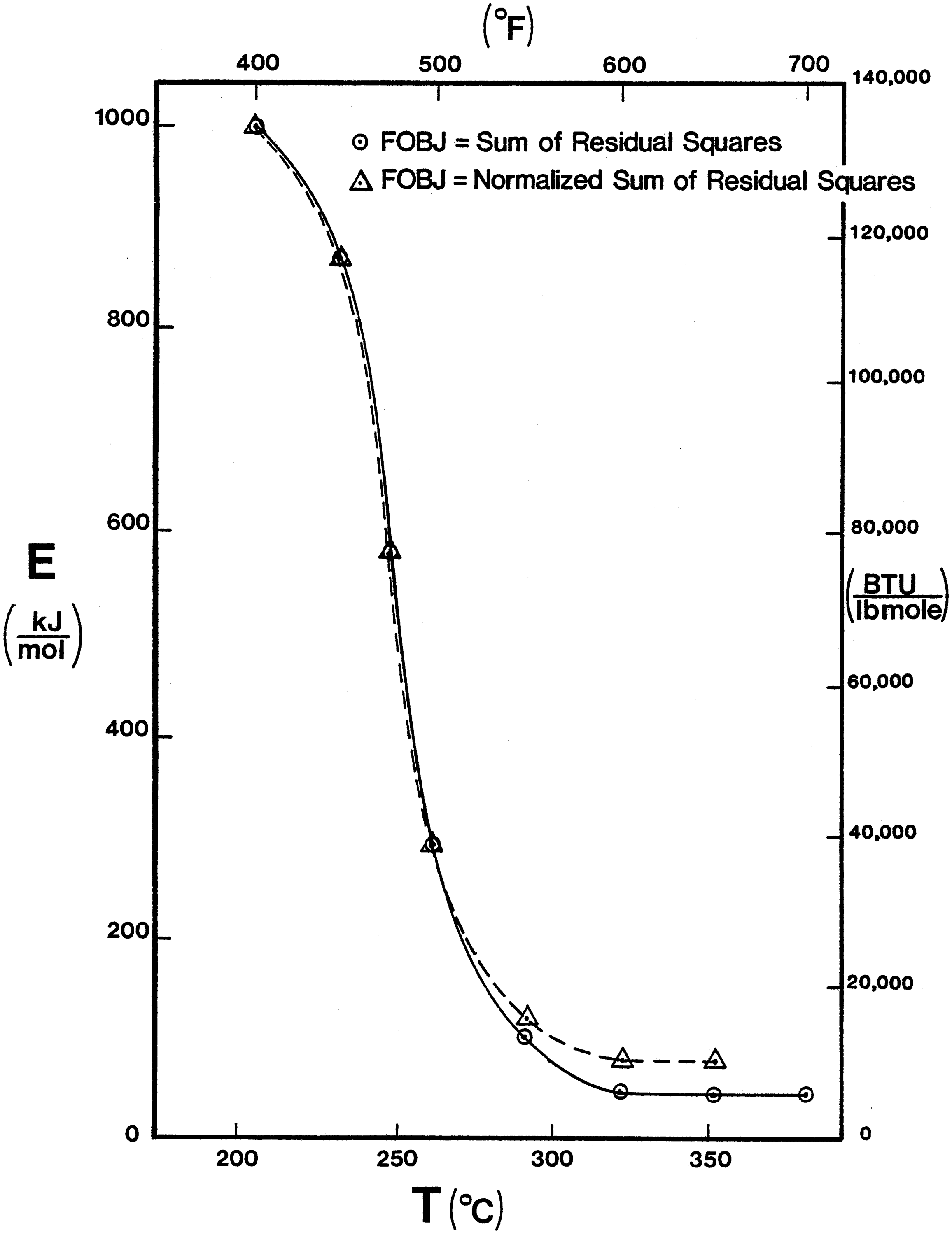

Figure 12. Global Model Activation Energy Dependence on Temperature

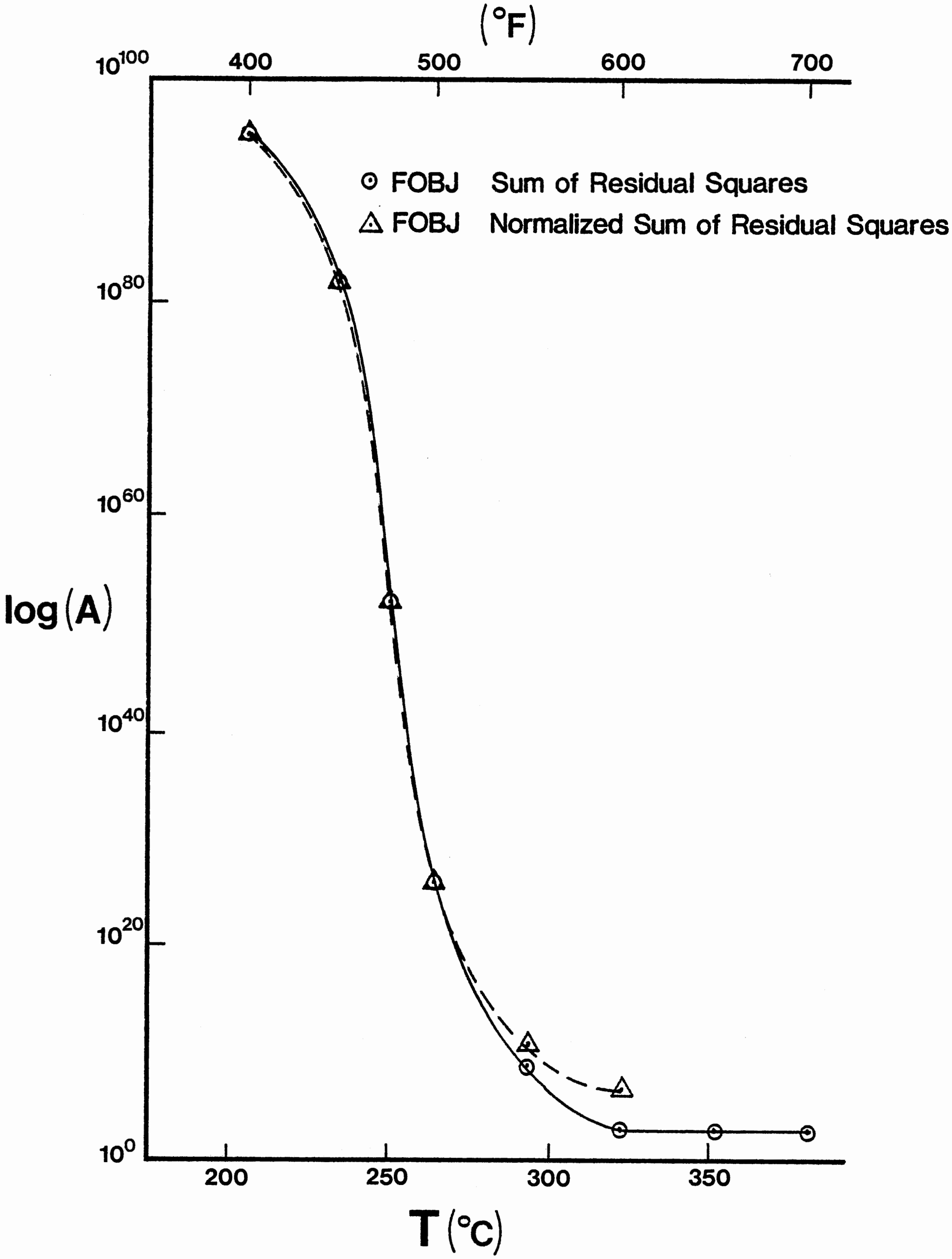

Figure 13. Global Model Pre-Exponential Constant Dependence on Temperature

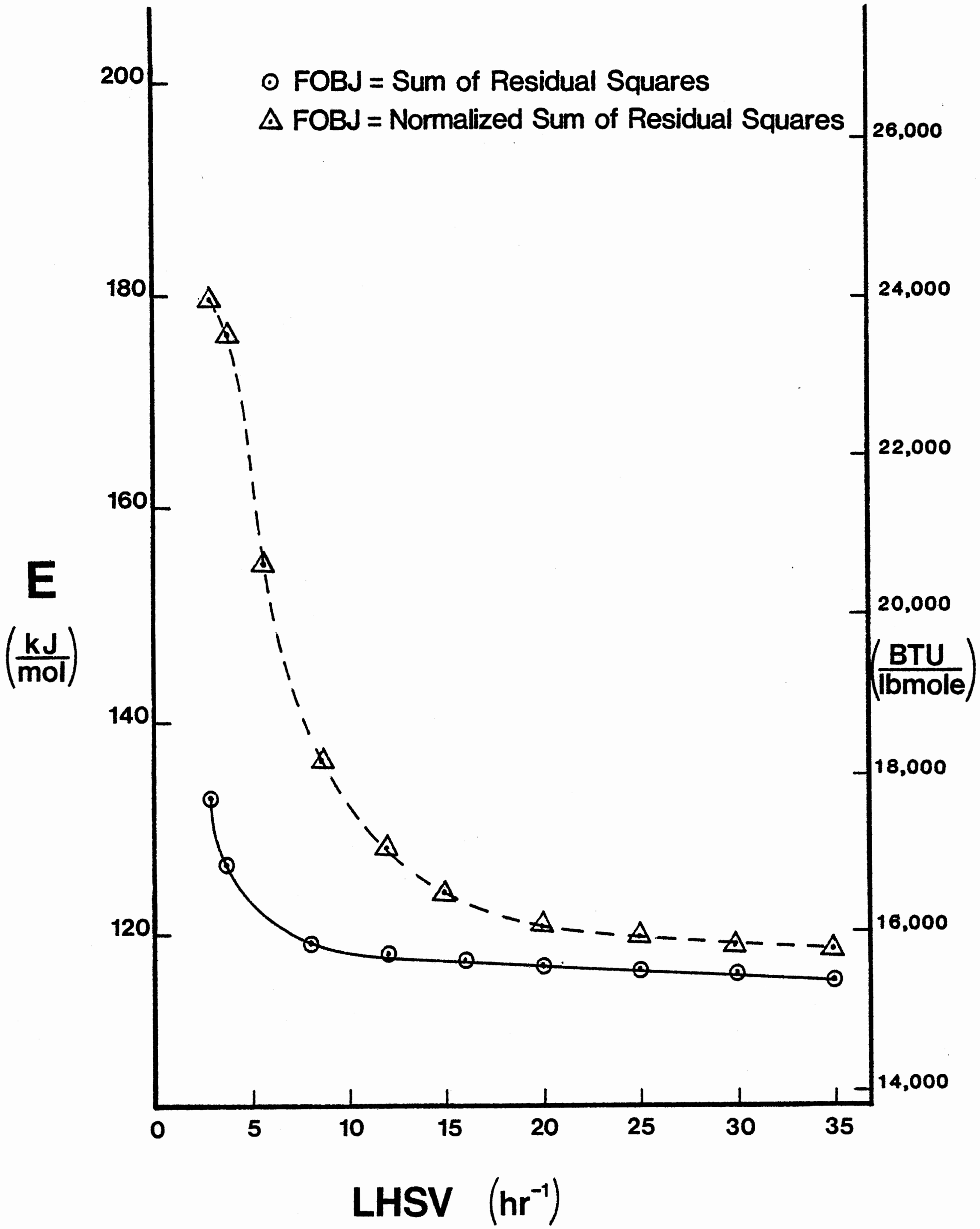

Figure 14. Global Model Activation Energy Dependence on Space Velocity

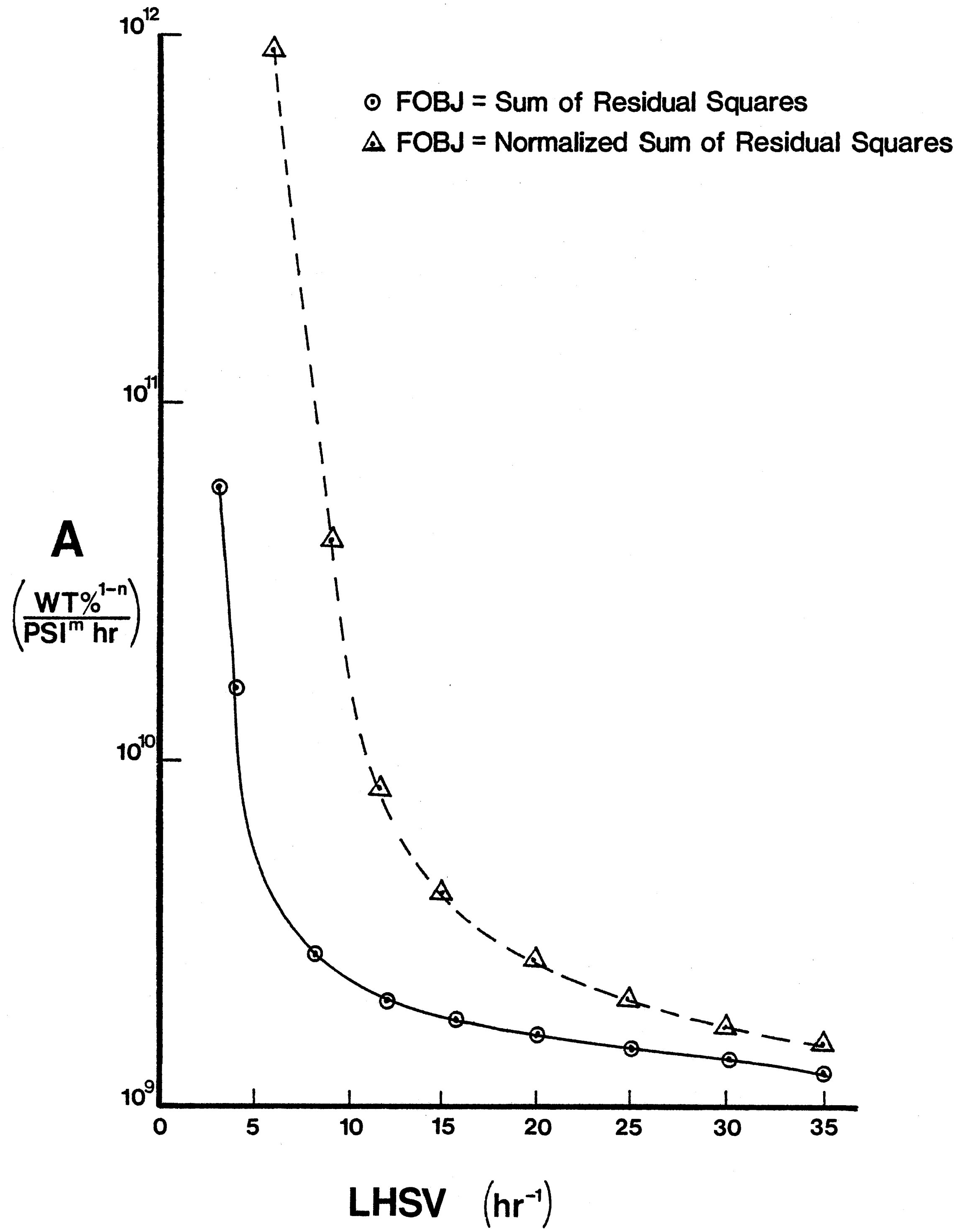

Figure 15. Global Model Pre-Exponential Constant Dependence on Space Velocity

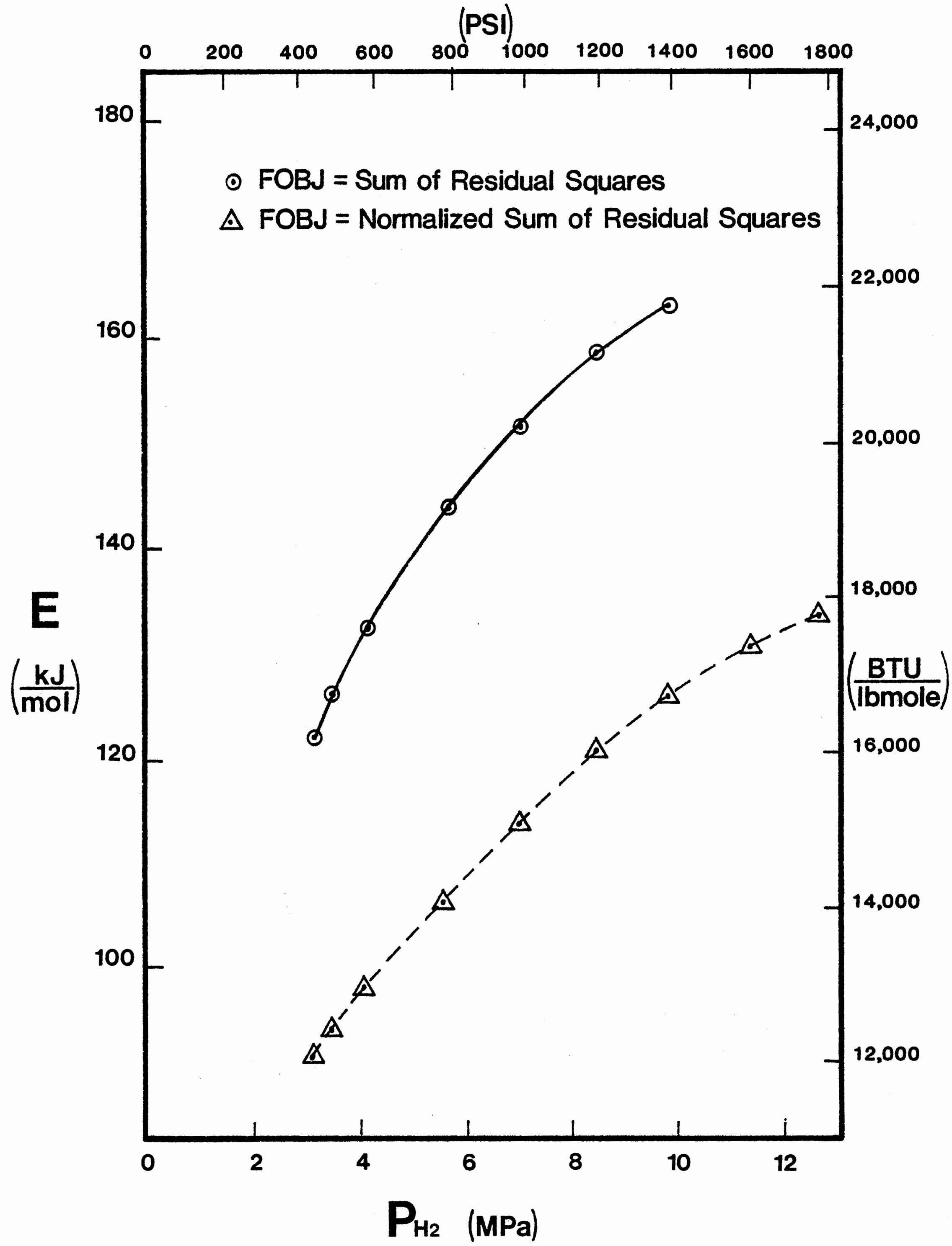

Figure 16. Global Model Activation Energy Dependence on Hydrogen Pressure

kinetics. The only such observation concerning this relationship would be that the global model parameters most closely approximate the intrinsic kinetic orders of DBT and hydrogen concentration dependence at high temperatures, high hydrogen pressures, and low space velocities.

CHAPTER V

SUMMARY AND CONCLUSIONS

Summary

An extensive survey of the literature related to the hydrotreatment of coal-derived liquids revealed a number of reports containing kinetic analyses. In these reports several different forms of global type rate equations were described from which a consensus opinion concerning their analyses was lacking. Although in most cases the authors reported acceptable data fit results for one of the global model forms, few authors made comparisons to other forms of the model. This left the determination of the best form in doubt. In many comparable studies contradictory opinions were offered.

In an attempt to learn the kintics of CDL hydrotreatment and to resolve the questions concerning the global rate expressions raised in the literature survey, evaluations of several kinetic rate models were performed. These evaluations were obtained through the analysis of appropriate hydrotreatment data fit results.

The values of the n-th order power-law or global kinetic model parameters were calculated which best described each of three separate sets of coal-liquid HDS, HDN, and HDO data. The resulting values of the pre-exponential constants (A), activation energies (E), orders of heteroatom concentration dependence (n), and orders of hydrogen pressure dependence (m), were scattered and inconsistent. Other observations from the global model CDL data fits were: values of n greater than one generally allowed the best fits to the experimental data; converged values of A, E, m, and n were dependent on the initial estimates of those values and on the form of the fitted function; the estimated values of the parameters included large confidence regions that were in some cases larger than the parameter value itself; and the goodness of fit was not highly dependent on the values of the model parameters, i.e., with a parameter fixed at some arbitrary value far from its "best fit" value only a slightly poorer fit resulted. These observations were concluded to be a characteristic of the global models, which are poorly conditioned for parameter estimation calculations.

The hyperbolic, or intrinsic kinetic model was unable to satisfactorily describe multiple reactant feeds unless they were treated as more than one separately reacting group. These multiple group forms were not investigated in this work.

A mathematical process model was developed to describe the HDS of a model CDL compound, dibenzothiophene. This model included the intrinsic rate expression found to be best suited for the description of the HDS of a single sulfur-containing hydrocarbon. This rate expression was derived from catalytic reaction theory in which two types of adsorption sites were assumed, one type of site for which sulfur containing molecules compete, and a second type of site on which the noncompetitive adsorption of hydrogen occurs. This process model was able to fit a set of experimental dibenzothiophene HDS data under isothermal conditions. The average deviation was less than two percent for each of five isothermal fits. This model was, however, unable to describe the same set of DBT HDS data under nonisothermal conditions due to an inadequate description of reaction product effects.

A parameter sensitivity study was conducted in which the n-th order global model parameters were calculated which allow the best fit to a hypothetical data set described by the dibenzothiophene HDS model mentioned above, and subsequently plotted as functions of the operating temperature, hydrogen pressure, and space velocity. Several observations were aparent from these curves: the global parameters were dependent upon the minimized objective function; the global parameters were dependent on the operating conditions at which they were calculated; and the global parameters revealed no directly corresponding relationship to the intrinsic kinetics of the system.

Conclusions

The principal conclusions of this work are:

1. The global kinetic model is capable of fitting coal-derived liquid hydrotreatment data with good accuracy.

2. Global kinetic models are poorly conditioned (do not allow their parameters to be sharply defined), resulting in: shallow parameter surface minima; large parameter confidence regions; and dependence of parameter values on the operating conditions at which they were calculated, the minimized objective function, and the fitted form of the rate equation.

3. There is no direct relationship between global and intrinsic parameters, specifically reaction orders, except under certain limited ranges of the operating conditions.

4. The conventional single group intrinsic rate expression is not capable of describing the hydrotreatment of a typical coal-derived

liquid.

5. The two type adsorption site intrinsic kinetic equation may be used to develop an accurate single compound HDS model under isothermal reaction conditions.

Recommendations

Two significant recommendations for further study related to this work were apparent to this author. First, the further development of the single component process model would be valuable to better describe product formation, hydrogen solubility, diffusion and the effectiveness factor, and flow and heat nonidealities. An experimental reactor specifically used to allow collection of the data necessary for proper refinement of this model would be helpful.

Second, a properly expanded set of parameter sensitivity curves would allow recognition of the specific forms of intrinsic kinetic expressions which best describe particular processes through the analysis of the n-th order global data fit results. The possibility of eliminating the trial and error search through possible descriptive intrinsic rate equations would make such an expansion of the parameter sensitivity study worthwhile.

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APPENDIX A

DERIVATION OF A LANGMUIR-HINSHELWOOD TYPE KINETIC RATE EQUATION FOR A SOLID-CATALYZED REACTION

Consider the following irreversible chemical reaction:

$$A + B \longrightarrow R + P \qquad [A-1]$$

Assume the following adsorption, reaction, desorption mechanism where s represents a catalyst adsorption site:

$$A + s \rightleftarrows As \qquad [A-2]$$

$$B + s \rightleftarrows Bs \qquad [A-3]$$

$$As + Bs \longrightarrow R + Ps + s \qquad [A-4]$$

$$Ps \rightleftarrows P + s \qquad [A-5]$$

Define the following terms:

C_i = concentration of species i in the liquid near the catalyst surface.

k_{if}, k_{ir} = forward and reverse rate constants for step i

r_i = rate of step i

K_i = equilibrium constant for step i

ϕ_i = fraction of total catalyst adsorption sites occupied by species i, where $\phi_s = 1 - \Sigma \phi_i$

If the reaction occurs near equilibrium conditions the step rates may be expressed as:

$$r_A = k_{Af}C_A(1 - \phi_A - \phi_B - \phi_P) - k_{Ar}\phi_A \qquad [A-6]$$

$$r_B = k_{Bf}C_B(1 - \phi_A - \phi_B - \phi_P) - k_{Br}\phi_B \qquad [A-7]$$

$$r = k_f \phi_A \phi_B \qquad [A-8]$$

$$r_P = k_{Pf}\phi_P - k_{Pr}C_P(1 - \phi_A - \phi_B - \phi_P \qquad [A-9]$$

Solving for equilibrium constants and fractional adsorption site coverages:

$$K_A = \frac{k_{Af}}{k_{Ar}} = \frac{\phi_A}{C_A(1-\phi_A-\phi_B-\phi_P)} \qquad [A-10]$$

$$\phi_A = K_A C_A(1 - \phi_A - \phi_B - \phi_P) = K_A C_A \phi_S \qquad [A-11]$$

$$K_B = \frac{k_{Bf}}{k_{Br}} = \frac{\phi_B}{C_B(1-\phi_A-\phi_B-\phi_P)} \qquad \text{[A-12]}$$

$$\phi_B = KBCB(1 - \phi A - \phi B - \phi P) = KBCB\ S \qquad \text{[A-13]}$$

$$K_P = \frac{k_{Pr}}{k_{Pf}} = \frac{\phi_P}{C_P(1-\phi_A-\phi_B-\phi_P)} \qquad \text{[A-14]}$$

$$\phi_P = KPCP(1 - \phi A - \phi B - \phi P) = KPCP\phi S \qquad \text{[A-15]}$$

The vacant catalyst site fraction may now be expressed as:

$$\phi S = 1 - KACA\phi S - KBCB\phi S - KPCP\phi S \qquad \text{[A-16]}$$

Solving for S:

$$\phi_S = \frac{1}{1 + K_AC_A + K_BC_B + K_PC_P} \qquad \text{[A-17]}$$

Substituting for ϕ_S in Equations (A-11,13):

$$\phi_A = \frac{K_AC_A}{1 + K_AC_A + K_BC_B + K_PC_P} \qquad \text{[A-18]}$$

$$\phi_B = \frac{K_BC_B}{1 + K_AC_A + K_BC_B + K_PC_P} \qquad \text{[A-19]}$$

Substituting for ϕ_A and ϕ_B in Equation (A-8):

$$r = \frac{kC_AC_B}{(1 + K_AC_A + K_BC_B + K_PC_P)^2} \qquad \text{[A-20]}$$

Combining constants:

$$r = \frac{kC_AC_B}{(1 + K_AC_A + K_BC_B + K_PC_P)^2} \qquad \text{[A-21]}$$

APPENDIX B

INTEGRATION OF PLUG FLOW DESIGN EQUATION WITH INTRINSIC RATE EQUATION

The ideal plug flow design equation is expressed as:

$$\frac{W}{f_{R1}} = \int_0^{X_R} \frac{dX_R}{r} \qquad [B-1]$$

where W is the weight of the catalyst, f_{R1} is the reactant feed rate, X_R is the reactant conversion, and r the reaction rate. The reaction rate equation used in this model is written below:

$$r = \frac{k\eta C_R C_H}{(1 + K_R\eta C_R + K_P C_P)(1 + K_H C_H)} \qquad [B-2]$$

Let:

$$X_R = 1 - C_{R2}/C_{R1} \qquad [B-3]$$

$$dX_R = -dC_R/C_{R1} \qquad [B-4]$$

$$\frac{-WC_{R1}}{f_{R1}} = \int_{C_{R1}}^{C_{R2}} \frac{dC_R}{r} \qquad [B-5]$$

$$\frac{-WC_{R1}}{f_{R1}} = \int_{C_{R1}}^{C_{R2}} \frac{(1 + K_R\eta C_R + K_P C_P)(1 + K_H C_H)}{k\eta C_R C_H} dC_R \qquad [B-6]$$

$$\frac{-WC_{R1} k\ C_H}{f_{R1}(1+K_H C_H)} = \int_{C_{R1}}^{C_{R2}} \frac{(1 + K_R\ C_R + K_P C_P)}{C_R} dC_R \qquad [B-7]$$

Define:

$$C_P = C_{R1} + C_{R2} + C_{P1} \qquad [B-8]$$

$$\frac{-WC_{R1} k\eta C_H}{f_{R1}(1+K_H C_H)} = \int_{C_{R1}}^{C_{R2}} \frac{((1 + k_P(C_{R1} + C_{P1})) + ((K_R\eta - K_P)C_R)}{C_R} \qquad [B-9]$$

$$\frac{-WC_{R1} k\eta C_H}{f_{R1}(1+K_H C_H)} = (1 + K_P(C_{R1} + C_{P1}))\ln\frac{C_{R2}}{C_{R1}}$$

$$+ (K_R\eta - K_P)(C_{R2} - C_{R1}) \qquad [B-10]$$

Solving for outlet concentration:

$$C_{R2} = C_{R1} + \frac{(1 + K_P(C_{R1} + C_{P1}))}{(K_R\eta - K_P)} \ln \frac{C_{R1}}{C_{R2}} - \frac{WC_{R1}k\ \eta C_H}{f_{R1}(1+K_HC_H)(K_R\eta-K_P)} \tag{B-11}$$

if f_{R1} and C_{R1} have units (wt/time) and (wt%) then:

$$f_{R1} = \frac{C_{R1}(\mathrm{LHSV})(V)(\rho)}{100} \tag{B-12}$$

Substituting for f_{R1} in Equation (B-11):

$$C_{R2} = C_{R1} + \frac{(1 + K_P(C_{R1} + C_{P1}))}{(k_R\eta - K_P)} \ln \frac{C_{R1}}{C_{R2}} - \frac{K(\eta)(C_H)(W)(100)}{(1 + K_HC_H)(K_R\eta - K_P)(\mathrm{LHSV})(V)(\rho)} \tag{B-13}$$

APPENDIX C

PARAMETER SENSITIVITY CALCULATION DATA

TABLE IX

PARAMETER SENSITIVITY - CONSTANT PRESSURE GLOBAL MODEL PARAMETERS

P_{H_2} psi	K_p wt%$^{1-n}$/hr	E Kcal/gmole	n	Average Error %	FOBJ (wt%)^2
450	2.143 E11	2.938 E4	1.222	1.513 E1	1.064 E-1
500	5.682 E11	3.042 E4	1.233	1.856 E1	9.244 E-2
600	3.184 E12	3.227 E4	1.246	2.685 E1	7.045 E-2
800	4.172 E13	3.502 E4	1.239	4.572 E1	4.230 E-2
1000	2.241 E14	3.680 E4	1.210	5.934 E1	2.811 E-2
1200	6.983 E14	3.800 E4	1.181	6.517 E1	2.141 E-2
1400	1.580 E15	3.885 E4	1.159	6.765 E1	1.841 E-2

$K_p = AP^m$

$\text{FOBJ} = \sum (C_{fit} - C_{dat})^2$

TABLE X

PARAMETER SENSITIVITY - CONSTANT PRESSURE GLOBAL MODEL PARAMETERS (NORMALIZED OBJECTIVE FUNCTION)

P_{H_2} psi	K_p wt%$^{1-n}$/hr	E Kcal/gmole	n	Average Error %	FOBJ
450	6.272 E8	2.237 E4	8.305 E-1	1.239 E1	1.385
500	1.107 E9	2.294 E4	8.576 E-1	1.280 E1	1.430
600	3.156 E9	2.401 E4	8.970 E-1	1.343 E1	1.512
800	1.937 E10	2.590 E4	9.425 E-1	1.411 E1	1.656
1000	9.068 E10	2.753 E4	9.656 E-1	1.431 E1	1.779
1200	3.486 E11	2.898 E4	9.775 E-1	1.429 E1	1.882
1400	1.153 E12	3.029 E4	9.831 E-1	1.421 E1	1.965
1600	3.366 E12	3.148 E4	9.850 E-1	1.397 E1	2.030
1800	8.718 E12	3.254 E4	9.848 E-1	1.382 E1	2.080
2000	1.981 E13	3.346 E4	9.839 E-1	1.374 E1	2.118

$K_p = AP^m$

$$\text{FOBJ} = \sum\left(\frac{C_{fit} - C_{dat}}{C_{dat}}\right)^2$$

TABLE XI

PARAMETER SENSITIVITY - CONSTANT SPACE VELOCITY GLOBAL MODEL PARAMETERS

LHSV hr^{-1}	A $wt\%^{1-n}/psi^{m}/hr$	E Kcal/gmole	m	n	Average Error %	FOBJ $(wt\%)^2$
3	6.030 E10	3.210 E4	6.303 E-1	8.915 E-1	3.287 E-1	3.422 E-2
4	1.562 E10	3.075 E4	6.650 E-1	8.208 E-1	1.181 E-1	3.873 E-2
8	2.557 E9	2.882 E4	7.148 E-1	5.951 E-1	3.290	3.091 E-2
12	2.004 E9	2.866 E4	7.412 E-1	5.428 E-1	1.456	1.841 E-2
16	1.645 E9	2.847 E4	7.523 E-1	5.090 E-1	9.297 E-1	1.150 E-2
20	1.452 E9	2.835 E4	7.589 E-1	4.937 E-1	7.020 E-1	2.782 E-3
25	1.314 E9	2.827 E4	7.645 E-1	4.914 E-1	5.417 E-1	5.198 E-3
30	1.227 E9	2.822 E4	7.684 E-1	5.002 E-1	4.425 E-1	3.713 E-3
35	1.163 E9	2.819 E4	7.714 E-1	5.157 E-1	3.747 E-1	2.783 E-3

$FOBJ = \sum (C_{fit} - C_{dat})^2$

TABLE XII

PARAMETER SENSITIVITY - CONSTANT SPACE VELOCITY GLOBAL MODEL PARAMETERS (NORMALIZED OBJECTIVE FUNCTION)

LHSV hr^{-1}	A $wt\%^{1-n}/psi^{m}/hr$	E Kcal/gmole	m	n	Average Error %	FOBJ
2	1.975 E14	4.309 E4	8.371 E-1	1.005	1.100 E-1	6.000 E-1
3	7.514 E13	4.250 E4	9.039 E-1	1.011	8.535	3.441 E-1
9	3.733 E10	3.313 E4	8.474 E-1	8.468 E-1	1.984	1.870 E-2
12	8.367 E9	3.104 E4	8.118 E-1	7.521 E-1	1.273	7.620 E-3
15	4.009 E9	3.000 E4	7.955 E-1	6.900 E-1	9.509 E-1	4.100 E-3
20	2.248 E9	2.919 E4	7.854 E-1	6.359 E-1	6.810 E-1	2.010 E-3
25	1.707 E9	2.882 E4	7.825 E-1	6.158 E-1	5.322 E-1	1.210 E-3
30	1.454 E9	2.863 E4	7.819 E-1	6.136 E-1	4.373 E-1	8.100 E-4
35	1.306 E9	2.851 E4	7.821 E-1	6.216 E-1	3.715 E-1	5.800 E-4

$$FOBJ = \sum \left(\frac{C_{fit} - C_{dat}}{C_{dat}} \right)^{2}$$

TABLE XIII

PARAMETER SENSITIVITY - CONSTANT TEMPERATURE GLOBAL MODEL PARAMETERS

T °F	K_t $wt\%^{1-n}/psi^m/hr$	m	n	Average Error %	FOBJ $(wt\%)^2$
450	3.329 E-6	1.332 E-1	1.055 E-1	1.339 E-2	5.559 E-6
475	3.011 E-4	2.026 E-1	6.059	4.613 E-2	5.791 E-5
500	3.722 E-3	2.898 E-1	3.591	1.348 E-1	4.001 E-4
550	2.985 E-2	4.944 E-1	1.484	7.557 E-1	5.118 E-3
600	5.359 E-2	6.810 E-1	9.333 E-1	6.003	9.221 E-3
650	7.077 E-2	8.403 E-1	7.048 E-1	1.048 E14	1.014 E-2
700	1.204 E-1	9.187 E-1	5.222 E-1	3.831 E9	9.689 E-4

$K_t = A \exp(-E/RT)$

$FOBJ = \sum (C_{fit} - C_{dat})^2$

TABLE XIV

PARAMETER SENSITIVITY - CONSTANT TEMPERATURE GLOBAL MODEL PARAMETERS (NORMALIZED OBJECTIVE FUNCTION)

T °F	K_t $\text{wt\%}^{1-n}/\text{psi}^m/\text{hr}$	m	n	Average Error %	FOBJ
400	6.293 E-9	4.680 E-2	1.574 E-1	1.847 E-3	6.354 E-8
450	3.334 E-6	1.331 E-1	1.055 E-1	1.339 E-2	5.559 E-6
475	3.022 E-4	2.023 E-1	6.057	4.615 E-2	5.791 E-5
500	3.760 E-3	2.886 E-1	3.588	1.349 E-1	4.003 E-4
550	3.157 E-2	4.863 E-1	1.477	7.476 E-1	5.210 E-3
600	7.623 E-2	6.277 E-1	9.730 E-1	3.858	3.325 E-2

$K_t = A \exp(-E/RT)$

$$\text{FOBJ} = \sum \left(\frac{C_{fit} - C_{dat}}{C_{dat}} \right)^2$$

TABLE XV

PRE-EXPONENTIAL CONSTANTS AND ACTIVATION ENERGIES CALCULATED FROM THE ARRHENIUS PLOT OF THE GLOBAL MODEL CONSTANT K_t

T °F	A $wt\%^{1-n}/psi^{m}/hr$	E Kcal/gmole	A $wt\%^{1-n}/psi^{m}/hr$	E Kcal/gmole
400	9.621 E94	2.317 E5	9.621 E94	2.317 E5
450	2.448 E81	2.009 E5	2.452 E81	2.009 E5
475	2.123 E52	1.327 E5	2.131 E52	1.327 E5
500	6.285 E25	6.889 E4	6.348 E25	6.889 E4
550	2.285 E8	2.538 E4	2.432 E9	2.795 E4
600	2.214 E2	9.745 E3	3.039 E5	1.779 E4
650	2.014 E2	9.745 E3	---	1.779 E4
700	2.431 E2	9.745 E3	---	1.779 E4

$$\text{FOBJ} = \sum (C_{fit} - C_{dat})^2 \qquad \text{FOBJ} = \sum \left(\frac{C_{fit} - C_{dat}}{C_{dat}}\right)^2$$

$K_t = A \exp(-E/RT)$

TABLE XVI

PRE-EXPONENTIAL CONSTANT AND ACTIVATION ENERGY CALCULATED FROM THE LINEAR REGRESSION OF LOGARITHMIC PLOT OF THE GLOBAL MODEL CONSTANT K_p VERSUS HYDROGEN PRESSURE

Slope = m	7.990	6.975
Standard error	2.123	1.417
Intercept = log A	-9.751	-9.844
Standard error	6.155	4.266
A ($wt\%^{1-n}/psi^{m}/hr$)	1.722 E-10	1.433 E-10
Coeff. of det.	0.993	0.997
FOBJ	$\sum (C_{fit} - C_{dat})^2$	$\sum \left(\frac{C_{fit} - C_{dat}}{C_{dat}} \right)^2$

APPENDIX D

LISTING OF THE MODIFIED MARQUARDT NONLINEAR DATA FIT PROGRAM

```
     $JOB              ,LIBLIST
 1          CALL MARQ
 2          STOP
 3          END

     $ENTRY
 4          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
     C  COPYRIGHT (C) 1981 J. P. CHANDLER                                       MARQ    4
     C                                                                          MARQ    5
     C  J. P. CHANDLER AND LEON W. JACKSON,                                     MARQ    6
     C              DEPARTMENT OF COMPUTING AND INFORMATION SCIENCES            MARQ    7
     C              OKLAHOMA STATE UNIVERSITY, STILLWATER, OKLAHOMA 74074       MARQ    8
     C                                                                          MARQ    9
     C  MARQ PERFORMS A NONLINEAR LEAST SQUARES FIT OF A USER-SUPPLIED          MARQ   10
     C  FUNCTION TO A GIVEN SET OF DATA, USING MARQUARDT-S METHOD, OR THE       MARQ   11
     C  GAUSS-NEWTON METHOD, OR A MODIFIED GAUSS-NEWTON METHOD.                 MARQ   12
     C                                                                          MARQ   13
     C UPDATE ADDED TO WATFIV LIBRARY BY J. HANSON, UCC USER SERVICES           MARQ   13
     C                                                                          MARQ   13
     C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *    MARQ   14
     C                                                                          MARQ   15
     C  INPUT QUANTITIES.....  FUNK,X(*),XMAX(*),XMIN(*),DELMN(*),NF,NTRAC,     MARQ   16
     C                              MASK(*),MATRX,NFMAX,NFLAT,KW,               MARQ   17
     C                              Y(*),YSIG(*),NPTS,LPCOL,                    MARQ   18
     C                              FLAMB,FNU,RELDF,METHD,KALCP,KORDF,          MARQ   19
     C                              MAXIT,LEQU,MXSUB                            MARQ   20
     C  OUTPUT QUANTITIES....  X(*),FOBJ,ERR(*,*),KFLAG,FIT(*)                  MARQ   21
     C  SCRATCH VECTOR.......  DELTX(*)
     C  UNUSED QUANTITIES (INCLUDED FOR COMPATIBILITY WITH STEPIT COMMON).      MARQ   22
     C                                  JVARY,NXTRA,NOREP,KERFL                 MARQ   23
     C                                                                          MARQ   24
     C      FUNK        --  THE NAME OF THE SUBROUTINE CALLED TO OBTAIN         MARQ   25
     C                           THE FITTED VALUES IF KALCP=0                   MARQ   25
     C      X(JX)       --  THE JX-TH PARAMETER                                 MARQ   27
     C      XMAX(JX)    --  THE UPPER LIMIT FOR X(JX)                           MARQ   28
     C      XMIN(JX)    --  THE LOWER LIMIT FOR X(JX)                           MARQ   29
     C      DELMN(JX)   --  THE CONVERGENCE TOLERANCE FOR X(JX)                 MARQ   30
     C      FOBJ        --  RETURNS THE FINAL VALUE OF PHI, THE WEIGHTED        MARQ   31
     C                           SUM OF SQUARES (PHI IS BEING MINIMIZED AS A    MARQ   32
     C                           FUNCTION OF THE X(JX))                         MARQ   33
     C      NV          --  THE NUMBER OF PARAMETERS                            MARQ   34
     C      NTRAC       --  USER PRINT CONTROL                                  MARQ   35
     C                           =-3, NO OUTPUT EXCEPT FATAL ERROR MESSAGES     MARQ   36
     C                           =-2, NO OUTPUT EXCEPT DIAGNOSTIC MESSAGES      MARQ   37
     C                           =-1, STANDARD OUTPUT EXCEPT FINAL FIT VALUES   MARQ   38
     C                           = 0, STANDARD OUTPUT                           MARQ   39
     C                           = 1, ALSO PRINTS RESULTS OF EACH ITERATION     MARQ   40
     C                           = 2, ALSO PRINTS THE COEFFICIENT MATRIX, QSAV  MARQ   41
     C                           = 3, ALSO PRINTS THE JACOBIAN MATRIX, P        MARQ   42
     C      MATRX       --  NONZERO IF STATISTICAL ERRORS ARE TO BE COMPUTED    MARQ   43
     C      MASK(JX)    --  NONZERO IF X(JX) IS TO BE HELD FIXED                MARQ   44
     C      NFMAX       --  THE MAXIMUM NUMBER OF FUNCTION COMPUTATIONS         MARQ   45
     C      NFLAT       --  NONZERO IF THE SEARCH IS TO TERMINATE WHEN TWO      MARQ   46
     C                           ITERATIONS GIVE IDENTICAL VALUES OF PHI        MARQ   47
     C      KW          --  THE LOGICAL UNIT NUMBER OF THE PRINTER              MARQ   48
     C      ERR(JX,KX)  --  RETURNS THE ERROR MATRIX                            MARQ   49
     C      KFLAG       --  RETURNED .GT. ZERO FOR A NORMAL EXIT,               MARQ   50
     C                           RETURNED .LT. ZERO FOR AN ABNORMAL EXIT        MARQ   51


     C                                                                          MARQ   52
     C      Y(JPT)      --  THE JPT-TH DATA ORDINATE                            MARQ   53
     C      YSIG(JPT)   --  THE EXPECTED ERROR IN Y(JPT)                        MARQ   54
     C      NPTS        --  THE NUMBER OF DATA OBSERVATIONS                     MARQ   55
     C      FIT(JPT)    --  THE JPT-TH FITTED VALUE                             MARQ   56
     C      FITSV       --  A SCRATCH VECTOR OF NPTS VALUES                     MARQ   57
     C      P(JPT,JX)   --  THE FIRST PARTIAL DERIVATIVE                        MARQ   58
     C                           OF FIT(JPT) WITH RESPECT TO X(JX)              MARQ   59
     C      LPDMA       --  THE FIRST DIMENSION OF THE ARRAY CONTAINING P       MARQ   60
     C                         (LPCOL MUST BE .GE. NPTS IF KALCP IS .GE. ZERO)MARQ   61
     C      LPDMB       --  THE SECOND DIMENSION OF THE ARRAY CONTAINING P      MARQ   62
     C                         (LPDMB MUST BE .GE. NV)                          MARQ   63
     C      FLAMB       --  MARQUARDT-S LAMBDA, THE RELATIVE AMOUNT BY WHICH    MARQ   64
     C                           THE DIAGONAL COEFFICIENTS OF THE NORMAL        MARQ   65
     C                           EQUATIONS ARE AUGMENTED                        MARQ   66
     C      FNU         --  MARQUARDT-S NU, THE FACTOR BY WHICH FLAMB IS        MARQ   67
     C                           CHANGED                                        MARQ   68
     C      RELDF       --  DETERMINES THE MAGNITUDE OF THE DIFFERENCING STEP   MARQ   69
     C      RELMN       --  RELATIVE CONVERGENCE CRITERION USED FOR EACH X(J)   MARQ   70
     C                           FOR WHICH DELMN(J) IS ZERO                     MARQ   71
     C      METHD       --  DETERMINES THE METHOD USED                          MARQ   72
     C                           =-1, MODIFIED GAUSS-NEWTON METHOD              MARQ   73
     C                           = 0, GAUSS-NEWTON METHOD                       MARQ   74
     C                           = 1, MODIFIED FORM OF MARQUARDT-S METHOD       MARQ   75
     C                           = 2, MARQUARDT-S METHOD                        MARQ   76
     C      KALCP       --  DETERMINES WHICH ROUTINE IS CALLED TO COMPUTE THE   MARQ   77
     C                           JACOBIAN MATRIX OF FIRST PARTIAL DERIVATIVES   MARQ   78
     C                           =-1, ONE ROW OF P RETURNED BY DERIV OR CALCD,  MARQ   79
     C                                   DERIV CALLS FOFX                       MARQ   80
     C                           = 0, ALL OF P RETURNED BY DERIV OR CALCD,      MARQ   81
     C                                   DERIV CALLS FUNK                       MARQ   82
     C                           = 1, ALL OF P RETURNED BY DERIV OR CALCD,      MARQ   83
     C                                   DERIV CALLS FOFX                       MARQ   84
     C      KORDF       --  DETERMINES HOW P IS TO BE CALCULATED                MARQ   85
     C                           = 1, FIRST ORDER APPROXIMATION USED BY DERIV   MARQ   86
     C                           = 2, SECOND ORDER APPROXIMATION USED BY DERIV  MARQ   87
     C                           = 3, ANALYTICAL DERIVATIVE SUPPLIED BY CALCD   MARQ   88
     C      MAXIT       --  THE MAXIMUM NUMBER OF ITERATIONS TO BE PERFORMED    MARQ   89
     C      LEQU        --  SAVES STORAGE IF ALL YSIG(JPT) ARE THE SAME         MARQ   90
     C                           =1 IF ALL YSIG(JPT) ARE EQUAL (IN THIS CASE    MARQ   91
     C                                ONLY YSIG(1) IS REFERENCED)               MARQ   92
     C                           =0 OTHERWISE                                   MARQ   93
     C      MXSUB       --  THE MAXIMUM NUMBER OF SUBITERATIONS PERMITTED       MARQ   94
     C      MXUPD       --  NOT USED AT PRESENT                                 MARQ   95
     C                                                                          MARQ   96
     C  MODIFICATIONS TO MARQUARDT-S METHOD...                                  MARQ   97
     C    1.  THE QUANTITY (1+LAMBDA) IS NOT ALLOWED TO INCREASE BY MORE        MARQ   98
     C         THAN A FACTOR OF FNULM, IN ANY SINGLE CHANGE.                    MARQ   99
     C    2.  WHEN CUTSTEPS ARE USED IN A LINE SEARCH (WHEN THE ANGLE           MARQ  100
     C         GAMMA .LT. GAMMA SUB ZERO), THE VALUE OF LAMBDA IS INCREASED.    MARQ  101
     C  IN BOTH THE MODIFIED MARQUARDT-S METHOD AND THE MODIFIED                MARQ  102
     C  GAUSS-NEWTON METHOD, A HALF STEP IS ATTEMPTED FOLLOWING EACH            MARQ  103
     C  SUCCESSFUL STEP.  THIS AVOIDS ONE FORM OF VERY SLOW CONVERGENCE.        MARQ  104
     C                                                                          MARQ  105
     C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *    MARQ  106
     C                                                                          MARQ  107
     C  THE FOLLOWING EXTERNAL STATEMENT IS REQUIRED BY SOME COMPILERS          MARQ  108
     C  (WATFIV, FOR EXAMPLE) AND FORBIDDEN BY OTHERS (MODCOMP II).             MARQ  109
 5          EXTERNAL FUNK                                                       MARQ  110
     C                                                                          MARQ  111
```

```
      DOUBLE PRECISION P,Y,YSIG,H,SCALE,XMAX,XMIN,DELTX,DELMN,
     *     ERR,FOBJ,FLAMB,FNU,RELDF,QSQRT,ARG,CRIT,FLDEF,RELMN,
     *     RLTOL,FACCL,HUGE,RZERO,RUNIT,RTWO,DELN,FMGN,FCUT,
     *     STFAC,PTERM,SCALJ,SA,PIVOT,EM,SUM,COSIN,SB,SC,HH,
     *     FRMIN,XMX,XMN,DENOM,FRAC,UPFAC,RLFAC,RSFAC,RMSQV,
     *     SDVMX,QMAX1,QMIN1,QABS,ARGB
      DOUBLE PRECISION X,XSAVE,XTEMP,GRAD,FIT,FITSV,
     *                  XSAV,SIG,RTERM,PHI,PHNEW,PHALF,XLIM
C
C  THE DIMENSIONS OF THE VECTORS AND MATRICES (AS OPPOSED TO ARRAYS)
C  ARE....
C       P(NPTS,NACTV) (OR P(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,METHQ,KALCP,KORDF,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
C  NO FLOATING POINT CONSTANTS ARE USED BEYOND THIS POINT.
C
      KFLAG=0
      NOREP=0
      ITER=0
      PHI=HUGE
      SC=HUGE
C
      IF(NTRAC.GE.-1) WRITE(KW,10)
   10 FORMAT(49H1MARQ....   BEGIN NONLINEAR LEAST SQUARES SOLUTION)
      NACTV=-99
      IF(NV.GT.0 .AND. NV.LE.NVMAX .AND. NV.LE.LPDMB .AND.
     *     NPTS.GE.1 .AND. (KALCP.LT.0 .OR. NPTS.LE.LPDMA)) GO TO 20
      KFLAG=-1
      GO TO 60
C
C  CHECK SOME INPUT QUANTITIES, AND SET THEM TO DEFAULT VALUES IF
C  DESIRED.
C                               NACTV ...  NUMBER OF ACTIVE X(J)
   20 NACTV=0
      DO 50 JX=1,NV
        DELN=QABS(DELMN(JX))
        IF(MASK(JX))50,30,50
   30   NACTV=NACTV+1
        IF(DELN.EQ.RZERO) DELN=QABS(RELMN*X(JX))
        IF(DELN.EQ.RZERO) DELN=RELMN
        IF(XMAX(JX).GT.XMIN(JX)) GO TO 40
        XMAX(JX)=HUGE
        XMIN(JX)=-HUGE
   40   X(JX)=QMAX1(XMIN(JX),QMIN1(XMAX(JX),X(JX)))
   50   DELMN(JX)=DELN
C
      IF(NACTV.GT.0) GO TO 80
      KFLAG=-2
   60 CONTINUE
      WRITE(KW,70)NV,NVMAX,NACTV,NPTS,LPDMA,LPDMB,KALCP
   70 FORMAT(//29H ILLEGAL INPUT VALUE IN MARQ.,4X,5H NV =,I3,4X,
     *     8H NVMAX =,I3,4X,8H NACTV =,I3/10X,7H NPTS =,I5,4X,8H LPDMA =,
     *     I5,4X,8H LPDMB =,I5,4X,8H KALCP =,I3)
      GO TO 1300
   80 CONTINUE
      IF(NTRAC.LT.-1) GO TO 150
      WRITE(KW,90)(MASK(J),J=1,NV)
   90 FORMAT(/10H MASK    = ,I7,7I13/(4X,8I13))
      WRITE(KW,100)(X(J),J=1,NV)
  100 FORMAT(/10H X       = ,8E13.5/(10X,8E13.5))
      WRITE(KW,110)(XMAX(J),J=1,NV)
  110 FORMAT(/10H XMAX    = ,8E13.5/(10X,8E13.5))
      WRITE(KW,120)(XMIN(J),J=1,NV)
  120 FORMAT(/10H XMIN    = ,8E13.5/(10X,8E13.5))
```

```
      WRITE(KW,130)(DELMN(J),J=1,NV)
  130 FORMAT(/10H DELMN  =  ,8E13.5/(10X,8E13.5))
      WRITE(KW,140)NV,NPTS,LPDMA,LPDMB,NTRAC,METHD,KALCP,KORDF,
     *     NFLAT,NFMAX,MAXIT,MXSUB,CRIT,RELDF,RELMN
  140 FORMAT(//5H NV =,I4,5X,7H NPTS =,I6,5X,8H LPDMA =,I6,5X,
     *   8H LPDMB =,I4,5X,8H NTRAC =,I2,5X,8H METHD =,I3,5X,8H KALCP =,
     *   I3//8H KORDF =,I2,5X,8H NFLAT =,I2,5X,8H NFMAX =,I7,5X,
     *   8H MAXIT =,I5,5X,8H MXSUB =,I4//7H CRIT =,E12.5,5X,8H RELDF =,
     *   E12.5,5X,8H RELMN =,E12.5)
  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=FLDEF
      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,8H 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,8E15.7/(6X,8E15.7))
C
C  COMPUTE QSAV AND GRAD.
C  QSAV, WHICH IS STORED IN ONE HALF OF THE ARRAY ERR(*,*), IS PT*P.
C  GRAD(*) IS HALF THE GRADIENT OF PHI.
C
        IF(LEQU.EQ.0) SIG=YSIG(JPT)
        RTERM=(FIT(JPT)-Y(JPT))/SIG**2
        DO 260 JX=1,NACTV
          GRAD(JX)=GRAD(JX)+P(KPT,JX)*RTERM
          PTERM=P(KPT,JX)/SIG**2
          DO 250 KX=1,JX
  250       ERR(JX,KX)=ERR(JX,KX)+P(KPT,KX)*PTERM
  260     CONTINUE
  270   CONTINUE
C                                RESTORE FIT IF IT WAS DESTROYED IN DERIV.
      IF(KORDF.NE.2) GO TO 280
      IF(KALCP.NE.0) GO TO 280
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)
      NF=NF+1
  280 NF=NF+NACTV
  290 NF=NF+NACTV
C
C  COMPUTE THE SCALE FACTORS AND STORE THEM IN DELTX(*).  SCALE GRAD.
C
      DO 300 JX=1,NACTV
        SCALJ=QSQRT(ERR(JX,JX))
        IF(SCALJ.EQ.RZERO) SCALJ=RUNIT
        DELTX(JX)=SCALJ
  300   GRAD(JX)=GRAD(JX)/SCALJ
      IF(NTRAC.GE.1) WRITE(KW,310)(GRAD(JX),JX=1,NACTV)
  310 FORMAT(/21H   SCALED GRADIENT =  ,8E15.7/(21X,8E15.7))
C
C  SCALE QSAV.  THE DIAGONAL ELEMENTS OF QSAV ARE SCALED TO UNITY.
C
      DO 355 JX=1,NACTV
        DO 350 KX=1,JX
          SA=ERR(JX,KX)/(DELTX(JX)*DELTX(KX))
          IF(KX.NE.JX) GO TO 320
          IF(SA.EQ.RZERO) GO TO 330
          SA=RUNIT
          GO TO 350
  320     IF(QABS(SA).LT.RUNIT-RLTOL) GO TO 350
  330     CONTINUE
          IF(NTRAC.GE.-2) WRITE(KW,340)JX,KX,SA,ITER
  340     FORMAT(36H ********  POSSIBLY DANGEROUS VALUE OF ,
     *     18H COEFFICIENT ...,5X,6H QSAV(,I3,1H,,I3,3H) =,E15.7,9X,
     *     10H ITERATION,I5)
  350     ERR(JX,KX)=SA
  355 CONTINUE
      IF(NTRAC.LT.2) GO TO 380
      WRITE(KW,360)
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      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
C                                                                        MARQ 360
C  COPY QSAV INTO Q AND GRAD INTO H, AND SET THE DIAGONAL ELEMENTS OF Q.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
          JO=0                                                           MARQ 366
          JT=0                                                           MARQ 367
          DO 460 JX=1,NV                                                 MARQ 368
            IF(MASK(JX).NE.0) GO TO 460                                  MARQ 369
            JO=JO+1                                                      MARQ 370
            IF(MASKT(JX).NE.0) GO TO 460                                 MARQ 371
            JT=JT+1                                                      MARQ 372
            H(JT)=-GRAD(JO)                                              MARQ 373
            KO=0                                                         MARQ 374
            KT=0                                                         MARQ 375
            DO 440 KX=1,JX                                               MARQ 376
              IF(MASK(KX).NE.0) GO TO 440                                MARQ 377
              KO=KO+1                                                    MARQ 378
              IF(MASKT(KX).NE.0) GO TO 440                               MARQ 379
              KT=KT+1                                                    MARQ 380
              SA=ERR(JO,KO)                                              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
      460   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
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            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)                                    MARQ 420
      520   H(J)=(H(J)-SUM)/PIVOT                                        MARQ 421
      530   CONTINUE                                                     MARQ 422
C                                                                        MARQ 423
C  IF THE COEFFICIENT MATRIX WAS RANK DEFICIENT, PRINT A MESSAGE.        MARQ 424
C                                                                        MARQ 425
          MRANK=NACT-NSMAL                                               MARQ 426
          IF(MRANK.EQ.NACT) GO TO 560                                    MARQ 427
          COSIN=HUGE                                                     MARQ 428
          IF(NTRAC.GE.-2) WRITE(KW,540)MRANK,NACT,ITER                   MARQ 429
      540 FORMAT(/41H RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.,9X,7H RANK =,MARQ 430
     *    I4,7X,18H ORDER OF MATRIX =,I4,9X,10H ITERATION,I5)            MARQ 431
          IF(MRANK.GT.0) GO TO 550                                       MARQ 432
          KFLAG=-4                                                       MARQ 433
          GO TO 1200                                                     MARQ 434
      550 IF(METHO.GT.0 .AND. MRANK.LT.KRANK) GO TO 660                  MARQ 435
C                                                                        MARQ 436
C  UNPACK AND DE-SCALE THE CORRECTION VECTOR H.                         MARQ 437
C  COMPUTE THE INNER PRODUCTS SA, SB, AND SC.                            MARQ 438
C                                                                        MARQ 439
      560 SA=RZERO                                                       MARQ 440
          SB=RZERO                                                       MARQ 441
          SC=RZERO                                                       MARQ 442
          KX=NV                                                          MARQ 443
          KO=NACTV                                                       MARQ 444
          KT=NACT                                                        MARQ 445
          DO 590 JX=1,NV                                                 MARQ 446
            HH=RZERO                                                     MARQ 447
            IF(MASK(KX).NE.0) GO TO 580                                  MARQ 448
            IF(MASKT(KX).NE.0) GO TO 570                                 MARQ 449
            HH=H(KT)                                                     MARQ 450
            SA=SA-HH*GRAD(KO)                                            MARQ 451
            SB=SB+HH*HH                                                  MARQ 452
            SC=SC+GRAD(KO)**2                                            MARQ 453
            HH=HH*FMGN/DELTX(KO)                                         MARQ 454
            KT=KT-1                                                      MARQ 455
      570   KO=KO-1                                                      MARQ 456
      580   H(KX)=HH                                                     MARQ 457
      590   KX=KX-1                                                      MARQ 458
C                                                                        MARQ 459
C  ADD THE CORRECTION VECTOR TO THE PARAMETER VECTOR AND                 MARQ 460
C  CHECK FOR CONSTRAINT VIOLATIONS.                                      MARQ 461
C  THIS IS THE ENTRY POINT FOLLOWING A CUTSTEP.                          MARQ 462
C                                                                        MARQ 463
      600 CONTINUE                                                       MARQ 464
          IF(NTRAC.GE.1) WRITE(KW,610)(H(JX),JX=1,NV)                    MARQ 465
      610 FORMAT(/7X,14H CORRECTION = ,6E15.7/(21X,6E15.7))              MARQ 466
          NACSV=NACT                                                     MARQ 467
          FRMIN=RUNIT                                                    MARQ 468
          NLOOP=0                                                        MARQ 469
          JXLIM=0                                                        MARQ 470
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  620 DO 720 JX=1,NV                                                    MARQ 471
        IF(MASKT(JX).NE.0) GO TO 720                                    MARQ 472
        XSAV=XSAVE(JX)                                                  MARQ 473
        XMX=XMAX(JX)                                                    MARQ 474
        XMN=XMIN(JX)                                                    MARQ 475
        HH=H(JX)                                                        MARQ 476
        IF((XSAV.LT.XMX .OR. HH.LE.RZERO) .AND.                         MARQ 477
     *     (XSAV.GT.XMN .OR. HH.GE.RZERO)) GO TO 640                    MARQ 478
        MASKT(JX)=1                                                     MARQ 479
        NACT=NACT-1                                                     MARQ 480
        X(JX)=XSAV                                                      MARQ 481
        IF(NTRAC.GE.-1) WRITE(KW,630)JX,XSAV,ITER                       MARQ 482
  630   FORMAT(/8H FIX  X(,I3,4H) = ,E12.5,22H TEMPORARILY, TO AVOID,   MARQ 483
     *   24H VIOLATING A CONSTRAINT.,26X,10H ITERATION,I5)              MARQ 484
        GO TO 720                                                       MARQ 485
  640   XLIM=XSAV+HH*FRMIN                                              MARQ 486
        IF(JX.NE.JXLIM) GO TO 650                                       MARQ 487
        IF(KBND)680,690,660                                             MARQ 488
  650   X(JX)=XLIM                                                      MARQ 489
        IF(XLIM.LE.XMX) GO TO 670                                       MARQ 490
  660   X(JX)=XMX                                                       MARQ 491
        JBND=1                                                          MARQ 492
        GO TO 690                                                       MARQ 493
  670   IF(XLIM.GE.XMN) GO TO 720                                       MARQ 494
  680   X(JX)=XMN                                                       MARQ 495
        JBND=-1                                                         MARQ 496
  690   IF(JX.NE.JXLIM) GO TO 710                                       MARQ 497
        IF(NTRAC.LT.-1) GO TO 720                                       MARQ 498
        WRITE(KW,700)JX,X(JX),FRMIN,ITER                                MARQ 499
  700   FORMAT(/28H CONSTRAINT VIOLATED BY X(,I3,                       MARQ 500
     *   20H).   VALUE RESET TO ,E15.8,24H USING CUTSTEP FACTOR = ,E12.5MARQ 501
     *   ,3X,8H ITER.,I5)                                               MARQ 502
        GO TO 720                                                       MARQ 503
  710   IF(NLOOP.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=JBND                                                       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 = ,5E15.7/(21X,5E15.7))                          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
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(/33X,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(METHO)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 860                                      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*RTWO,FNU)                                         MARQ 581
      IF(METHO.EQ.1) UPFAC=DMIN1(UPFAC,FNULM*RUNIT/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) =,E12.5,28X,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
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C
C  COSIN IS GREATER THAN CRIT.  CUT THE MAGNITUDE OF THE STEP, H.
C
  880 STFAC=STFAC/FCUT
      IF(METHD.GE.0) GO TO 890
      FMGN=FMGN/FCUT
      GO TO 900
  890 IF(METHD.EQ.1) FLAMB=FLAMB*RTWO
  900 DO 910 JX=1,NV
  910   H(JX)=(X(JX)-XSAVE(JX))/FCUT
      FCUT=FCUT*FACCL
      IF(NTRAC.GE.1) WRITE(KW,920)JSUB,COSIN,STFAC
  920 FORMAT(/18H **** SUBITERATION,I3,4X,16H TAKE CUT STEPS.,4X,
     *   13H COS(GAMMA) =,E12.5,5X,17H CUTSTEP FACTOR =,E12.5)
C
C                                GO BACK AND TRY A SMALLER CUTSTEP.
      GO TO 800
C
C  THE VALUE OF PHI HAS DECREASED.  TRY A HALF STEP.
C
  830 IF(METHD.EQ.0 .OR  METHD.EQ.2) GO TO 1080
      DO 840 JX=1,NV
        XTEMP(JX)=X(JX)
        IF(MASK(JX).NE.0) GO TO 840
        X(JX)=XSAVE(JX)+(X(JX)-XSAVE(JX))/RTWO
        X(JX)=DMAX1(XMIN(JX),DMIN1(XMAX(JX),X(JX)))
  840   CONTINUE
      DO 850 JPT=1,NPTS
  850   FITSV(JPT)=FIT(JPT)
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHALF)
      NF=NF+1
C
C  USE QUADRATIC INTERPOLATION, IN ORDER TO TRY TO REFINE THE
C  POSITION OF THE MINIMUM OF PHI.
C
      RLFAC=RUNIT
      DENOM=RTWO*((PHNEW-PHALF)-(PHALF-PHI))
      STFAC=RZERO
      IF(DENOM.LE.RZERO) GO TO 860
      STFAC=(PHI-PHNEW)/DENOM
      RSFAC=(RUNIT+STFAC)/RTWO
C
C                                DO NOT EXTRAPOLATE.
      IF(STFAC.GE.RUNIT) STFAC=RZERO
  860 DO 870 JX=1,NV
        H(JX)=X(JX)
  870   X(JX)=X(JX)+(XTEMP(JX)-X(JX))*STFAC
      IF(PHALF.GE.PHNEW) GO TO 1010
      RLFAC=RUNIT/RTWO
      JSUB=JSUB+1
      DO 880 JX=1,NV
  880 XTEMP(JX)=H(JX)
      DO 990 JPT=1,NPTS
  990   FITSV(JPT)=FIT(JPT)
      IF(NTRAC.GE.1) WRITE(KW,1000)PHNEW,PHALF
 1000 FORMAT(/21H HALF STEP SUCCEEDED.,15X,8H PHNEW =,E15.8,18X,
     *   8H PHALF =,E15.8)
      PHNEW=PHALF
 1010 IF(STFAC.EQ.RZERO) GO TO 1020
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)


      NF=NF+1
      IF(PHI.LT.PHNEW) GO TO 1060
 1020 DO 1030 JX=1,NV
 1030   X(JX)=XTEMP(JX)
      DO 1040 JPT=1,NPTS
 1040   FIT(JPT)=FITSV(JPT)
      IF(STFAC.EQ.RZERO) GO TO 1060
      IF(NTRAC.LT.1) GO TO 1080
      WRITE(KW,1050)RSFAC,PHI
 1050 FORMAT(/25H QUADRATIC INTERPOLATION.,22X,8H RSFAC =,E12.5,12X,
     *   6H PHI =,E15.8)
      GO TO 1080
 1060 RLFAC=RSFAC
      PHNEW=PHI
      IF(NTRAC.GE.1) WRITE(KW,1070)RLFAC,PHI
 1070 FORMAT(/35H QUADRATIC INTERPOLATION SUCCEEDED.,12X,8H RLFAC =,
     *   E12.5,12X,6H PHI =,E15.8)
 1080 IF(RLFAC.LE.RZERO) GO TO 1090
      FLAMB=FLAMB/RLFAC
      IF(METHD.LT.0) FMGN=FMGN*RLFAC
C
C  THE STEP IS ACCEPTED.  TEST FOR CONVERGENCE IF NO CONSTRAINT
C  BECAME ACTIVE DURING THIS ITERATION.
C
 1090 CONTINUE
      IF(NTRAC.GE.1) WRITE(KW,1100)ITER,PHNEW
 1100 FORMAT(/16H END   ITERATION,I5,58X,6H PHI =,E15.8)
      PHI=PHNEW
      IF(JXLIM.GT.0) GO TO 1130
      DO 1110 JX=1,NV
        IF(MASK(JX).NE.0) GO TO 1110
        IF(DABS(X(JX)-XSAVE(JX)).GT.DELMN(JX)) GO TO 1130
 1110   CONTINUE
      KFLAG=1
      IF(NTRAC.LT.-1) GO TO 1200
      WRITE(KW,1120)
 1120 FORMAT(//38H CONVERGED WHEN THE STEP BECAME SMALL.)
      GO TO 1200
C
C  THE ITERATION HAS NOT YET CONVERGED.
C
 1130 IF(ITER.LT.MAXIT) GO TO 1150
      KFLAG=-6
      WRITE(KW,1140)MAXIT
 1140 FORMAT(//46H MAXIMUM NUMBER OF ITERATIONS REACHED IN MARQ.,5X,
     *   6H MAXIT =,I5)
      GO TO 1200
C
C  IF SUBITERATIONS WERE NOT PERFORMED THIS ITERATION, DECREASE LAMBDA.
C
 1150 IF(NF.GE.NFMAX) GO TO 1180
      IF(JSUB.GT.0) GO TO 1160
      FMGN=DMIN1(FMGN*RTWO,RUNIT)
      SCALJ=RUNIT+FLAMB
      IF(SCALJ.GT.RUNIT) FLAMB=FLAMB/DOWNU
      UPNU=DOWNU
      DOWNU=DMIN1(DOWNU*RTWO,FNU)
      GO TO 1170
 1160 IF(METHD.NE.1) GO TO 1170
      UPNU=FNULM
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      DOWNU=FNULM                                                       MARO 711
 1170 CONTINUE                                                          MARO 712
C                                 GO BACK AND DO ANOTHER ITERATION.     MARO 713
      GO TO 170                                                         MARO 714
 1180 KFLAG=-7                                                          MARO 715
      WRITE(KW,1190)NFMAX                                               MARO 716
 1190 FORMAT(//23H NF HAS REACHED NFMAX =,I7,9H IN MARO.)               MARO 717
C                                                                       MARO 718
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * MARO 719
C                                                                       MARO 720
C  THE ITERATION HAS TERMINATED.                                        MARO 721
C  PRINT OUT THE DATA, FITTED VALUES, AND RESIDUALS.                    MARO 722
C  COMPUTE AND PRINT THE STANDARD DEVIATION OF THE DATA FROM THE FIT.   MARO 723
C                                                                       MARO 724
 1200 CONTINUE                                                          MARO 725
      SC=DSQRT(SC)                                                      MARO 726
      IF(NTRAC.LT.-1) GO TO 1290                                        MARO 727
      WRITE(KW,1210)ITER,NF,PHI,FMGN,FLAMB,SC                           MARO 728
 1210 FORMAT(/1X,I4,11H ITERATIONS,7X,5H NF =,I5,9X,6H PHI =,E15.8,10X, MARO 729
     *    7H FMGN =,E12.5,7X,9H LAMBDA =,E12.5//9X,15H NORM OF SCALED,  MARO 730
     *    18H GRADIENT VECTOR =,E12.5)                                  MARO 731
      WRITE(KW,760)(X(JX),JX=1,NV)                                      MARO 732
      IF(NTRAC.GE.0) WRITE(KW,1220)                                     MARO 733
 1220 FORMAT(///14X,1HJ,8X,5H Y(J),14X,7H FIT(J),10X,                   MARO 734
     *    12H Y(J)-FIT(J),7X,8H YSIG(J),11X,13H (Y-FIT)/YSIG/1H )       MARO 735
      SIG=YSIG(1)                                                       MARO 736
      RMSDV=RZERO                                                       MARO 737
      SDVMX=RZERO                                                       MARO 738
      DO 1240 JPT=1,NPTS                                                MARO 739
        IF(LEQU.EQ.0) SIG=YSIG(JPT)                                     MARO 740
        YY=Y(JPT)                                                       MARO 741
        PTERM=YY-FIT(JPT)                                               MARO 742
        RTERM=PTERM/SIG                                                 MARO 743
        IF(NTRAC.GE.0) WRITE(KW,1230)JPT,YY,FIT(JPT),PTERM,SIG,RTERM    MARO 744
 1230   FORMAT(5X,I10,5X,E15.8,5X,E15.8,5X,E12.5,5X,E12.5,10X,E12.5)    MARO 745
        RMSDV=RMSDV+RTERM**2                                            MARO 746
 1240   SDVMX=DMAX1(SDVMX,DABS(RTERM))                                  MARO 747
      DENOM=NPTS-NACTV                                                  MARO 748
      WRITE(KW,1250)DENOM                                               MARO 749
 1250 FORMAT(//32H NUMBER OF DEGREES OF FREEDOM =  ,E12.5 )             MARO 750
      IF(DENOM.LE.RZERO) GO TO 1270                                     MARO 751
      RMSDV=DSQRT(RMSDV/DENOM)                                          MARO 752
      WRITE(KW,1260)RMSDV                                               MARO 753
 1260 FORMAT(/43H R.M.S. SCALED DEVIATION OF DATA FROM FIT =,E12.5)     MARO 754
 1270 CONTINUE                                                          MARO 755
      WRITE(KW,1280)SDVMX                                               MARO 756
 1280 FORMAT(/27H MAXIMUM SCALED DEVIATION =,E12.5)                     MARO 757
C                                                                       MARO 758
C  CALL FUNC TO SET THE FINAL VALUES.                                   MARO 759
C                                                                       MARO 760
 1290 CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                              MARO 761
      FOBJ=PHI                                                          MARO 762
C                                                                       MARO 763
C  CALL MOERR TO PRINT THE PARAMETER ERRORS AND CORRELATIONS.           MARO 764
C  A DUMMY ROUTINE MAY BE SUBSTITUTED FOR MOERR IF THESE ARE NOT NEEDED.MARO 765
C                                                                       MARO 766
      IF(MATRX.EQ.0) RETURN                                             MARO 767
      CALL MOERR (NACTV,NPTS)                                           MARO 768
C                                                                       MARO 769
 1300 RETURN                                                            MARO 770



C  END MARO.                                                            MARO 771
      END                                                               MARO 772

      SUBROUTINE FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                        FUNC    1
C                                                                       FUNC    2
C   UPDATED BY J. CHANDLER, OSU 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 FITM.  FUNC    3
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 /NLLS4/ 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 FOFX(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(/26H ERROR IN MARO....    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,P,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 MARO 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
```

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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
C   INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES                  DERIV   2
C                                                                       DERIV   2
C   DERIV 4.1         A.N.S.I. STANDARD FORTRAN         MAY 1981        DERIV   3
C                                                                       DERIV   4
C   DERIV COMPUTES THE JACOBIAN MATRIX P USING FINITE DIFFERENCES.      DERIV   5
C                                                                       DERIV   6
C   P(J,K) IS THE PARTIAL DERIVATIVE OF FIT(J) WITH RESPECT TO X(K).    DERIV   7
C   IF KORDF.EQ.1, DERIV USES A NONCENTRAL DIFFERENCE FORMULA.          DERIV   8
C   IF KORDF.EQ.2, DERIV USES A CENTRAL DIFFERENCE FORMULA.             DERIV   9
C   KORDF.EQ.1 IS ABOUT TWICE AS FAST AS KORDF.EQ.2, BUT LESS ACCURATE. DERIV  10
C                                                                       DERIV  11
      DOUBLE PRECISION P,XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,                DERIV  12
     *      FLAMB,FNU,RELDF,RELMN,RZERO                                 DERIV  13
      DOUBLE PRECISION X,FIT,FITSV,DEL,TWODL,XSAVE,FX0,FX1              DERIV  14
C                                                                       DERIV  15
      DIMENSION FIT(1),FITSV(1),P(LPDMA,LPDMB)                          DERIV  16
C                                                                       DERIV  17
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20),       DERIV  18
     *      ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),                    DERIV  19
     *      NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW                DERIV  20
      COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDF,MAXIT,     DERIV  21
     *      LEQU,MXSUB,MXUPD                                            DERIV  22
C                                                                       DERIV  23
      RZERO=0.                                                          DERIV  24
      JVARY=0                                                           DERIV  25
C                                                                       DERIV  26
C   SAVE FIT IF KALCP.GE.0 .                                            DERIV  27
C                                                                       DERIV  28
      IF(KALCP.LT.0) GO TO 20                                           DERIV  29
      DO 10 J=1,NPTS                                                    DERIV  30
   10   FITSV(J)=FIT(J)                                                 DERIV  31
C                                                                       DERIV  32
C   LOOP OVER THE ACTIVE PARAMETERS X(JX).                              DERIV  33
C                                                                       DERIV  34
   20 KX=0                                                              DERIV  35
      DO 150 JX=1,NV                                                    DERIV  36
        IF(MASK(JX).NE.0) GO TO 150                                     DERIV  37
        KX=KX+1                                                         DERIV  38
        DEL=RELDF*X(JX)                                                 DERIV  39
        IF(DEL.EQ.RZERO) DEL=RELDF                                      DERIV  40
        XSAVE=X(JX)                                                     DERIV  41
        X(JX)=XSAVE+DEL                                                 DERIV  42
        TWODL=DEL+DEL                                                   DERIV  43
        IF(KALCP)110,30,80                                              DERIV  44
C                                                                       DERIV  45
C   KALCP.EQ.0 .  COMPUTE P, ONE COLUMN AT A TIME.                      DERIV  46
C                                                                       DERIV  47
   30   CALL FUNK (FIT)                                                 DERIV  48
        IF(KORDF.EQ.2) GO TO 50                                         DERIV  49
        DO 40 J=1,NPTS                                                  DERIV  50
   40     P(J,KX)=(FIT(J)-FITSV(J))/DEL                                 DERIV  51

        GO TO 140                                                       DERIV  52
C                                                                       DERIV  53
C   KALCP.EQ.0 AND KORDF.EQ.2 .  IN THIS CASE, THE INPUT VALUES OF      DERIV  54
C   FIT(J) WILL BE DESTROYED.                                           DERIV  55
C                                                                       DERIV  56
   50   X(JX)=XSAVE-DEL                                                 DERIV  57
        DO 60 J=1,NPTS                                                  DERIV  58
   60     FITSV(J)=FIT(J)                                               DERIV  59
        JVARY=JX                                                        DERIV  60
        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 MOERR (NACTV,NPTS)                                     MOERR   1
C                                                                       MOERR   2
C   UPDATED BY J. CHANDLER, OSU DEPARTMENT OF COMPUTING AND             MOERR   2
C   INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES                  MOERR   2
C                                                                       MOERR   2
C   MOERR 3.0         A.N.S.I. STANDARD FORTRAN         MAY 1981        MOERR   3
C                                                                       MOERR   4
C   MOERR IS CALLED BY MARQ TO COMPUTE AND PRINT APPROXIMATE VALUES OF  MOERR   5
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C  THE PARAMETER ERRORS AND CORRELATIONS.
C
C  FOR THE MEANING OF THE -MAXIMUM VARIANCE INFLATION FACTOR- BELOW,
C  SEE...       D. W. MARQUARDT AND R. D. SNEE,
C               RIDGE REGRESSION IN PRACTICE,
C               THE AMERICAN STATISTICIAN 29 (1975) 3-20
C
C  INPUT QUANTITIES.....  KW,ERR(*,*),NACTV,DELTX(*),NPTS,NV,NTRAC,
C                         MASK(*),FOBJ
C  OUTPUT QUANTITIES....  ERR(*,*)
C
      DOUBLE PRECISION H,SCALE,XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,
     *     QSQRT,ARG,RZERO,RUNIT,HUGE,PIVOT,Q,VIFMX,ER,TEMP,
     *     DENOM,SCFAC,RESCL          ,X
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
C
      QSQRT(ARG)=DSQRT(ARG)
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
      RZERO=0.
      RUNIT=1.
      HUGE=1.E30
C                               PRINT QSAV.
      IF(NTRAC.LT.-1) GO TO 40
      WRITE(KW,10)
   10 FORMAT(///18H SUBROUTINE MOERR.//28H QSAV (PT*P, SCALED, WHERE,
     *   23H P IS THE JACOBIAN)....)
      DO 30 JX=1,NACTV
        WRITE(KW,20)JX,(ERR(JX,KX),KX=1,JX)
   20   FORMAT(/1X,I3,2X,6E15.7/(6X,6E15.7))
   30   CONTINUE
C
C  COMPUTE THE SCALED ERROR MATRIX, WHICH IS THE INVERSE OF QSAV.
C  INVERT QSAV USING THE GAUSS-JORDAN METHOD WITHOUT PIVOTING.
C  F. L. BAUER AND C. REINSCH, P. 45 IN -LINEAR ALGEBRA-
C  BY J. H. WILKINSON AND C. REINSCH (SPRINGER-VERLAG, 1971)
C  ERR(*,NV+1) IS USED AS A SCRATCH VECTOR.
C
   40 NVPLU=NV+1
      NSMAL=0
      DO 130 LINV=1,NACTV
        L=(NACTV+1)-LINV
        PIVOT=ERR(1,1)
        IF(PIVOT.LE.RZERO) NSMAL=NSMAL+1
        IF(NACTV.LT.2) GO TO 90
        DO 80 K=2,NACTV
          Q=ERR(K,1)
          IF(PIVOT.NE.RZERO) GO TO 50
          ERR(K,NVPLU)=RZERO
          GO TO 70
   50     IF(K.GT.L) GO TO 60
          ERR(K,NVPLU)=-Q/PIVOT
          GO TO 70
   60     ERR(K,NVPLU)=Q/PIVOT
   70     DO 80 M=2,K
   80       ERR(K-1,M-1)=ERR(K,M)+Q*ERR(M,NVPLU)


   90   IF(PIVOT.NE.RZERO) GO TO 100
        ERR(NACTV,NACTV)=RZERO
        GO TO 110
  100   ERR(NACTV,NACTV)=RUNIT/PIVOT
  110   IF(NACTV.LT.2) GO TO 130
        DO 120 K=2,NACTV
  120     ERR(NACTV,K-1)=ERR(K,NVPLU)
  130   CONTINUE
C
      NRANK=NACTV-NSMAL
      IF(NRANK.LT.NACTV) WRITE(KW,140)NRANK,NACTV
  140 FORMAT(//51H THE SECOND DERIVATIVE MATRIX IS SINGULAR IN MOERR.,
     *   5X,7H RANK =,I3,7X,8H ORDER =,I3//24H THEREFORE ALL PARAMETER,
     *    21H ERRORS ARE INFINITE.)
C
C                             UNPACK THE ERROR MATRIX INTO THE UPPER
C                                 TRIANGLE OF ERR(*,*), DE-SCALING IT.
      JV=0
      VIFMX=RZERO
      DO 190 JX=1,NV
        IF(MASK(JX).EQ.0) JV=JV+1
        KV=0
        DO 180 KX=1,JX
          ER=RZERO
          IF(MASK(JX).NE.0 .OR. MASK(KX).NE.0) GO TO 180
          KV=KV+1
          TEMP=RZERO
          DENOM=DELTX(JV)*DELTX(KV)
          IF(DENOM.EQ.RZERO) GO TO 150
          TEMP=ERR(JV,KV)
          ER=TEMP/DENOM
  150     IF(JX.NE.KX) GO TO 180
          IF(TEMP.GT.RZERO) GO TO 170
          IF(NTRAC.GE.-2) WRITE(KW,160)JX,KX,TEMP
  160     FORMAT(/6H THE (,I3,1H,,I3,23H) ELEMENT OF QSAV**-1 =,E13.5,
     *     5X,45H THEREFORE ALL PARAMETER ERRORS ARE INFINITE.)
          TEMP=-TEMP
  170     IF(TEMP.GT.VIFMX) VIFMX=TEMP
  180     ERR(KX,JX+1)=ER
  190   CONTINUE
C                              COMPUTE AND PRINT THE STANDARD ERRORS.
      NDF=NPTS-NACTV
      SCFAC=HUGE
      IF(NDF.LE.0) GO TO 200
      SCFAC=NDF
      SCFAC=QSQRT(FOBJ/SCFAC)
  200 RESCL=NDF+NDF
      IF(RESCL.GT.RZERO) RESCL=QSQRT(RESCL)
      IF(NTRAC.LT.-1) GO TO 340
      WRITE(KW,210)NDF,NDF,RESCL,FOBJ,SCFAC
  210 FORMAT(///41H NUMBER OF DEGREES OF FREEDOM (N.D.F.) =  ,
     *    14H(NPTS-NACTV) =,I5//24H EXPECTED VALUE OF PHI =  ,
     *    38H N.D.F  PLUS OR MINUS SQRT(2*N.D.F.) =,I5,
     *    15H  PLUS OR MINUS,E12.5//22H ACTUAL VALUE OF PHI =,E12.5//
     *    38H RESCALING FACTOR = SQRT(PHI/N.D.F.) =,E12.5)
      WRITE(KW,220)VIFMX
  220 FORMAT(///36H MAXIMUM VARIANCE INFLATION FACTOR =,E12.5///
     *    32H APPROXIMATE STANDARD ERRORS  .../68X,9H RESCALED/12X,1HJ,
     *    6X,7HMASK(J),9X,4HX(J),14X,5HERROR,12X,5HERROR)
      RESCL=HUGE
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823         DO 270 JX=1,NV                                                      MOERR126
824           SCALJ=RUNIT                                                       MOERR127
825           ER=ERR(JX,JX+1)                                                   MOERR128
826           IF(ER)230,250,240                                                 MOERR129
827     230   ER=-DSQRT(-ER)                                                    MOERR130
828           SCALJ=-ER                                                         MOERR131
829           GO TO 250                                                         MOERR132
830     240   ER=DSQRT(ER)                                                      MOERR133
831           SCALJ=ER                                                          MOERR134
832     250   IF(NDF.GT.0 .AND. NRANK.EQ.NACTV) RESCL=SCFAC*ER                  MOERR135
833           DELTX(JX)=SCALJ                                                   MOERR136
834           WRITE(KW,260)JX,MASK(JX),X(JX),ER,RESCL                           MOERR137
835     260   FORMAT(/10X,I3,I10,6X,E16.8,4X,E13.5,4X,E13.5)                    MOERR138
836     270   CONTINUE                                                          MOERR139
      C                               COMPUTE AND PRINT THE CORRELATIONS.       MOERR140
837         IF(NV.LT.2) GO TO 340                                               MOERR141
838         WRITE(KW,280)(K,K=1,NV)                                             MOERR142
839     280 FORMAT(///45H LOWER TRIANGLE OF THE CORRELATION MATRIX....//12X,    MOERR143
         *     7H K .....,I5,7I13/(11X,8I13))                                   MOERR144
840         WRITE(KW,290)(MASK(K),K=1,NV)                                       MOERR145
841     290 FORMAT(/7X,12H MASK(K)....,I5,7I13/(11X,8I13))                      MOERR146
842         WRITE(KW,300)                                                       MOERR147
843     300 FORMAT(/3X,1HJ,4X,7HMASK(J) )                                       MOERR148
844         DO 330 JX=1,NV                                                      MOERR149
845           DO 310 KX=1,JX                                                    MOERR150
846     310     ERR(KX,1)=ERR(KX,JX+1)/(DELTX(JX)*DELTX(KX))                    MOERR151
847           WRITE(KW,320)JX,MASK(JX),(ERR(KX,1),KX=1,JX)                      MOERR152
848     320   FORMAT(/1X,I3,I8,5X,8E13.5/(17X,8E13.5))                          MOERR153
849     330   CONTINUE                                                          MOERR154
      C                               RESCALE ERR AND SYMMETRIZE IT.            MOERR155
850     340 SCFAC=SCFAC**2                                                      MOERR156
851         IF(SCFAC.LT.RUNIT) SCFAC=RUNIT                                      MOERR157
852         DO 350 JX=1,NV                                                      MOERR158
853           DO 350 KX=1,JX                                                    MOERR159
854             ERR(JX,KX)=ERR(KX,JX+1)*SCFAC                                   MOERR160
855     350     ERR(KX,JX)=ERR(JX,KX)                                           MOERR161
      C                                                                         MOERR162
856         RETURN                                                              MOERR163
      C  END MOERR.                                                             MOERR164
857         END                                                                 MOERR165

858         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, P,     FOFXDUM8
      C  BE STORED.                                                             FOFXDUM9
      C                                                                         FOFXDU10
859         DOUBLE PRECISION X,F                                                FOFXDU11
860         DIMENSION X(20)                                                     FOFXDU12
861         RETURN                                                              FOFXDU13
862         END                                                                 FOFXDU14
***ERROR***  WRONG NUMBER OF ARGUMENTS IN REFERENCE TO SUBPROGRAM MARQ


      PROGRAM WAS EXECUTING LINE      1 IN ROUTINE M/PROG WHEN TERMINATION OCCURRED

STATEMENTS EXECUTED=        1

CORE USAGE        OBJECT CODE=   37568 BYTES,ARRAY AREA=    5076 BYTES,TOTAL AREA AVAILABLE=  129024  BYTES

DIAGNOSTICS        NUMBER OF ERRORS=        1, NUMBER OF WARNINGS=        0, NUMBER OF EXTENSIONS=        9

COMPILE TIME=     0.32 SEC,EXECUTION TIME=     0.01 SEC,      14.17.10     FRIDAY        22 JUL 83    WATFIV - MAR 1980 V2L0

      $STOP
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     $JOB              ,LIBLIST
   1         CALL STSET
   2         STOP
   3         END

     $ENTRY
   4         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, KAUPE, 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
   5         DOUBLE PRECISION XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,FLAMB,FNU,   STSETM14
        *        RELDF,RELMN,RZERO,HUGE        ,X                         STSETM15
     C                                                                    STSETM16
   6         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
   7         COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDF,MAXIT, STSETM20
        *        LEQU,MXSUB,MXUPD                                         STSETM21
     C                                                                    STSETM22
     C                             KW ...  LOGICAL UNIT NUMBER OF THE PRINTER STSETM23
   8         KW=6                                                         STSETM24
   9         NVMAX=20                                                     STSETM25
     C                             THE USER MUST SET NV AFTER CALLING STSET.  STSETM26
  10         NV=-1                                                        STSETM27
  11         HUGE=1.E30                                                   STSETM28
  12         RZERO=0.                                                     STSETM29
  13         NTRAC=0                                                      STSETM30
  14         NFMAX=32767                                                  STSETM31
  15         MAXIT=20                                                     STSETM32
  16         MXSUB=25                                                     STSETM33
  17         METHD=1                                                      STSETM34
  18         KALCP=0                                                      STSETM35
  19         KORDF=1                                                      STSETM36
  20         LEQU=0                                                       STSETM37
  21         NFLAT=1                                                      STSETM38
  22         MATRX=106                                                    STSETM39
  23         NXTRA=0                                                      STSETM40
  24         FLAMB=1.                                                     STSETM41
  25         FNU=10.                                                      STSETM42
  26         RELDF=1.E-6                                                  STSETM43
  27         RELMN=1.E-6                                                  STSETM44
     C                                                                    STSETM45
  28         DO 10 JX=1,NVMAX                                             STSETM46
  29           X(JX)=RZERO                                                STSETM47
  30           XMAX(JX)=HUGE                                              STSETM48
  31           XMIN(JX)=-HUGE                                             STSETM49
  32           DELTX(JX)=RZERO                                            STSETM50
  33           DELMN(JX)=RZERO                                            STSETM51


  34           MASK(JX)=0                                                 STSETM52
  35      10   CONTINUE                                                   STSETM53
     C                                                                    STSETM54
  36         RETURN                                                       STSETM55
  37         END                                                          STSETM56
STATEMENTS EXECUTED=      163
CORE USAGE       OBJECT CODE=    1384 BYTES,ARRAY AREA=    4356 BYTES,TOTAL AREA AVAILABLE=  128024  BYTES
DIAGNOSTICS        NUMBER OF ERRORS=       0, NUMBER OF WARNINGS=       0, NUMBER OF EXTENSIONS=       0
COMPILE TIME=    0.02 SEC,EXECUTION TIME=    0.01 SEC,     14.18.45    FRIDAY       22 JUL 83    WATFIV - MAR 1980 V2L0

        C$STOP
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$JOB               ,LIBLIST
      CALL STEPT
      STOP
      END

$ENTRY
      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
      EXTERNAL FUNK                                                     STMARQ17
C                                                                       STMARQ18
      DOUBLE PRECISION FIT,FITSV          ,Y,YSIG,P                     STMARQ19
C                                                                       STMARQ20
      DIMENSION P(300,20),FITSV(300)                                    STMARQ21
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS                      STMARQ22
C                                                                       STMARQ23
      LPDMA=300                                                         STMARQ24
      LPDMB=20                                                          STMARQ25
C                                                                       STMARQ26
      CALL MARQ (FUNK,Y,YSIG,NPTS,FIT,FITSV,P,LPDMA,LPDMB)              STMARQ27
C                                                                       STMARQ28
      RETURN                                                            STMARQ29
      END                                                               STMARQ30

      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
C  COPYRIGHT (C) 1981 J. P. CHANDLER                                    MARQ   4
C                                                                       MARQ   5
C  J. P. CHANDLER AND LEON W. JACKSON,                                  MARQ   6
C              DEPARTMENT OF COMPUTING AND INFORMATION SCIENCES         MARQ   7
C              OKLAHOMA STATE UNIVERSITY, STILLWATER, OKLAHOMA 74074    MARQ   8
C                                                                       MARQ   9
C  MARQ PERFORMS A NONLINEAR LEAST SQUARES FIT OF A USER-SUPPLIED       MARQ  10
C  FUNCTION TO A GIVEN SET OF DATA, USING MARQUARDT-S METHOD, OR THE    MARQ  11
C  GAUSS-NEWTON METHOD, OR A MODIFIED GAUSS-NEWTON METHOD.              MARQ  12
C                                                                       MARQ  13
C UPDATE ADDED TO WATFIV LIBRARY BY J. HANSON, UCC USER SERVICES        MARQ  13
C                                                                       MARQ  13
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * MARQ  14
C                                                                       MARQ  15
C  INPUT QUANTITIES.....  FUNK,X(*),XMAX(*),XMIN(*),DELMN(*),NF,NTRAC,  MARQ  16
C                              MASK(*),MATRX,NFMAX,NFLAT,KW,            MARQ  17
C                              Y(*),YSIG(*),NPTS,LPCOL,                 MARQ  18


C                              FLAMB,FNU,RELDF,METHD,KALCP,KORDF,       MARQ  19
C                              MAXIT,LEQU,MXSUB                         MARQ  20
C  OUTPUT QUANTITIES....  X(*),FOBJ,ERR(*,*),KFLAG,FIT(*)               MARQ  21
C  SCRATCH VECTOR.......  DELTX(*)
C  UNUSED QUANTITIES (INCLUDED FOR COMPATIBILITY WITH STEPIT COMMON)....MARQ  22
C                                 JVARY,NXTRA,NOREP,KERFL               MARQ  23
C                                                                       MARQ  24
C     FUNK        --  THE NAME OF THE SUBROUTINE CALLED TO OBTAIN       MARQ  25
C                           THE FITTED VALUES IF KALCP=0                MARQ  26
C     X(JX)       --  THE JX-TH PARAMETER                               MARQ  27
C     XMAX(JX)    --  THE UPPER LIMIT FOR X(JX)                         MARQ  28
C     XMIN(JX)    --  THE LOWER LIMIT FOR X(JX)                         MARQ  29
C     DELMN(JX)   --  THE CONVERGENCE TOLERANCE FOR X(JX)               MARQ  30
C     FOBJ        --  RETURNS THE FINAL VALUE OF PHI, THE WEIGHTED      MARQ  31
C                           SUM OF SQUARES (PHI IS BEING MINIMIZED AS A MARQ  32
C                           FUNCTION OF THE X(JX))                      MARQ  33
C     NV          --  THE NUMBER OF PARAMETERS                          MARQ  34
C     NTRAC       --  USER PRINT CONTROL                                MARQ  35
C                           =-3, NO OUTPUT EXCEPT FATAL ERROR MESSAGES  MARQ  36
C                           =-2, NO OUTPUT EXCEPT DIAGNOSTIC MESSAGES   MARQ  37
C                           =-1, STANDARD OUTPUT EXCEPT FINAL FIT VALUESMARQ  38
C                           = 0, STANDARD OUTPUT                        MARQ  39
C                           = 1, ALSO PRINTS RESULTS OF EACH ITERATION  MARQ  40
C                           = 2, ALSO PRINTS THE COEFFICIENT MATRIX, OSAVMARQ  41
C                           = 3, ALSO PRINTS THE JACOBIAN MATRIX, P     MARQ  42
C     MATRX       --  NONZERO IF STATISTICAL ERRORS ARE TO BE COMPUTED  MARQ  43
C     MASK(JX)    --  NONZERO IF X(JX) IS TO BE HELD FIXED              MARQ  44
C     NFMAX       --  THE MAXIMUM NUMBER OF FUNCTION COMPUTATIONS       MARQ  45
C     NFLAT       --  NONZERO IF THE SEARCH IS TO TERMINATE WHEN TWO    MARQ  46
C                           ITERATIONS GIVE IDENTICAL VALUES OF PHI     MARQ  47
C     KW          --  THE LOGICAL UNIT NUMBER OF THE PRINTER            MARQ  48
C     ERR(JX,KX)  --  RETURNS THE ERROR MATRIX                          MARQ  49
C     KFLAG       --  RETURNED .GT. ZERO FOR A NORMAL EXIT,             MARQ  50
C                           RETURNED .LT. ZERO FOR AN ABNORMAL EXIT     MARQ  51
C                                                                       MARQ  52
C     Y(JPT)      --  THE JPT-TH DATA ORDINATE                          MARQ  53
C     YSIG(JPT)   --  THE EXPECTED ERROR IN Y(JPT)                      MARQ  54
C     NPTS        --  THE NUMBER OF DATA OBSERVATIONS                   MARQ  55
C     FIT(JPT)    --  THE JPT-TH FITTED VALUE                           MARQ  56
C     FITSV       --  A SCRATCH VECTOR OF NPTS VALUES                   MARQ  57
C     P(JPT,JX)   --  THE FIRST PARTIAL DERIVATIVE                      MARQ  58
C                           OF FIT(JPT) WITH RESPECT TO X(JX)           MARQ  59
C     LPDMA       --  THE FIRST DIMENSION OF THE ARRAY CONTAINING P     MARQ  60
C                         (LPCOL MUST BE .GE. NPTS IF KALCP IS .GE. ZERO)MARQ  61
C     LPDMB       --  THE SECOND DIMENSION OF THE ARRAY CONTAINING P    MARQ  62
C                         (LPDMB MUST BE .GE. NV)                       MARQ  63
C     FLAMB       --  MARQUARDT-S LAMBDA, THE RELATIVE AMOUNT BY WHICH  MARQ  64
C                           THE DIAGONAL COEFFICIENTS OF THE NORMAL     MARQ  65
C                           EQUATIONS ARE AUGMENTED                     MARQ  66
C     FNU         --  MARQUARDT-S NU, THE FACTOR BY WHICH FLAMB IS      MARQ  67
C                           CHANGED                                     MARQ  68
C     RELDF       --  DETERMINES THE MAGNITUDE OF THE DIFFERENCING STEP MARQ  69
C     RELMN       --  RELATIVE CONVERGENCE CRITERION USED FOR EACH X(J) MARQ  70
C                           FOR WHICH DELMN(J) IS ZERO                  MARQ  71
C     METHD       --  DETERMINES THE METHOD USED                        MARQ  72
C                           =-1, MODIFIED GAUSS-NEWTON METHOD           MARQ  73
C                           = 0, GAUSS-NEWTON METHOD                    MARQ  74
C                           = 1, MODIFIED FORM OF MARQUARDT-S METHOD    MARQ  75
C                           = 2, MARQUARDT-S METHOD                     MARQ  76
C     KALCP       --  DETERMINES WHICH ROUTINE IS CALLED TO COMPUTE THE MARQ  77
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C                              JACOBIAN MATRIX OF FIRST PARTIAL DERIVATIVES  MARQ  78
C                              =-1, ONE ROW OF P RETURNED BY DERIV OR CALCD, MARQ  79
C                                     DERIV CALLS FOFX                       MARQ  80
C                              = 0, ALL OF P RETURNED BY DERIV OR CALCD,     MARQ  81
C                                     DERIV CALLS FUNK                       MARQ  82
C                              = 1, ALL OF P RETURNED BY DERIV OR CALCD,     MARQ  83
C                                     DERIV CALLS FOFX                       MARQ  84
C     KORDF       --  DETERMINES HOW P IS TO BE CALCULATED                   MARQ  85
C                              = 1, FIRST ORDER APPROXIMATION USED BY DERIV  MARQ  86
C                              = 2, SECOND ORDER APPROXIMATION USED BY DERIV MARQ  87
C                              = 3, ANALYTICAL DERIVATIVE SUPPLIED BY CALCD  MARQ  88
C     MAXIT       --  THE MAXIMUM NUMBER OF ITERATIONS TO BE PERFORMED       MARQ  89
C     LEQU        --  SAVES STORAGE IF ALL YSIG(JPT) ARE THE SAME            MARQ  90
C                              =1 IF ALL YSIG(JPT) ARE EQUAL (IN THIS CASE   MARQ  91
C                                   ONLY YSIG(1) IS REFERENCED)              MARQ  92
C                              =0 OTHERWISE                                  MARQ  93
C     MXSUB       --  THE MAXIMUM NUMBER OF SUBITERATIONS PERMITTED          MARQ  94
C     MXUPD       --  NOT USED AT PRESENT                                    MARQ  95
C                                                                            MARQ  96
C  MODIFICATIONS TO MARQUARDT-S METHOD...                                    MARQ  97
C    1.   THE QUANTITY (1+LAMBDA) IS NOT ALLOWED TO INCREASE BY MORE         MARQ  98
C         THAN A FACTOR OF FNULM, IN ANY SINGLE CHANGE.                      MARQ  99
C    2.   WHEN CUTSTEPS ARE USED IN A LINE SEARCH (WHEN THE ANGLE            MARQ 100
C         GAMMA .LT. GAMMA SUB ZERO), THE VALUE OF LAMBDA IS INCREASED.      MARQ 101
C  IN BOTH THE MODIFIED MARQUARDT-S METHOD AND THE MODIFIED                  MARQ 102
C  GAUSS-NEWTON METHOD, A HALF STEP IS ATTEMPTED FOLLOWING EACH              MARQ 103
C  SUCCESSFUL STEP.  THIS AVOIDS ONE FORM OF VERY SLOW CONVERGENCE.          MARQ 104
C                                                                            MARQ 105
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *  MARQ 106
C                                                                            MARQ 107
C  THE FOLLOWING EXTERNAL STATEMENT IS REQUIRED BY SOME COMPILERS            MARQ 108
C  (WATFIV, FOR EXAMPLE) AND FORBIDDEN BY OTHERS (MODCOMP II).               MARQ 109
      EXTERNAL FUNK                                                          MARQ 110
C                                                                            MARQ 111
      DOUBLE PRECISION P,Y,YSIG,H,SCALE,XMAX,XMIN,DELTX,DELMN,               MARQ 112
     *     ERR,FOBJ,FLAMB,FNU,RELDF,QSQRT,ARG,CRIT,FLDEF,RELMN,              MARQ 113
     *     RLTOL,FACCL,HUGE,RZERO,RUNIT,RTWO,DELN,FMGN,FCUT,                 MARQ 114
     *     STFAC,PTERM,SCALJ,SA,PIVOT,EM,SUM,COSIN,SB,SC,HH,                 MARQ 115
     *     FRMIN,XMX,XMN,DENOM,FRAC,UPFAC,RLFAC,RSFAC,RMSDV,                 MARQ 116
     *     SDVMX,QMAX1,QMIN1,QABS,ARGB                                       MARQ 117
      DOUBLE PRECISION X,XSAVE,XTEMP,GRAD,FIT,FITSV,                         MARQ 118
     *                 XSAV,SIG,RTERM,PHI,PHNEW,PHALF,XLIM                   MARQ 119
C                                                                            MARQ 120
C  THE DIMENSIONS OF THE VECTORS AND MATRICES (AS OPPOSED TO ARRAYS)         MARQ 121
C  ARE....                                                                   MARQ 122
C        P(NPTS,NACTV) (OR P(1,NACTV) IF KALCP.EQ.-1),                       MARQ 123
C        FITSV(NPTS) (OR FITSV(1) IF KALCP.EQ.-1)                            MARQ 124
C        X(NV),XMAX(NV),XMIN(NV),DELMN(NV),ERR(NV,NV+1),                     MARQ 125
C        XSAVE(NV),H(NV),MASKT(NV),                                          MARQ 126
C        GRAD(NACTV),SCALE(NACTV),                                           MARQ 127
C        Y(NPTS),FIT(NPTS),YSIG(NPTS) (OR YSIG(1) IF LEQU.NE.0),             MARQ 128
C  WHERE NACTV IS THE NUMBER OF ACTIVE (UNMASKED) X(J).                      MARQ 129
C                                                                            MARQ 130
      DIMENSION P(LPDMA,LPDMB)                                               MARQ 131
      DIMENSION Y(1),YSIG(1),FIT(1),FITSV(1)                                 MARQ 132
      DIMENSION XSAVE(20),H(20),GRAD(20),MASKT(20),XTEMP(20)                 MARQ 133
C                                                                            MARQ 134
C  USER COMMON.....                                                          MARQ 135
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20),            MARQ 136
     *     ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),                          MARQ 137
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     *     NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW                      MARQ 138
C                                                                            MARQ 139
C  MARQ COMMON.....                                                          MARQ 140
      COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDF,MAXIT,          MARQ 141
     *     LEQU,MXSUB,MXUPD                                                  MARQ 142
C                                                                            MARQ 143
C  SET THE LIBRARY FUNCTIONS FOR DOUBLE PRECISION (DSQRT, DABS, DMAX1,       MARQ 144
C  DMIN1) OR FOR SINGLE PRECISION (SQRT, ABS, AMAX1, AMIN1).                 MARQ 145
C                                                                            MARQ 146
      QSQRT(ARG)=DSQRT(ARG)                                                  MARQ 147
      QABS(ARG)=DABS(ARG)                                                    MARQ 148
      QMAX1(ARG,ARGB)=DMAX1(ARG,ARGB)                                        MARQ 149
      QMIN1(ARG,ARGB)=DMIN1(ARG,ARGB)                                        MARQ 150
C                                                                            MARQ 151
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *  MARQ 152
C                                                                            MARQ 153
C  SET FIXED QUANTITIES ....                                                 MARQ 154
C                                                                            MARQ 155
C  NVMAX IS THE MAXIMUM PERMISSIBLE VALUE OF NV.  IT IS ALSO THE             MARQ 156
C  DIMENSION OF THE ARRAYS X, XMAX, XMIN, MASK, DELMN,                       MARQ 157
C  XSAVE, H, MASKT, GRAD, AND SCALE, AND THE FIRST DIMENSION OF ERR.         MARQ 158
C  THE SECOND DIMENSION OF ERR IS NVMAX+1.                                   MARQ 159
C                                                                            MARQ 160
      NVMAX=20                                                               MARQ 161
C                                 CRIT ...  COSINE OF MARQUARDT-S CRITICAL   MARQ 162
C                                                ANGLE, GAMMA SUB ZERO       MARQ 163
      CRIT=.70711                                                            MARQ 164
C                                 FLDEF ...  DEFAULT VALUE FOR FLAMB         MARQ 165
      FLDEF=1.                                                               MARQ 166
C                                 RLTOL ...  TOLERANCE FOR A WARNING MESSAGE MARQ 167
      RLTOL=1.E-4                                                            MARQ 168
C                                 FACCL ...  ACCELERATION FACTOR FOR FCUT    MARQ 169
      FACCL=2.                                                               MARQ 170
C                                 FNULM ...  LIMIT ON THE FACTOR BY WHICH    MARQ 171
C                                     (1+FLAMB) MAY CHANGE                   MARQ 172
      FNULM=2.                                                               MARQ 173
C                                 HUGE ...  A VERY LARGE REAL NUMBER         MARQ 174
C                                     (DEFAULT VALUE FOR XMAX AND -XMIN)     MARQ 175
      HUGE=1.E30                                                             MARQ 176
C                                                                            MARQ 177
      RZERO=0.                                                               MARQ 178
      RUNIT=1.                                                               MARQ 179
      RTWO=2.                                                                MARQ 180
C                                                                            MARQ 181
C  NO FLOATING POINT CONSTANTS ARE USED BEYOND THIS POINT.                   MARQ 182
C                                                                            MARQ 183
      KFLAG=0                                                                MARQ 184
      NOREP=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. (KALCP.LT.0 .OR. NPTS.LE.LPDMA)) GO TO 20         MARQ 194
      KFLAG=-1                                                               MARQ 195
      GO TO 60                                                               MARQ 196
C                                                                            MARQ 197
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C  CHECK SOME INPUT QUANTITIES, AND SET THEM TO DEFAULT VALUES IF        MARO 198
C  DESIRED.                                                              MARO 199
C                             NACTV ...  NUMBER OF ACTIVE X(J)           MARO 200
   20 NACTV=0                                                            MARO 201
      DO 50 JX=1,NV                                                      MARO 202
        DELN=DABS(DELMN(JX))                                             MARO 203
        IF(MASK(JX))50,30,50                                             MARO 204
   30   NACTV=NACTV+1                                                    MARO 205
        IF(DELN.EQ.RZERO) DELN=DABS(RELMN*X(JX))                         MARO 206
        IF(DELN.EQ.RZERO) DELN=RELMN                                     MARO 207
        IF(XMAX(JX).GT.XMIN(JX)) GO TO 40                                MARO 208
        XMAX(JX)=HUGE                                                    MARO 209
        XMIN(JX)=-HUGE                                                   MARO 210
   40   X(JX)=DMAX1(XMIN(JX),DMIN1(XMAX(JX),X(JX)))                      MARO 211
   50   DELMN(JX)=DELN                                                   MARO 212
C                                                                        MARO 213
      IF(NACTV.GT.0) GO TO 80                                            MARO 214
      KFLAG=-2                                                           MARO 215
   60 CONTINUE                                                           MARO 216
      WRITE(KW,70)NV,NVMAX,NACTV,NPTS,LPDMA,LPDMB,KALCP                  MARO 217
   70 FORMAT(//29H ILLEGAL INPUT VALUE IN MARO.,4X,5H NV =,I3,4X,        MARO 218
     *   8H NVMAX =,I3,4X,8H NACTV =,I3/10X,7H NPTS =,I5,4X,8H LPDMA =, MARO 219
     *   I5,4X,8H LPDMB =,I5,4X,8H KALCP =,I3)                           MARO 220
      GO TO 1300                                                         MARO 221
   80 CONTINUE                                                           MARO 222
      IF(NTRAC.LT.-1) GO TO 150                                          MARO 223
      WRITE(KW,90)(MASK(J),J=1,NV)                                       MARO 224
   90 FORMAT(/10H MASK    =,I7,7I13/(4X,8I13))                           MARO 225
      WRITE(KW,100)(X(J),J=1,NV)                                         MARO 226
  100 FORMAT(/10H X       =,8E13.5/(10X,8E13.5))                         MARO 227
      WRITE(KW,110)(XMAX(J),J=1,NV)                                      MARO 228
  110 FORMAT(/10H XMAX    =,8E13.5/(10X,8E13.5))                         MARO 229
      WRITE(KW,120)(XMIN(J),J=1,NV)                                      MARO 230
  120 FORMAT(/10H XMIN    =,8E13.5/(10X,8E13.5))                         MARO 231
      WRITE(KW,130)(DELMN(J),J=1,NV)                                     MARO 232
  130 FORMAT(/10H DELMN   =,8E13.5/(10X,8E13.5))                         MARO 233
      WRITE(KW,140)NV,NPTS,LPDMA,LPDMB,NTRAC,METHD,KALCP,KORDF,          MARO 234
     *      NFLAT,NFMAX,MAXIT,MXSUB,CRIT,RELDF,RELMN                     MARO 235
  140 FORMAT(//5H NV =,I4,5X,7H NPTS =,I6,5X,8H LPDMA =,I6,5X,           MARO 236
     *   8H LPDMB =,I4,5X,8H NTRAC =,I2,5X,8H METHD =,I3,5X,8H KALCP =, MARO 237
     *   I3//8H KORDF =,I2,5X,8H NFLAT =,I2,5X,8H NFMAX =,I7,5X,         MARO 238
     *   8H MAXIT =,I5,5X,8H MXSUB =,I4//7H CRIT =,E12.5,5X,8H RELDF =,  MARO 239
     *   E12.5,5X,8H RELMN =,E12.5)                                      MARO 240
  150 JVARY=0                                                            MARO 241
C                                                                        MARO 242
C  SET FMGN.  IF NECESSARY, RESET FLAMB AND/OR FACCL.                    MARO 243
C                                                                        MARO 244
      FMGN=RUNIT                                                         MARO 245
      UPNU=FNU                                                           MARO 246
      DOWNU=FNU                                                          MARO 247
      IF(FLAMB.LE.RZERO) FLAMB=FLDEF                                     MARO 248
      IF(METHD.LE.0) FLAMB=RZERO                                         MARO 249
      IF(METHD.NE.1) FACCL=RUNIT                                         MARO 250
C                                                                        MARO 251
C  COMPUTE THE INITIAL GOODNESS OF FIT OF THE MODEL TO THE DATA.         MARO 252
C  CALL FUNC TO CALCULATE THE VECTOR OF FITTED VALUES.                   MARO 253
C                                                                        MARO 254
      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                               MARO 255
C                                                                        MARO 256
C                             NF ...  EQUIVALENT NUMBER OF CALLS TO FUNC MARO 257


      NF=1                                                               MARO 258
      IF(NTRAC.GE.-1) WRITE(KW,160)PHI,FLAMB                             MARO 259
  160 FORMAT(//27H PHI (THE SUM OF SQUARES) =,E15.8,57X,9H LAMBDA =,     MARO 260
     *   E12.5//1H )                                                     MARO 261
C                                                                        MARO 262
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *    MARO 263
C                                                                        MARO 264
C  BEGIN THE NEXT ITERATION.                                             MARO 26
C  THIS IS THE ENTRY POINT AFTER A SUCCESSFUL STEP IF THE CONVERGENCE    MARO 266
C  CRITERION IS NOT MET.                                                 MARO 267
C                                                                        MARO 268
  170 JSUB=0                                                             MARO 269
      FCUT=RTWO                                                          MARO 270
      ITER=ITER+1                                                        MARO 271
      IF(NTRAC.GE.1) WRITE(KW,180)ITER,FMGN,FLAMB                        MARO 272
  180 FORMAT(//16H BEGIN ITERATION,I5,44X,7H FMGN =,E12.5,15X,           MARO 273
     *   9H LAMBDA =,E12.5)                                              MARO 274
      IF(NTRAC.GE.3) WRITE(KW,190)                                       MARO 275
  190 FORMAT(/28H P (THE JACOBIAN MATRIX)..../1H )                       MARO 276
C                                                                        MARO 277
C                             INITIALIZE FOR THIS ITERATION.             MARO 278
      STFAC=RUNIT                                                        MARO 279
      DO 200 JX=1,NACTV                                                  MARO 280
        GRAD(JX)=RZERO                                                   MARO 281
        DO 200 KX=1,JX                                                   MARO 282
  200     ERR(JX,KX)=RZERO                                               MARO 283
C                                                                        MARO 284
C  CALL DERIV (OR CALCD) TO COMPUTE THE JACOBIAN MATRIX, P.              MARO 285
C  DERIV IS CALLED NPTS TIMES IF KALCP=-1.                               MARO 286
C                                                                        MARO 287
      SIG=YSIG(1)                                                        MARO 288
      DO 270 JPT=1,NPTS                                                  MARO 289
        KPT=JPT                                                          MARO 290
        IF(KALCP.LT.0) GO TO 210                                         MARO 291
        IF(JPT.NE.1) GO TO 230                                           MARO 292
  210   KPT=1                                                            MARO 293
        IF(KORDF.LE.2) GO TO 220                                         MARO 294
        CALL CALCD (JPT,P,LPDMA,LPDMB)                                   MARO 295
        GO TO 230                                                        MARO 296
  220   CALL DERIV (JPT,FUNK,NPTS,FIT,FITSV,P,LPDMA,LPDMB)               MARO 297
  230   CONTINUE                                                         MARO 298
        IF(NTRAC.GE.3) WRITE(KW,240)JPT,(P(KPT,JX),JX=1,NACTV)           MARO 299
  240   FORMAT(1X,I3,2X,6E15.7/(6X,6E15.7))                              MARO 300
C                                                                        MARO 301
C  COMPUTE QSAV AND GRAD.                                                MARO 302
C  QSAV, WHICH IS STORED IN ONE HALF OF THE ARRAY ERR(*,*), IS PT*P.     MARO 303
C  GRAD(*) IS HALF THE GRADIENT OF PHI.                                  MARO 304
C                                                                        MARO 305
        IF(LEQU.EQ.0) SIG=YSIG(JPT)                                      MARO 306
        RTERM=(FIT(JPT)-Y(JPT))/SIG**2                                   MARO 307
        DO 260 JX=1,NACTV                                                MARO 308
          GRAD(JX)=GRAD(JX)+P(KPT,JX)*RTERM                              MARO 309
          PTERM=P(KPT,JX)/SIG**2                                         MARO 310
          DO 250 KX=1,JX                                                 MARO 311
  250       ERR(JX,KX)=ERR(JX,KX)+P(KPT,KX)*PTERM                        MARO 312
  260     CONTINUE                                                       MARO 313
  270   CONTINUE                                                         MARO 314
C                             RESTORE FIT IF IT WAS DESTROYED IN DERIV.  MARO 315
      IF(KORDF.NE.2) GO TO 290                                           MARO 316
      IF(KALCP.NE.0) GO TO 280                                           MARO 317
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      CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)                              MARO 318
      NF=NF+1                                                           MARO 319
  280 NF=NF+NACTV                                                       MARO 320
  290 NF=NF+NACTV                                                       MARO 321
C                                                                       MARO 322
C  COMPUTE THE SCALE FACTORS AND STORE THEM IN DELTX(*).  SCALE GRAD.   MARO 323
C                                                                       MARO 324
      DO 300 JX=1,NACTV                                                 MARO 325
        SCALJ=DSQRT(ERR(JX,JX))                                         MARO 326
        IF(SCALJ.EQ.RZERO) SCALJ=RUNIT                                  MARO 327
        DELTX(JX)=SCALJ                                                 MARO 328
  300   GRAD(JX)=GRAD(JX)/SCALJ                                         MARO 329
      IF(NTRAC.GE.1) WRITE(KW,310)(GRAD(JX),JX=1,NACTV)                 MARO 330
  310 FORMAT(/21H   SCALED GRADIENT = ,8E15.7/(21X,8E15.7))             MARO 331
C                                                                       MARO 332
C  SCALE QSAV.  THE DIAGONAL ELEMENTS OF QSAV ARE SCALED TO UNITY.      MARO 333
C                                                                       MARO 334
      DO 355 JX=1,NACTV                                                 MARO 335
        DO 350 KX=1,JX                                                  MARO 336
          SA=ERR(JX,KX)/(DELTX(JX)*DELTX(KX))                           MARO 337
          IF(KX.NE.JX) GO TO 320                                        MARO 338
          IF(SA.EQ.RZERO) GO TO 330                                     MARO 339
          SA=RUNIT                                                      MARO 340
          GO TO 350                                                     MARO 341
  320     IF(DABS(SA).LT.RUNIT-RLTOL) GO TO 350                         MARO 342
  330     CONTINUE                                                      MARO 343
          IF(NTRAC.GE.-2) WRITE(KW,340)JX,KX,SA,ITER                    MARO 344
  340     FORMAT(38H ********  POSSIBLY DANGEROUS VALUE OF ,            MARO 345
     *      16H COEFFICIENT....,5X,6H QSAV(,I3,1H,,I3,3H) =,E15.7,9X,   MARO 346
     *      10H ITERATION,I5)                                           MARO 347
  350     ERR(JX,KX)=SA                                                 MARO 348
  355 CONTINUE
      IF(NTRAC.LT.2) GO TO 380                                          MARO 349
      WRITE(KW,360)                                                     MARO 350
  360 FORMAT(/49H QSAV (PT*P, SCALED, WHERE P IS THE JACOBIAN)..../1H ) MARO 351
      DO 370 JX=1,NACTV                                                 MARO 352
  370   WRITE(KW,240)JX,(ERR(JX,KX),KX=1,JX)                            MARO 353
  380 DO 390 JX=1,NV                                                    MARO 354
  390   XSAVE(JX)=X(JX)                                                 MARO 355
C                                     INITIALIZE MASKT AND NACT.        MARO 356
  400 NACT=NACTV                                                        MARO 357
      DO 410 JX=1,NV                                                    MARO 358
  410   MASKT(JX)=MASK(JX)                                              MARO 359
C                                                                       MARO 360
C  COPY QSAV INTO Q AND GRAD INTO H, AND SET THE DIAGONAL ELEMENTS OF Q.MARO 361
C  THIS IS THE ENTRY POINT FOR SUBITERATIONS IN WHICH FLAMB IS          MARO 362
C  INCREASED OR CONSTRAINTS ARE IMPOSED.                                MARO 363
C                                                                       MARO 364
  420 KRANK=0                                                           MARO 365
      JQ=0                                                              MARO 386
      JT=0                                                              MARO 367
      DO 450 JX=1,NV                                                    MARO 368
        IF(MASK(JX).NE.0) GO TO 450                                     MARO 369
        JQ=JQ+1                                                         MARO 370
        IF(MASKT(JX).NE.0) GO TO 450                                    MARO 371
        JT=JT+1                                                         MARO 372
        H(JT)=-GRAD(JQ)                                                 MARO 373
        KQ=0                                                            MARO 374
        KT=0                                                            MARO 375
        DO 440 KX=1,JX                                                  MARO 376
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          IF(MASK(KX).NE.0) GO TO 440                                   MARO 377
          KQ=KQ+1                                                       MARO 378
          IF(MASKT(KX).NE.0) GO TO 440                                  MARO 379
          KT=KT+1                                                       MARO 380
          SA=ERR(JQ,KQ)                                                 MARO 381
          IF(KX.NE.JX .OR. SA.EQ.RZERO) GO TO 430                       MARO 382
          SA=RUNIT+FLAMB                                                MARO 383
          KRANK=KRANK+1                                                 MARO 384
  430     ERR(KT,JT+1)=SA                                               MARO 385
  440     CONTINUE                                                      MARO 386
  450   CONTINUE                                                        MARO 387
C                                                                       MARO 388
C  SOLVE THE NORMAL EQUATIONS FOR H, THE CORRECTION VECTOR.             MARO 389
C                                                                       MARO 390
      NSMAL=0                                                           MARO 391
      NMU=NACT-1                                                        MARO 392
      IF(NMU.EQ.0) GO TO 490                                            MARO 393
C                                                                       MARO 394
C                                     REDUCE THE SYSTEM TO TRIANGULAR FORM,  MARO 395
C                                        UTILIZING THE SYMMETRY OF THE MATRIX. MARO 396
      DO 480 J=1,NMU                                                    MARO 397
        PIVOT=ERR(J,J+1)                                                MARO 398
        IF(PIVOT.EQ.RZERO) GO TO 480                                    MARO 399
        JPU=J+1                                                         MARO 400
        DO 470 K=JPU,NACT                                               MARO 401
          EM=ERR(J,K+1)/PIVOT                                           MARO 402
          IF(EM.EQ.RZERO) GO TO 470                                     MARO 40
          DO 460 L=K,NACT                                               MARO 404
  460       ERR(K,L+1)=ERR(K,L+1)-ERR(J,L+1)*EM                         MARO 405
  470     H(K)=H(K)-H(J)*EM                                             MARO 406
  480   CONTINUE                                                        MARO 407
C                                     DO THE BACK SOLUTION.             MARO 408
  490 DO 530 JINV=1,NACT                                                MARO 409
        J=(NACT+1)-JINV                                                 MARO 410
        PIVOT=ERR(J,J+1)                                                MARO 411
        IF(PIVOT.LE.RZERO) NSMAL=NSMAL+1                                MARO 412
        IF(PIVOT.NE.RZERO) GO TO 500                                    MARO 413
        H(J)=RZERO                                                      MARO 414
        GO TO 530                                                       MARO 415
  500   SUM=RZERO                                                       MARO 416
        IF(J.EQ.NACT) GO TO 520                                         MARO 417
        JPU=J+1                                                         MARO 418
        DO 510 K=JPU,NACT                                               MARO 419
  510     SUM=SUM+ERR(J,K+1)*H(K)                                       MARO 420
  520   H(J)=(H(J)-SUM)/PIVOT                                           MARO 421
  530   CONTINUE                                                        MARO 422
C                                                                       MARO 423
C   IF THE COEFFICIENT MATRIX WAS RANK DEFICIENT, PRINT A MESSAGE.      MARO 424
C                                                                       MARO 425
      MRANK=NACT-NSMAL                                                  MARO 426
      IF(MRANK.EQ.NACT) GO TO 560                                       MARO 427
      COSIN=HUGE                                                        MARO 428
      IF(NTRAC.GE.-2) WRITE(KW,540)MRANK,NACT,ITER                      MARO 429
  540 FORMAT(/41H RANK-DEFICIENT NORMAL EQUATIONS IN MARO.,9X,7H RANK =,MARO 430
     *    I4,7X,18H ORDER OF MATRIX =,I4,9X,10H ITERATION,I5)           MARO 431
      IF(MRANK.GT.0) GO TO 550                                          MARO 432
      KFLAG=-4                                                          MARO 433
      GO TO 1200                                                        MARO 434
  550 IF(METHD.GT.0 .AND. MRANK.LT.KRANK) GO TO 880                     MARO 435
C                                                                       MARO 436
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C  UNPACK AND DE-SCALE THE CORRECTION VECTOR H.                         MARQ 437
C  COMPUTE THE INNER PRODUCTS SA, SB, AND SC.                           MARQ 438
C                                                                       MARQ 439
  550 SA=RZERO                                                          MARQ 440
      SB=RZERO                                                          MARQ 441
      SC=RZERO                                                          MARQ 442
      KX=NV                                                             MARQ 443
      KQ=NACTV                                                          MARQ 444
      KT=NACT                                                           MARQ 445
      DO 590 JX=1,NV                                                    MARQ 446
        HH=RZERO                                                        MARQ 447
        IF(MASK(KX).NE.0) GO TO 580                                     MARQ 448
        IF(MASKT(KX).NE.0) GO TO 570                                    MARQ 449
        HH=H(KT)                                                        MARQ 450
        SA=SA-HH*GRAD(KQ)                                               MARQ 451
        SB=SB+HH*HH                                                     MARQ 452
        SC=SC+GRAD(KQ)**2                                               MARQ 453
        HH=HH*FMGN/DELTX(KQ)                                            MARQ 454
        KT=KT-1                                                         MARQ 455
  570   KQ=KQ-1                                                         MARQ 456
  580   H(KX)=HH                                                        MARQ 457
  590   KX=KX-1                                                         MARQ 458
C                                                                       MARQ 459
C  ADD THE CORRECTION VECTOR TO THE PARAMETER VECTOR AND                MARQ 460
C  CHECK FOR CONSTRAINT VIOLATIONS.                                     MARQ 461
C  THIS IS THE ENTRY POINT FOLLOWING A CUTSTEP.                         MARQ 462
C                                                                       MARQ 463
  600 CONTINUE                                                          MARQ 464
      IF(NTRAC.GE.1) WRITE(KW,610)(H(JX),JX=1,NV)                       MARQ 465
  610 FORMAT(/7X,14H CORRECTION = ,6E15.7/(21X,6E15.7))                 MARQ 466
      NACSV=NACT                                                        MARQ 467
      FRMIN=RUNIT                                                       MARQ 468
      NLOOP=0                                                           MARQ 469
      JXLIM=0                                                           MARQ 470
  620 DO 720 JX=1,NV                                                    MARQ 471
        IF(MASKT(JX).NE.0) GO TO 720                                    MARQ 472
        XSAV=XSAVE(JX)                                                  MARQ 473
        XMX=XMAX(JX)                                                    MARQ 474
        XMN=XMIN(JX)                                                    MARQ 475
        HH=H(JX)                                                        MARQ 476
        IF((XSAV.LT.XMX .OR. HH.LE.RZERO) .AND.                         MARQ 477
     *     (XSAV.GT.XMN .OR. HH.GE.RZERO)) GO TO 640                    MARQ 478
        MASKT(JX)=1                                                     MARQ 479
        NACT=NACT-1                                                     MARQ 480
        X(JX)=XSAV                                                      MARQ 481
        IF(NTRAC.GE.-1) WRITE(KW,630)JX,XSAV,ITER                       MARQ 482
  630   FORMAT(/8H FIX  X(,I3,4H) = ,E12.5,22H TEMPORARILY, TO AVOID,   MARQ 483
     *   24H VIOLATING A CONSTRAINT.,26X,10H ITERATION,I5)              MARQ 484
        GO TO 720                                                       MARQ 485
  640   XLIM=XSAV+HH*FRMIN                                              MARQ 486
        IF(JX.NE.JXLIM) GO TO 650                                       MARQ 487
        IF(KBND)680,650,660                                             MARQ 488
  650   X(JX)=XLIM                                                      MARQ 489
        IF(XLIM.LE.XMX) GO TO 670                                       MARQ 490
  660   X(JX)=XMX                                                       MARQ 491
        JBND=1                                                          MARQ 492
        GO TO 690                                                       MARQ 493
  670   IF(XLIM.GE.XMN) GO TO 720                                       MARQ 494
  680   X(JX)=XMN                                                       MARQ 495
        JBND=-1                                                         MARQ 496

  690   IF(JX.NE.JXLIM) GO TO 710                                       MARQ 497
        IF(NTRAC.LT.-1) GO TO 720                                       MARQ 498
        WRITE(KW,700)JX,X(JX),FRMIN,ITER                                MARQ 499
  700   FORMAT(/28H CONSTRAINT VIOLATED BY X(,I3,                       MARQ 500
     *   20H).   VALUE RESET TO ,E15.8,24H USING CUTSTEP FACTOR = ,E12.5MARQ 501
     *   ,3X,5H ITER.,I5)                                               MARQ 502
        GO TO 720                                                       MARQ 503
  710   IF(NLOOP.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=JBND                                                       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
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(/33X,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
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      IF(JSUB.GT.MXSUB) GO TO 810                                       MARQ 557
      IF(METHD)880,1080,850                                             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 860                                      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*RTWO,FNU)                                         MARQ 581
      IF(METHD.EQ.1) UPFAC=DMIN1(UPFAC,FNULM+RUNIT/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) =,E12.5,28X,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
      FMGN=FMGN/FCUT                                                    MARQ 596
      GO TO 900                                                         MARQ 597
  890 IF(METHD.EQ.1) FLAMB=FLAMB*RTWO                                   MARQ 598
  900 DO 910 JX=1,NV                                                    MARQ 599
  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) =,E12.5,5X,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 1090                         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)=DMAX1(XMIN(JX),DMIN1(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 1080                                     MARQ 657
      IF(NTRAC.LT.1) GO TO 1080                                         MARQ 658
      WRITE(KW,1050)RSFAC,PHI                                           MARQ 659
 1050 FORMAT(/25H QUADRATIC INTERPOLATION.,22X,8H RSFAC =,E12.5,12X,    MARQ 660
     *    8H 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,8H 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,I5,38X,6H PHI =,E15.8)
      PHI=PHNEW
      IF(JXLIM.GT.0) GO TO 1130
      DO 1110 JX=1,NV
        IF(MASK(JX).NE.0) GO TO 1110
        IF(DABS(X(JX)-XSAVE(JX)).GT.DELMN(JX)) GO TO 1130
 1110   CONTINUE
      KFLAG=1
      IF(NTRAC.LT.-1) GO TO 1200
      WRITE(KW,1120)
 1120 FORMAT(//38H CONVERGED WHEN THE STEP BECAME SMALL.)
      GO TO 1200
C
C  THE ITERATION HAS NOT YET CONVERGED.
C
 1130 IF(ITER.LT.MAXIT) GO TO 1150
      KFLAG=-6
      WRITE(KW,1140)MAXIT
 1140 FORMAT(//46H MAXIMUM NUMBER OF ITERATIONS REACHED IN MARQ.,5X,
     *   8H MAXIT =,I5)
      GO TO 1200
C
C  IF SUBITERATIONS WERE NOT PERFORMED THIS ITERATION, DECREASE LAMBDA.
C
 1150 IF(NF.GE.NFMAX) GO TO 1180
      IF(JSUB.GT.0) GO TO 1160
      FMGN=DMIN1(FMGN*RTWO,RUNIT)
      SCALJ=RUNIT+FLAMB
      IF(SCALJ.GT.RUNIT) FLAMB=FLAMB/DOWNU
      UPNU=DOWNU
      DOWNU=DMIN1(DOWNU*RTWO,FNU)
      GO TO 1170
 1160 IF(METHD.NE.1) GO TO 1170
      UPNU=FNULM
      DOWNU=FNULM
 1170 CONTINUE
C                                GO BACK AND DO ANOTHER ITERATION.
      GO TO 170
 1180 KFLAG=-7
      WRITE(KW,1190)NFMAX
 1190 FORMAT(//23H NF HAS REACHED NFMAX =,I7,9H IN MARQ.)
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C  THE ITERATION HAS TERMINATED.
C  PRINT OUT THE DATA, FITTED VALUES, AND RESIDUALS.
C  COMPUTE AND PRINT THE STANDARD DEVIATION OF THE DATA FROM THE FIT.
C
 1200 CONTINUE
      SC=DSQRT(SC)
      IF(NTRAC.LT.-1) GO TO 1290
      WRITE(KW,1210)ITER,NF,PHI,FMGN,FLAMB,SC
 1210 FORMAT(/1X,I4,11H ITERATIONS,7X,5H NF =,I5,9X,6H PHI =,E15.8,10X,
     *    7H FMGN =,E12.5,7X,9H LAMBDA =,E12.5//8X,15H NORM OF SCALED,
     *    18H GRADIENT VECTOR =,E12.5)
      WRITE(KW,780)(X(JX),JX=1,NV)
      IF(NTRAC.GE.0) WRITE(KW,1220)
 1220 FORMAT(///14X,1HJ,9X,5H Y(J),14X,7H FIT(J),10X,
     *    12H Y(J)-FIT(J),7X,8H YSIG(J),11X,13H (Y-FIT)/YSIG/1H )
      SIG=YSIG(1)

      RMSDV=RZERO
      SDVMX=RZERO
      DO 1240 JPT=1,NPTS
        IF(LEQU.EQ.0) SIG=YSIG(JPT)
        YY=Y(JPT)
        PTERM=YY-FIT(JPT)
        RTERM=PTERM/SIG
        IF(NTRAC.GE.0) WRITE(KW,1230)JPT,YY,FIT(JPT),PTERM,SIG,RTERM
 1230   FORMAT(5X,I10,5X,E15.8,5X,E15.8,5X,E12.5,5X,E12.5,10X,E12.5)
        RMSDV=RMSDV+RTERM**2
 1240   SDVMX=DMAX1(SDVMX,DABS(RTERM))
      DENOM=NPTS-NACTV
      WRITE(KW,1250)DENOM
 1250 FORMAT(//32H NUMBER OF DEGREES OF FREEDOM = ,E12.5 )
      IF(DENOM.LE.RZERO) GO TO 1270
      RMSDV=DSQRT(RMSDV/DENOM)
      WRITE(KW,1260)RMSDV
 1260 FORMAT(/43H R.M.S. SCALED DEVIATION OF DATA FROM FIT =,E12.5)
 1270 CONTINUE
      WRITE(KW,1280)SDVMX
 1280 FORMAT(/27H MAXIMUM SCALED DEVIATION =,E12.5)
C
C  CALL FUNC TO SET THE FINAL VALUES.
C
 1290 CALL FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)
      FOBJ=PHI
C
C  CALL MQERR TO PRINT THE PARAMETER ERRORS AND CORRELATIONS.
C  A DUMMY ROUTINE MAY BE SUBSTITUTED FOR MQERR IF THESE ARE NOT NEEDED.
C
      IF(MATRX.EQ.0) RETURN
      CALL MQERR (NACTV,NPTS)
C
 1300 RETURN
C  END MARQ
      END

      SUBROUTINE FUNC (FUNK,Y,YSIG,NPTS,FIT,PHI)
C
C   UPDATED BY J. CHANDLER, OSU DEPARTMENT OF COMPUTING AND
C   INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES, MAY 1981
C
C  FUNC CALLS FUNK OR FOFX TO COMPUTE THE ARRAY OF FITTED VALUES FITM.
C
      DOUBLE PRECISION Y,YSIG,XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,
     *      FLAMB,FNU,RELDF,RELMN
      DOUBLE PRECISION X,FIT,F,PHI,SIG
C
      DIMENSION Y(1),YSIG(1),FIT(1)
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
      IF(KALCP.NE.0) GO TO 10
C
      CALL FUNK (FIT)
```

```
      GO TO 30
C
   10 DO 20 JPT=1,NPTS
        CALL FOFX(JPT,NV,X,F)
   20   FIT(JPT)=F
C
   30 PHI=RZERO
      SIG=YSIG(1)
      DO 50 JPT=1,NPTS
        IF(LEQU.EQ.0) SIG=YSIG(JPT)
C
C                            CHECK FOR AN ILLEGAL VALUE OF SIG.
        IF(SIG.GT.RZERO) GO TO 50
        WRITE(KW,40)LEQU,JPT,SIG
   40   FORMAT(/28H ERROR IN MARQ....   LEQU = ,I1,5X,8H JPT =,I5,5X,
     *   7H YSIG =,E13.5,14H IS .LE. ZERO.)
        STOP
C
   50   PHI=PHI+((FIT(JPT)-Y(JPT))/SIG)**2
C
      RETURN
C  END FUNC.
      END

      SUBROUTINE CALCD (JPT,P,LPDMA,LPDMB)
C
C  UPDATE BY J. CHANDLER, MAY 1981, OSU COMPUTER SCIENCE
C  DEPARTMENT--J. HANSON, UCC USER SERVICES
C
C  THIS IS A DUMMY VERSION OF SUBROUTINE CALCD.
C  A NON-DUMMY VERSION OF CALCD MAY BE USED (OPTIONALLY) TO SUPPLY
C  TO MARQ ANALYTIC VALUES OF THE ELEMENTS OF THE JACOBIAN MATRIX,
C  INSTEAD OF APPROXIMATING THEM BY FINITE DIFFERENCES.
C  HOWEVER, MOST USERS PREFER TO USE FINITE DIFFERENCES.
C
      DOUBLE PRECISION P
      DIMENSION P(LPDMA,LPDMB)
      RETURN
      END

      SUBROUTINE DERIV (JPT,FUNK,NPTS,FIT,FITSV,P,LPDMA,LPDMB)
C
C  UPDATED BY J. CHANDLER, OSU DEPARTMENT OF COMPUTING AND
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
        CALL FUNK (FIT)
        JVARY=0
        DO 70 J=1,NPTS
   70     P(J,KX)=(FITSV(J)-FIT(J))/TWODL
        GO TO 140
C
C  KALCP.GT.0 .  COMPUTE P, ONE ELEMENT AT A TIME.
C
   80   DO 100 J=1,NPTS
          CALL FOFX (J,NV,X,FX1)
          IF(KORDF.EQ.2) GO TO 90
          P(J,KX)=(FX1-FITSV(J))/DEL
          GO TO 100
   90     X(JX)=XSAVE-DEL
          CALL FOFX (J,NV,X,FX0)
          P(J,KX)=(FX1-FX0)/TWODL
          X(JX)=XSAVE+DEL
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  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,FXO)                                        DERIV 89
        P(1,KX)=(FX1-FXO)/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 MOERR (NACTV,NPTS)                                     MOERR  1
C                                                                       MOERR  2
C  UPDATED BY J. CHANDLER, OSU DEPARTMENT OF COMPUTING AND              MOERR  2
C  INFORMATION SCIENCES--J. HANSON, UCC USER SERVICES                   MOERR  2
C                                                                       MOERR  2
C  MOERR 3.0         A.N.S.I. STANDARD FORTRAN         MAY 1981         MOERR  3
C                                                                       MOERR  4
C  MOERR IS CALLED BY MARQ TO COMPUTE AND PRINT APPROXIMATE VALUES OF   MOERR  5
C  THE PARAMETER ERRORS AND CORRELATIONS                                MOERR  6
C                                                                       MOERR  7
C  FOR THE MEANING OF THE -MAXIMUM VARIANCE INFLATION FACTOR- BELOW,    MOERR  8
C  SEE...       D. W. MARQUARDT AND R. D. SNEE,                         MOERR  9
C               RIDGE REGRESSION IN PRACTICE,                           MOERR 10
C               THE AMERICAN STATISTICIAN 29 (1975) 3-20                MOERR 11
C                                                                       MOERR 12
C  INPUT QUANTITIES.....  KW,ERR(*,*),NACTV,DELTX(*),NPTS,NV,NTRAC,     MOERR 13
C                         MASK(*),FOBJ                                  MOERR 14
C  OUTPUT QUANTITIES....  ERR(*,*)                                      MOERR 15
C                                                                       MOERR 16
      DOUBLE PRECISION H,SCALE,XMAX,XMIN,DELTX,DELMN,ERR,FOBJ,          MOERR 17
     *     QSQRT,ARG,RZERO,RUNIT,HUGE,PIVOT,Q,VIFMX,ER,TEMP,            MOERR 18
     *     DENOM,SCFAC,RESCL          ,X                                MOERR 19
C                                                                       MOERR 20
      COMMON /CSTEP/ X(20),XMAX(20),XMIN(20),DELTX(20),DELMN(20),       MOERR 21
     *     ERR(20,21),FOBJ,NV,NTRAC,MATRX,MASK(20),                     MOERR 22
     *     NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW                 MOERR 23
C                                                                       MOERR 24
      QSQRT(ARG)=DSQRT(ARG)                                             MOERR 25
C                                                                       MOERR 26
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * MOERR 27
C                                                                       MOERR 28
      RZERO=0.                                                          MOERR 29
      RUNIT=1.                                                          MOERR 30
      HUGE=1.E30                                                        MOERR 31


C                                     PRINT OSAV.                       MOERR 32
      IF(NTRAC.LT.-1) GO TO 40                                          MOERR 33
      WRITE(KW,10)                                                      MOERR 34
   10 FORMAT(///18H SUBROUTINE MOERR.//28H OSAV (PT*P, SCALED, WHERE,   MOERR 35
     *     23H P IS THE JACOBIAN)....)                                  MOERR 36
      DO 30 JX=1,NACTV                                                  MOERR 37
        WRITE(KW,20)JX,(ERR(JX,KX),KX=1,JX)                             MOERR 38
   20   FORMAT(/1X,I3,2X,8E15.7/(6X,8E15.7))                            MOERR 39
   30   CONTINUE                                                        MOERR 40
C                                                                       MOERR 41
C  COMPUTE THE SCALED ERROR MATRIX, WHICH IS THE INVERSE OF OSAV.       MOERR 42
C  INVERT OSAV USING THE GAUSS-JORDAN METHOD WITHOUT PIVOTING.          MOERR 43
C  F. L. BAUER AND C. REINSCH, P. 45 IN -LINEAR ALGEBRA-                MOERR 44
C  BY J. H. WILKINSON AND C. REINSCH (SPRINGER-VERLAG, 1971)            MOERR 45
C  ERR(*,NV+1) IS USED AS A SCRATCH VECTOR.                             MOERR 46
C                                                                       MOERR 47
   40 NVPLU=NV+1                                                        MOERR 48
      NSMAL=0                                                           MOERR 49
      DO 130 LINV=1,NACTV                                               MOERR 50
        L=(NACTV+1)-LINV                                                MOERR 51
        PIVOT=ERR(1,1)                                                  MOERR 52
        IF(PIVOT.LE.RZERO) NSMAL=NSMAL+1                                MOERR 53
        IF(NACTV.LT.2) GO TO 90                                         MOERR 54
        DO 80 K=2,NACTV                                                 MOERR 55
          Q=ERR(K,1)                                                    MOERR 56
          IF(PIVOT.NE.RZERO) GO TO 50                                   MOERR 57
          ERR(K,NVPLU)=RZERO                                            MOERR 58
          GO TO 70                                                      MOERR 59
   50     IF(K.GT.L) GO TO 60                                           MOERR 60
          ERR(K,NVPLU)=-Q/PIVOT                                         MOERR 61
          GO TO 70                                                      MOERR 62
   60     ERR(K,NVPLU)=Q/PIVOT                                          MOERR 63
   70     DO 80 M=2,K                                                   MOERR 64
   80       ERR(K-1,M-1)=ERR(K,M)+Q*ERR(M,NVPLU)                        MOERR 65
   90   IF(PIVOT.NE.RZERO) GO TO 100                                    MOERR 66
        ERR(NACTV,NACTV)=RZERO                                          MOERR 67
        GO TO 110                                                       MOERR 68
  100   ERR(NACTV,NACTV)=RUNIT/PIVOT                                    MOERR 69
  110   IF(NACTV.LT.2) GO TO 130                                        MOERR 70
        DO 120 K=2,NACTV                                                MOERR 71
  120     ERR(NACTV,K-1)=ERR(K,NVPLU)                                   MOERR 72
  130   CONTINUE                                                        MOERR 73
C                                                                       MOERR 74
      NRANK=NACTV-NSMAL                                                 MOERR 75
      IF(NRANK.LT.NACTV) WRITE(KW,140)NRANK,NACTV                       MOERR 76
  140 FORMAT(//51H THE SECOND DERIVATIVE MATRIX IS SINGULAR IN MOERR.,  MOERR 77
     *   9X,7H RANK =,I3,7X,8H ORDER =,I3//24H THEREFORE ALL PARAMETER, MOERR 78
     *   21H ERRORS ARE INFINITE.)                                      MOERR 79
C                                                                       MOERR 80
C                                  UNPACK THE ERROR MATRIX INTO THE UPPER MOERR 81
C                                      TRIANGLE OF ERR(*,*), DE-SCALING IT MOERR 82
      JV=0                                                              MOERR 83
      VIFMX=RZERO                                                       MOERR 84
      DO 180 JX=1,NV                                                    MOERR 85
        IF(MASK(JX).EQ.0) JV=JV+1                                       MOERR 86
        KV=0                                                            MOERR 87
        DO 180 KX=1,JX                                                  MOERR 88
          ER=RZERO                                                      MOERR 89
          IF(MASK(JX).NE.0 .OR. MASK(KX).NE.0) GO TO 180                MOERR 90
          KV=KV+1                                                       MOERR 91
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```
                TEMP=RZERO                                                  MOERR 92
                DENOM=DELTX(JV)*DELTX(KV)                                   MOERR 93
                IF(DENOM.EQ.RZERO) GO TO 150                                MOERR 94
                TEMP=ERR(JV,KV)                                             MOERR 95
                ER=TEMP/DENOM                                               MOERR 96
      150       IF(JX.NE.KX) GO TO 180                                      MOERR 97
                IF(TEMP.GT.RZERO) GO TO 170                                 MOERR 98
                IF(NTRAC.GE.-2) WRITE(KW,160)JX,KX,TEMP                     MOERR 99
      160       FORMAT(/6H THE (,I3,1H,,I3,23H) ELEMENT OF OSAV**-1 =,E13.5, MOERR100
         *       5X,45H THEREFORE ALL PARAMETER ERRORS ARE INFINITE.)       MOERR101
                TEMP=-TEMP                                                  MOERR102
      170       IF(TEMP.GT.VIFMX) VIFMX=TEMP                                MOERR103
      180       ERR(KX,JX+1)=ER                                             MOERR104
      190     CONTINUE                                                      MOERR105
    C                               COMPUTE AND PRINT THE STANDARD ERRORS.  MOERR106
            NDF=NPTS-NACTV                                                  MOERR107
            SCFAC=HUGE                                                      MOERR108
            IF(NDF.LE.0) GO TO 200                                          MOERR109
            SCFAC=NDF                                                       MOERR110
            SCFAC=DSQRT(FOBJ/SCFAC)                                         MOERR111
      200 RESCL=NDF+NDF                                                     MOERR112
            IF(RESCL.GT.RZERO) RESCL=DSQRT(RESCL)                           MOERR113
            IF(NTRAC.LT.-1) GO TO 340                                       MOERR114
            WRITE(KW,210)NDF,NDF,RESCL,FOBJ,SCFAC                           MOERR115
      210 FORMAT(///41H NUMBER OF DEGREES OF FREEDOM (N.D.F.) = ,           MOERR116
         *    14H(NPTS-NACTV) =,I5//24H EXPECTED VALUE OF PHI = ,           MOERR117
         *    38H N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =,I5,                 MOERR118
         *    15H  PLUS OR MINUS,E12.5//22H ACTUAL VALUE OF PHI =,E12.5//   MOERR119
         *    38H RESCALING FACTOR = SQRT(PHI/N.D.F.) =,E12.5)              MOERR120
            WRITE(KW,220)VIFMX                                              MOERR121
      220 FORMAT(///36H MAXIMUM VARIANCE INFLATION FACTOR =,E12.5///        MOERR122
         *    32H APPROXIMATE STANDARD ERRORS..../68X,9H RESCALED/12X,1HJ,  MOERR123
         *    8X,7HMASK(J),9X,4HX(J),14X,5HERROR,12X,5HERROR)               MOERR124
            RESCL=HUGE                                                      MOERR125
            DO 270 JX=1,NV                                                  MOERR126
              SCALJ=RUNIT                                                   MOERR127
              ER=ERR(JX,JX+1)                                               MOERR128
              IF(ER)230,250,240                                             MOERR129
      230     ER=-DSQRT(-ER)                                                MOERR130
              SCALJ=-ER                                                     MOERR131
              GO TO 250                                                     MOERR132
      240     ER=DSQRT(ER)                                                  MOERR133
              SCALJ=ER                                                      MOERR134
      250     IF(NDF.GT.0 .AND. NRANK.EQ.NACTV) RESCL=SCFAC*ER              MOERR135
              DELTX(JX)=SCALJ                                               MOERR136
              WRITE(KW,260)JX,MASK(JX),X(JX),ER,RESCL                       MOERR137
      260     FORMAT(/10X,I3,I10,8X,E16.8,4X,E13.5,4X,E13.5)                MOERR138
      270     CONTINUE                                                      MOERR139
    C                               COMPUTE AND PRINT THE CORRELATIONS.     MOERR140
            IF(NV.LT.2) GO TO 340                                           MOERR141
            WRITE(KW,280)(K,K=1,NV)                                         MOERR142
      280 FORMAT(///45H LOWER TRIANGLE OF THE CORRELATION MATRIX....//12X,  MOERR143
         *    7H K ....,I5,7I13/(11X,8I13))                                 MOERR144
            WRITE(KW,290)(MASK(K),K=1,NV)                                   MOERR145
      290 FORMAT(/7X,12H MASK(K)....,I6,7I13/(11X,8I13))                    MOERR146
            WRITE(KW,300)                                                   MOERR147
      300 FORMAT(/3X,1HJ,4X,7HMASK(J) )                                     MOERR148
            DO 330 JX=1,NV                                                  MOERR149
              DO 310 KX=1,JX                                                MOERR150
      310       ERR(KX,1)=ERR(KX,JX+1)/(DELTX(JX)*DELTX(KX))                MOERR151


              WRITE(KW,320)JX,MASK(JX),(ERR(KX,1),KX=1,JX)                  MOERR152
      320     FORMAT(/1X,I3,I8,5X,8E13.5/(17X,8E13.5))                      MOERR153
      330     CONTINUE                                                      MOERR154
    C                               RESCALE ERR AND SYMMETRIZE IT.          MOERR155
      340 SCFAC=SCFAC**2                                                    MOERR156
            IF(SCFAC.LT.RUNIT) SCFAC=RUNIT                                  MOERR157
            DO 350 JX=1,NV                                                  MOERR158
              DO 350 KX=1,JX                                                MOERR159
                ERR(JX,KX)=ERR(KX,JX+1)*SCFAC                               MOERR160
      350       ERR(KX,JX)=ERR(JX,KX)                                       MOERR161
    C                                                                       MOERR162
            RETURN                                                          MOERR163
    C  END MOERR.                                                           MOERR164
            END                                                             MOERR165

            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, P,   FOFXDUM8
    C  BE STORED.                                                           FOFXDUM9
    C                                                                       FOFXDU10
            DOUBLE PRECISION X,F                                            FOFXDU11
            DIMENSION X(20)                                                 FOFXDU12
            RETURN                                                          FOFXDU13
            END                                                             FOFXDU14
***ERROR***  WRONG NUMBER OF ARGUMENTS IN REFERENCE TO SUBPROGRAM STEPT

        PROGRAM WAS EXECUTING LINE      1 IN ROUTINE M/PROG WHEN TERMINATION OCCURRED

STATEMENTS EXECUTED=        1

CORE USAGE        OBJECT CODE=   37992 BYTES,ARRAY AREA=   62864 BYTES,TOTAL AREA AVAILABLE=  129024  BYTES

DIAGNOSTICS         NUMBER OF ERRORS=        1, NUMBER OF WARNINGS=        0, NUMBER OF EXTENSIONS=        9

COMPILE TIME=     0.33 SEC,EXECUTION TIME=     0.01 SEC,      14.21.51     FRIDAY        22 JUL 83    WATFIV - MAR 1980 V2L0

        CSSTOP
```

APPENDIX E

LISTING OF GLOBAL MODEL PROGRAM AND DATA FIT CALCULATION RESULTS

```
$JOB
C
C
C      ******************************
C      *                            *
C      *  2-ND ORDER GLOBAL MODEL   *
C      *                            *
C      *  DATA FROM HECK AND STEIN  *
C      *                            *
C      *  HYDRODESULFURIZATION      *
C      *                            *
C      *  SRC RECYCLE SOLVENT       *
C      *                            *
C      *  HDS-9A CATALYST           *
C      *                            *
C      ******************************
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL EXFIT
      DOUBLE PRECISION X,FIT
      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,METHO,KALCP,KORDF,
     *MAXIT,LEQU,MXSUE,MXUPD
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
      COMMON /CSTOR/ T(70),P(70),ALHSV(70),C1(70),X1(70)
      KR=5
      KW=6
      FL=1.
      CALL STSET
      MAXIT=200
      NV=3
      XMIN(1)=0.0
      X(1)=1.0E10
      X(2)=6.0E04
      X(3)=1.5
      NTRAC=0
      WRITE(KW,50)
   50 FORMAT(/////10X,'TEMPERATURE',5X,'PRESSURE',9X,'LHSV',9X,'IN. CONC
     *.',5X,'FIN. CONC.',//14X,'(R)',10X,'(PSI)',10X,'(1/HR)',10X,'(WT%)
     *',10X,'(WT%)')
      READ(KR,100)NPTS
  100 FORMAT(I5)
      DO 110 K=1,NPTS
      READ(KR,120)T(K),P(K),ALHSV(K),C1(K),Y(K)
  120 FORMAT(7X,5F10.5)
  110 T(K)=T(K)+460.
      WRITE(KW,125)NPTS,(K,T(K),P(K),ALHSV(K),C1(K),Y(K),K=1,NPTS)
  125 FORMAT(//1X,I5//(1X,I5,5E16.5))
      CALL STEPT (EXFIT)
      DEV=0.0
      PE=0.0
      SOS=0.0
      DO 130 L=1,NPTS
      DEV=DEV+DABS(FIT(L)-Y(L))/NPTS
      PE=PE+DABS(FIT(L)-Y(L))/NPTS/Y(L)*100.
  130 SOS=SOS+(FIT(L)-Y(L))**2
      WRITE(KW,135)


  135 FORMAT(1H1,/////5X,'2-ND ORDER GLOBAL MODEL PARAMETERS',/)
      WRITE(KW,140)X(1),X(2),X(3)
  140 FORMAT(//5X,'A = ',E10.4,3X,'PSI**(-M)/WT%/HR',//5X,'E = ',E10.4,3
     *X,'BTU/LBMOLE',//5X,'M = ',E10.4)
      WRITE(KW,150)DEV,PE,FOBJ,SOS
  150 FORMAT(////5X,'MEAN DEVIATION = ',E10.4,//5X,'AVG. PERCENT ERROR =
     * ',E10.4,//5X,'FOBJ = ',E10.4,//5X,'SUM OF SQUARES = ',E10.4,////)
      STOP
      END

      SUBROUTINE EXFIT (FITM)
      IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION X,FIT,QEXP,DEXP,ARG,FITM,FF
      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(70),P(70),ALHSV(70),C1(70),X1(70)
      QEXP(ARG)=DEXP(ARG)
      FOBJ=0.
      R=1.987
      DO 200 J=1,NPTS
      YSIG(J)=1.0
      FF=1./(X(1)*QEXP(-X(2)/(R*T(J)))*P(J)**X(3)/ALHSV(J)+1./C1(J))
      FITM(J)=FF
  200 FOBJ=FOBJ+((FF-Y(J))/YSIG(J))**2
      RETURN
      END

$ENTRY
```

```
          TEMPERATURE     PRESSURE         LHSV          IN. CONC.      FIN. CONC.

              (R)           (PSI)         (1/HR)          (WT%)           (WT%)


   18

    1   0.118800D 04    0.250000D 04    0.193000D 01    0.410000D 00    0.200000D-01
    2   0.113300D 04    0.250000D 04    0.211000D 01    0.410000D 00    0.300000D-01
    3   0.125800D 04    0.250000D 04    0.204000D 01    0.410000D 00    0.100000D-01
    4   0.118900D 04    0.250000D 04    0.450000D 00    0.410000D 00    0.100000D-01
    5   0.113300D 04    0.250000D 04    0.510000D 00    0.410000D 00    0.200000D-01
    6   0.118800D 04    0.250000D 04    0.530000D 00    0.410000D 00    0.100000D-01
    7   0.118100D 04    0.180000D 04    0.480000D 00    0.410000D 00    0.100000D-01
    8   0.118800D 04    0.120000D 04    0.490000D 00    0.410000D 00    0.100000D-01
    9   0.123400D 04    0.120000D 04    0.500000D 00    0.410000D 00    0.100000D-01
   10   0.113600D 04    0.120000D 04    0.510000D 00    0.410000D 00    0.300000D-01
   11   0.113000D 04    0.120000D 04    0.102000D 01    0.410000D 00    0.500000D-01
   12   0.119100D 04    0.120000D 04    0.990000D 00    0.410000D 00    0.200000D-01
   13   0.123400D 04    0.120000D 04    0.105000D 01    0.410000D 00    0.100000D-01
   14   0.123300D 04    0.180000D 04    0.102000D 01    0.410000D 00    0.200000D-01
   15   0.124100D 04    0.250000D 04    0.970000D 00    0.410000D 00    0.100000D-01
   16   0.119300D 04    0.250000D 04    0.105000D 01    0.410000D 00    0.100000D-01
   17   0.115900D 04    0.250000D 04    0.202000D 01    0.410000D 00    0.200000D-01
```

```
 18     0.12390D 04     0.25000D 04     0.18500D 01     0.41000D 00     0.20000D-01
```

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

MASK    :        0              0              0

X       :    0.10000D 11   0.80000D 05   0.15000D 01

XMAX    :    0.10000D 31   0.10000D 31   0.10000D 31

XMIN    :    0.00000D 00  -0.10000D 31  -0.10000D 31

DELMN   :    0.10000D 03   0.80000D-03   0.15000D-07

NY :    2       NPTS :     18       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) : 0.73886055D-02                                                 LAMBDA : 0.10000D 01


CONSTRAINT VIOLATED BY X(   1).    VALUE RESET TO  0.000000000D 00 USING CUTSTEP FACTOR :  0.68129D-01     ITER.    1

CONSTRAINT VIOLATED BY X(   1).    VALUE RESET TO  0.000000000D 00 USING CUTSTEP FACTOR :  0.49731D 00     ITER.    2

CONVERGED WHEN THE STEP BECAME SMALL.
 114 ITERATIONS         NF :  831          PHI : 0.57890530D-03            FMGN : 0.10000D 01         LAMBDA : 0.12714D-02
         NORM OF SCALED GRADIENT VECTOR : 0.34752D-10
               X :    0.4484035D 03   0.2896095D 05   0.1373746D 01

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

          1      0.19999990E-01     0.18866652D-01      0.11334D-02      0.10000D 01           0.11334D-02
          2      0.29999990E-01     0.35797389D-01     -0.57974D-02      0.10000D 01          -0.57974D-02
          3      0.99999970E-02     0.10296628D-01     -0.29663D-03      0.10000D 01          -0.29663D-03
          4      0.99999970E-02     0.45135459D-02      0.54865D-02      0.10000D 01           0.54865D-02
          5      0.19999990E-01     0.92659199D-02      0.10734D-01      0.10000D 01           0.10734D-01
          6      0.99999970E-02     0.53598801D-02      0.46401D-02      0.10000D 01           0.46401D-02
          7      0.99999970E-02     0.78085638D-02      0.21914D-02      0.10000D 01           0.21914D-02
          8      0.99999970E-02     0.13584259D-01     -0.35843D-02      0.10000D 01          -0.35843D-02
          9      0.99999970E-02     0.87000503D-02      0.12999D-02      0.10000D 01           0.12999D-02
         10      0.29999990E-01     0.23666501D-01      0.63335D-02      0.10000D 01           0.63335D-02
         11      0.49999990E-01     0.47538945D-01      0.24611D-02      0.10000D 01           0.24611D-02
         12      0.19999990E-01     0.25295595D-01     -0.52956D-02      0.10000D 01          -0.52956D-02
         13      0.99999970E-02     0.17853379D-01     -0.78534D-02      0.10000D 01          -0.78534D-02
         14      0.19999990E-01     0.10227084D-01      0.97729D-02      0.10000D 01           0.97729D-02
         15      0.99999970E-02     0.58025690D-02      0.41974D-02      0.10000D 01           0.41974D-02
         16      0.99999970E-02     0.99714730D-02      0.28525D-04      0.10000D 01           0.28525D-04
         17      0.19999990E-01     0.26329388D-01     -0.63294D-02      0.10000D 01          -0.63294D-02
         18      0.19999990E-01     0.11714340D-01      0.82857D-02      0.10000D 01           0.82857D-02
```

```
NUMBER OF DEGREES OF FREEDOM =  0.15000D 02

R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.62124D-02

MAXIMUM SCALED DEVIATION = 0.10734D-01


SUBROUTINE MOERR.

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

  1    0.1000000D 01

  2   -0.9995185D 00  0.1000000D 01

  3    0.9988310D 00 -0.9981991D 00  0.1000000D 01


NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    15

EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =    15  PLUS OR MINUS 0.54772D 01

ACTUAL VALUE OF PHI = 0.57891D-03

RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.62124D-02


MAXIMUM VARIANCE INFLATION FACTOR = 0.16159D 04


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

          1          0       0.44640348D 03      0.23152D 06       0.14383D 04

          2          0       0.28980953D 05      0.96143D 06       0.59727D 04

          3          0       0.13737458D 01      0.36188D 02       0.22481D 00


LOWER TRIANGLE OF THE CORRELATION MATRIX....

           K ....     1             2             3

      MASK(K)....     0             0             0

  J   MASK(J)

  1      0        0.10000D 01

  2      0        0.85741D 00  0.10000D 01

  3      0       -0.58773D 00 -0.10066D 00  0.10000D 01





    2-ND ORDER GLOBAL MODEL PARAMETERS


    A = 0.4464D 03   PSI**(-M)/WT%/HR

    E = 0.2898D 05   BTU/LBMOLE

    M = 0.1374D 01


    MEAN DEVIATION = 0.4752D-02

    AVG. PERCENT ERROR = 0.3049D 02

    FOBJ = 0.5789D-03

    SUM OF SQUARES = 0.5789D-03


STATEMENTS EXECUTED=  196907

CORE USAGE        OBJECT CODE=   43376 BYTES,ARRAY AREA=   65484 BYTES,TOTAL AREA AVAILABLE=  174080  BYTES

DIAGNOSTICS        NUMBER OF ERRORS=       0, NUMBER OF WARNINGS=       0, NUMBER OF EXTENSIONS=      10

COMPILE TIME=     0.28 SEC,EXECUTION TIME=     2.53 SEC,      11.21.33     SATURDAY      23 JUL 83     WATFIV - MAR 1980 V2L0

         C$STOP
```

APPENDIX F

LISTING OF DIBENZOTHIOPHENE PROCESS MODEL PROGRAM AND DATA FIT CALCULATION RESULTS

```
$JOB
C     ******************************************************************
C     *                                                              *
C     *  DIBENZOTHIOPHENE HDS MODEL                                    *
C     *                                                              *
C     *  2-TYPE SITE INTRINSIC RATE EXPRESSION (BRODERICK)             *
C     *                                                              *
C     *  ISOTHERMAL FIT                                                *
C     *                                                              *
C     *  DATA FROM ESPINO                                              *
C     *                                                              *
C     ******************************************************************
C
C     ******************************************************************
C     *                                                              *
C     *                                                              *
C     *                        GLOSSARY                                *
C     *                                                              *
C     *  A(J)=SIMPLIFICATION TERM FOR INTEGRATED RATE EQUATION         *
C     *  AH2=PRE-EXPONENTIAL CONSTANT FOR HYDROGEN EQUILIBRIUM CONSTANT*
C     *       (1/WT%)                                                  *
C     *  ALHSV(J)=LIQUID HOURLY SPACE VELOCITY FOR DATA POINT J (1/HR) *
C     *  ALHSV1(J)=J-TH VALUE IN LIQUID HOURLY SPACE VELOCITY GROUP    *
C     *       (1/HR)                                                   *
C     *  AP=PRE-EXPONENTIAL CONSTANT FOR PRODUCT EQUILIBRIUM CONSTANT  *
C     *       (1/WT%)                                                  *
C     *  AR=PRE-EXPONENTIAL CONSTANT FOR REACTANT EQUILIBRIUM CONSTANT *
C     *       (1/WT%)                                                  *
C     *  ARX=PRE-EXPONENTIAL CONSTANT FOR REACTION RATE CONSTANT       *
C     *       (GRAM/GRAM CAT/HR)                                       *
C     *  B(J)=SIMPLIFICATION TERM FOR INTEGRATED RATE EQUATION (1/WT%) *
C     *  CF1-4=CALCULATED OUTLET CONCENTRATION IN CONVERGENCE LOOP(WT%)*
C     *  CG1-4=ASSUMED OUTLET CONCENTRATION IN CONVERGENCE LOOP (WT%)  *
C     *  CR(J,K)=CONVERGED VALUE FOR OUTLET CONCENTRATION FOR DATA     *
C     *       POINT J, GROUP K (WT%)                                   *
C     *  CP1=WEIGHT PERCENT PRODUCT INTRODUCED IN FEED (WT%)           *
C     *  CRAD=CATALYST PARTICLE RADIUS (CM)                            *
C     *  CR22=OUTLET CONCENTRATION FOR DATA POINT 22 (WT%)             *
C     *  CR1=INLET CONCENTRATION (WT%)                                 *
C     *  CSTORE=STORAGE VARIABLE FOR OUTLET CONCENTRATION IN EFF FACTOR*
C     *       LOOP (WT%)                                               *
C     *  C1(J)=INLET CONCENTRATION (WT%)                               *
C     *  DAB(J)=FREE LIQUID DIFFUSIVITY OF A IN SOLVENT B (SQ CM/SEC)  *
C     *  DEFF(J)=EFFECTIVE DIFFUSIVITY OF A IN SOLVENT B (SQ CM/SEC)   *
C     *  DEL=INCREMENTAL CHANGE IN ASSUMED OUTLET CONCENTRATION (WT%)  *
C     *  DEN=DENSITY OF LIQUID AT TREF (GRAM/CC)                       *
C     *  DENS(J)=DENSITY OF LIQUID AT DATA POINT J (GRAM/CC)           *
C     *  D1-D5=CONSTANTS USED IN LIQUID DENSITY CALCULATION            *
C     *  E=EFFECTIVENESS FACTOR                                        *
C     *  E1(J)=EFFECTIVENESS FACTOR FOR DATA POINT J                   *
C     *  EH2(J)=HYDROGEN HEAT OF ADSORPTION (CAL/GMOLE)                *
C     *  EP(J)=PRODUCT HEAT OF ADSORPTION (CAL/GMOLE)                  *
C     *  ER(J)=REACTANT HEAT OF ADSORPTION (CAL/GMOLE)                 *
C     *  ERX(J)=REACTION ACTIVATION ENERGY (CAL/GMOLE)                 *
C     *  FF=FUNCTION TO BE FITTED                                      *
C     *  FITM(J)=FITTED VALUE FOR J-TH DATA POINT                      *
C     *  FL=INITIAL VALUE OF FLAMB, THE RELATIVE AMOUNT BY WHICH THE   *
C     *       DIAGONAL COEFFICIENTS ARE AUGMENTED                      *
C     *  FOBJ=RETURNS THE FINAL VALUE OF PHI, THE WEIGHTED SUM OF      *
C     *       SQUARES                                                  *


C     *  H=CONSTANT USED IN EFFECTIVENESS FACTOR CALCULATION           *
C     *  K1=CONSTANT USED IN DIFFUSIVITY CALCULATION                   *
C     *  KH2(J)=HYDROGEN ADSORPTION EQUILIBRIUM CONSTANT (1/WT%)       *
C     *  KH2REF=HYDROGEN ADSORPTION EQUILIBRIUM CONSTANT AT REFERENCE  *
C     *       TEMPERATURE (1/PSI)                                      *
C     *  KNTP=COUNTER FOR PRESSURE GROUP IN DATA SET GENERATOR         *
C     *  KNTT=COUNTER FOR TEMPERATURE GROUP IN DATA SET GENERATOR      *
C     *  KOB=OBSERVED REACTION RATE CONSTANT (1/HR)                    *
C     *  KOUNT=COUNTER IN OUTLET CONCENTRATION CONVERGENCE LOOP        *
C     *  KOWNT=COUNTER IN EFFECTIVENESS FACTOR CALCULATION             *
C     *  KP(J)=PRODUCT ADSORPTION EQUILIBRIUM CONSTANT (1/WT%)         *
C     *  KR=LOGICAL UNIT NUMBER FOR THE READER                         *
C     *  KRE(J)=REACTANT ADSORPTION EQUILIBRIUM CONSTANT (1/WT%)       *
C     *  KRX(J)=REACTION EQUILIBRIUM CONSTANT (GRAM/GRAM CAT/HR)       *
C     *  KW=LOGICAL UNIT NUMBER OF THE PRINTER                         *
C     *  LL=MEMBER NUMBER FOR LIQUID HOURLY SPACE VELOCITY GROUP       *
C     *  LP=MEMBER NUMBER FOR PRESSURE GROUP                           *
C     *  LT=MEMBER NUMBER FOR TEMPERATURE GROUP                        *
C     *  M=NUMBER OF DIFFERENT SETS OF ADSORPTION EQUILIBRIUM TERMS    *
C     *  MASK(J)=NONZERO IF X(J) IS TO BE HELD CONSTANT                *
C     *  MATRX=NONZERO IF STATISTICAL ERRORS ARE TO BE CALCULATED      *
C     *  MAX=MAXIMUM ITERATIONS IN OUTLET CONCENTRATION LOOP           *
C     *  MAXE=MAXIMUM NO. OF ITERATIONS IN THE EFF. FACTOR CALCULATION *
C     *  MAXIT=MAXIMUM ITERATIONS IN MARQUARDT DATA FIT                *
C     *  METHD=DETERMINES CONVERGENCE METHOD USED IN DATA FIT          *
C     *  MN=NO. OF COMBINATIONS OF M AND N                             *
C     *  MWB=MOLECULAR WEIGHT OF SOLVENT LIQUID (G/GMOLE)              *
C     *  MWH2=MOLECULAR WEIGHT OF HYDROGEN (G/GMOLE)                   *
C     *  MWP=MOLECULAR WEIGHT OF REACTION PRODUCT (G/GMOLE)            *
C     *  MWR=MOLECULAR WEIGHT OF REACTANT (G/GMOLE)                    *
C     *  MWS=MOLECULAR WEIGHT OF ELEMENTAL SULFUR (G/GMOLE)            *
C     *  N=NUMBER OF DIFFERENT SETS OF VALUES FOR ACTIVATION ENERGY    *
C     *       AND HEATS OF ADSORPTION                                  *
C     *  NL=NUMBER OF MEMBERS IN LIQUID HOURLY SPACE VELOCITY GROUP    *
C     *  NM=LOGICAL UNIT NUMBER IN OUTLET CONCENTRATION STORAGE ARRAY  *
C     *  NP=NUMBER OF MEMBERS IN PRESSURE GROUP                        *
C     *  NPTS=NUMBER OF POINTS IN THE DATA SET                         *
C     *  NT=NUMBER OF MEMBERS IN TEMPERATURE GROUP                     *
C     *  NTEMP=NUMBER OF TEMPERATURES AT WHICH A UNIQUE FIT IS TO BE   *
C     *       MADE                                                     *
C     *  NTRAC=USER PRINT CONTROL                                      *
C     *  NV=NUMBER OF PARAMETERS IN FUNCTION TO BE FIT                 *
C     *  P(J)=PRESSURE FOR DATA POINT J (PSI)                          *
C     *  P1(J)=J-TH VALUE IN PRESSURE GROUP (PSI)                      *
C     *  PC=CRITICAL PRESSURE OF SOLVENT (ATM)                         *
C     *  PRAD=AVERAGE CATALYST PORE RADIUS (ANGSTROMS)                 *
C     *  Q=CONSTANT USED IN VISCOSITY CALCULATION                      *
C     *  R=IDEAL GAS CONSTANT (CAL/GMOLE/K)                            *
C     *  R=IDEAL GAS CONSTANT                                          *
C     *  RP(J)=RATIO OF KP(J) : KH2REF AT THE REFERENCE TEMPERATURE    *
C     *  RR(J)=RATIO OF KR(J) : KH2REF AT THE REFERENCE TEMPERATURE    *
C     *  S(J)=SOLUBILITY OF HYDROGEN IN SOLVENT (WT%)                  *
C     *  S1=CONSTANT USED IN SOLUBILITY CALCULATION                    *
C     *  S2=CONSTANT USED IN SOLUBILITY CALCULATION                    *
C     *  SIZ=SIZE OF REACTANT MOLECULE (ANGSTROMS)                     *
C     *  T(J)=TEMPERATURE FOR DATA POINT J (R)                         *
C     *  T1(J)=J-TH VALUE IN TEMPERATURE GROUP (R)                     *
C     *  TC=CRITICAL TEMPERATURE OF SOLVENT (K)                        *
C     *  TEMP(J)=J-TH OF NT DIFFERENT TEMPERATURES IN THE DATA SET (F) *
C     *  TERM(J)=SIMPLIFICATION TERM FOR INTEGRATED RATE EQUATION      *
```

```
C      *  TK(J)=TEMPERATURE FOR DATA POINT J (K)                       *
C      *  TOR=CATALYST TORTUOSITY FACTOR                               *
C      *  TR=REDUCED TEMPERATURE                                       *
C      *  VA=MOLAR VOLUME OF REACTANT AT ITS NORMAL BOILING POINT      *
C      *         (CC/GMOLE)                                            *
C      *  VB=MOLAR VOLUME OF SOLVENT AT ITS NORMAL BOILING POINT       *
C      *         (CC/GMOLE)                                            *
C      *  VBREF=MOLAR VOLUME OF SOLVENT AT 20 C  (CC/GMOLE)            *
C      *  VF=CATALYST VOID FRACTION OR POROSITY                        *
C      *  VIS(J)=VISCOSITY OF LIQUID AT DATA POINT J (CP)              *
C      *  VO1=CONSTANT USED IN VISCOSITY CALCULATION                   *
C      *  VO2=CONSTANT USED IN VISCOSITY CALCULATION                   *
C      *  VR=VOLUME OF EMPTY REACTOR (CC)                              *
C      *  W=ACENTRIC FACTOR FOR SOLVENT                                *
C      *  WT=WEIGHT OF CATALYST (G)                                    *
C      *  X(J)=J-TH PARAMETER                                          *
C      *  XMAX(J)=MAXIMUM VALUE FOR J-TH PARAMETER                     *
C      *  XMIN(J)=MINIMUM VALUE FOR THE J-TH PARAMETER                 *
C      *  Y(J)=J-TH DATA ORDINATE                                      *
C      *  YSIG(J)=EXPECTED ERROR IN Y(J)                               *
C      *  ZZ=REFERENCE DATA POINT                                      *
C      *                                                               *
C      *****************************************************************
C
       IMPLICIT REAL*8 (A-H,O-Z)
       INTEGER ZZ
       REAL*8 KRX,KH2,KP,KRE,KH2REF,K1,H,KOB,KNUM
       REAL*8 KROKP
       DIMENSION ERX(20),EH2(20),EP(20),ER(20),RP(20),RR(20),KRX(27),
      *KH2(27),KP(27),KRE(27),A(27),B(27),CR(4,27)
       EXTERNAL EXFIT
       DOUBLE PRECISION X,FIT
       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,MXSUE,MXUPD
       COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
       COMMON /CSTOR/ T(27),P(27),ALHSV(27),C1(27),TERM(27),T1(10),P1(10)
      *,ALHSV1(10),E1(27),DAB(27),DEFF(27),S(27),VIS(27),TEMP(10),C2(27),
      *DENS(27),DEV,CP1,WT,VR,HI,TK(27),X1(27),DEV1,DEV2,C2C(27),C2D(27)
       DIMENSION KROKP(27)
       QEXP(ARG)=DEXP(ARG)
       CALL STSET
C
C
C
C
C      ***********************
C      *                     *
C      * MARQUARDT VARIABLES *
C      *                     *
C      ***********************
C
       FL=1.
       KR=5
       KW=6
       MATRX=1
       MAXIT=200
       NFMAX=1000



       MAXIT=60
       METHD=1
       NTRAC=0
       NV=3
C      ***********************************
C      *                                 *
C      *  MODEL CONSTANTS AND VARIABLES  *
C      *                                 *
C      ***********************************
C
       ARX=-1.0
       CP1=0.0
       CRAD=0.0106
       CR22=0.5
       CR1=2.43
       KH2REF=4.10D-04
       M=1
       MWB=132.206
       MWH2=2.016
       MWP=34.08
       MWR=184.27
       MWS=32.064
       N=1
       MN=M*N
       NL=1
       NP=1
       NT=1
       NPTS=NT*NP*NL
       NTEMP=1
       PC=34.7
       PRAD=14.0
       R=1.9872
       S1=716.0
       S2=12.24
       SI2=10.0
       TC=719.0
       TOR=2.5
       TREF=525.0
       TREFL=293.0
       VA=182.0
       VB=147.0
       VBREF=135.87
       VF=0.5
       VR=15.0
       W=0.303
       WT=6.0
       ZZ=1
C
C      *****************************************************************
C      *                                                               *
C      *  INPUT=1  IF DATA IS TO BE HYPOTHETICALLY GENERATED           *
C      *  INPUT=2  IF DATA IS TO BE SUPPLIED                           *
C      *                                                               *
C      *  DATA MAY BE GENERATED IN TWO MANNERS                         *
C      *      1 SUPPLY ALL PRE-EXPONENTIAL AND EXPONENTIAL CONSTANTS   *
C      *      2 SUPPLY EXPONENTIAL CONSTANTS AND RATIOS OF EQUILIBRIUM *
C      *          CONSTANTS AT A SPECIFIED REFERENCE TEMPERATURE       *
C      *                                                               *
C      *****************************************************************
       INPUT=1
```

```
      INPUT=2
C
      KNUM=17.5D-8
      IF (VA/VB.GE.2.5) KNUM=6.2D-8
      IF (VA/VB.LE.1.0) KNUM=25.2D-8
      TR=TREF/TC
      D1=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D2=.29607-.09045*TR-.04842*TR*TR
      TR=TREFL/TC
      D3=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D4=.29607-.09045*TR-.04842*TR*TR
      D5=D1*(1.-W*D2)/D3/(1.-W*D4)
      DEN=MWB/D5/VBREF
      KH2REF=KH2REF/DEXP(-S1/625.-S2)*MWH2/DEN
C
C
C
C     ***************************************
C     *                                     *
C     * READ TEMPERATURES, PRESSURES, LHSVS *
C     *                                     *
C     ***************************************
C
      IF (INPUT.EQ.1) GO TO 90
      READ(KR,50)NPTS
   50 FORMAT(I5)
      L=0
   70 L=L+1
      IF (L.EQ.(NPTS+1)) GO TO 311
      READ(KR,80)T(L),P(L),ALHSV(L),C1(L),Y(L)
   80 FORMAT(7X,5F10.5)
      NM=1
      X1(L)=1.-Y(L)/C1(L)
      C2(L)=Y(L)
      CR(NM,L)=C2(L)
      CG2=C2(L)
      Y(L)=(1./X1(L))*DLOG(1./(1.-X1(L)))
      T(L)=T(L)+460.
      TK(L)=T(L)/1.8
      S(L)=DEXP(-S1/TK(L)-S2)*P(L)*100.
      TR=TK(L)/TC
      D1=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D2=.29607-.09045*TR-.04842*TR*TR
      TR=TREFL/TC
      D3=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D4=.29607-.09045*TR-.04842*TR*TR
      D5=D1*(1.-W*D2)/D3/(1.-W*D4)
      DENS(L)=MWB/D5/VBREF
      GO TO 285
   90 DO 110 K=1,NTEMP
      READ(KR,100)TEMP(K)
  100 FORMAT(7X,F10.5)
  110 CONTINUE
      DO 130 K=1,NP
      READ(KR,120)P1(K)
  120 FORMAT(7X,F10.5)



  130 CONTINUE
      DO 150 K=1,NL
      READ(KR,140)ALHSV1(K)
  140 FORMAT(7X,F10.5)
  150 CONTINUE
C
C
C
C     ***************************************************************
C     *                                                             *
C     * READ ACTIVATION ENERGY, HEATS OF ADSORPTION, AND RATIOS FOR *
C     * RELATIVE ADSORPTION CONSTANTS AT REFERENCE TEMPERATURE      *
C     *                                                             *
C     ***************************************************************
C
      READ(KR,160)(ERX(K),EH2(K),EP(K),ER(K),K=1,N)
  160 FORMAT(7X,4F10.1)
      READ(KR,170)(RP(K),RR(K),K=1,M)
  170 FORMAT(7X,2F10.3)
C
C
C
C     *******************************************************************
C     *                                                                 *
C     * START LOOPS-DATA SET GENERATED FROM EACH E-SET, K-RATIO COMB.   *
C     * J  E-SET                                                        *
C.    * K  K-RATIO                                                      *
C     * KK TEMPERATURE                                                  *
C     * L  DATA POINT                                                   *
C     *                                                                 *
C     *******************************************************************
C
      J=0
   72 J=J+1
      K=0
   73 K=K+1
      KK=0
   74 KK=KK+1
      DO 175 L=1,NT
      T1(L)=TEMP(KK)+460.
  175 CONTINUE
C
C
C
C             **********************************************
C             *                                            *
C             * COMBINE TEMP, PRESS, LHSV TO FORM DATA SET *
C             *                                            *
C             **********************************************
C
      LT=1
      LP=1
      LL=1
      KNTT=0
      KNTP=0
      DO 210 L=1,NPTS
      KNTT=KNTT+1
      KNTP=KNTP+1
      T(L)=T1(LT)
      P(L)=P1(LP)
```

```
      ALHSV(L)=ALHSV1(LL)
      IF (KNTT.NE.NP*NL) GO TO 180
      KNTT=0
      LT=LT+1
  180 IF (LP.NE.NP) GO TO 190
      IF (KNTP.EQ.NL) LP=0
  190 IF (KNTP.NE.NL) GO TO 200
      KNTP=0
      LP=LP+1
  200 IF (LL.EQ.NL) LL=0
      LL=LL+1
  210 CONTINUE
C
C
C
C              *****************************************
C              *                                       *
C              * START EQUILIBRIUM CONSTANT CALCULATIONS *
C              *                                       *
C              * PRE-EXPONENTIAL CONSTANTS             *
C              * ARX-REACTION                          *
C              * AH2-HYDROGEN                          *
C              * AP -PRODUCT                           *
C              * AR -REACTANT                          *
C              *                                       *
C              * EQUILIBRIUM CONSTANTS                 *
C              *                                       *
C              * KRX-REACTION                          *
C              * KH2-HYDROGEN ADSORPTION               *
C              * KP -PRODUCT ADSORPTION                *
C              * KR -REACTANT ADSORPTION               *
C              *                                       *
C              *****************************************
C
      AH2=0.0
      AH2=KH2REF/DEXP(EH2(J)/R/625.0)*DEN/MWH2/100.
      AP=RP(K)*KH2REF/DEXP(EP(J)/R/625.0)*DEN/MWS/100.
      AR=0.0
      AR=RR(K)*KH2REF/DEXP(ER(J)/R/625.0)*DEN/MWS/100.
      DO 220 L=1,NPTS
      TK(L)=T(L)/1.8
      S(L)=DEXP(-S1/TK(L)-S2)*P(L)*100.
      TR=TK(L)/TC
      D1=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D2=.29607-.09045*TR-.04842*TR*TR
      TR=TREFL/TC
      D3=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D4=.29607-.09045*TR- 04842*TR*TR
      D5=D1*(1.-W*D2)/D3/(1 -W*D4)
      DENS(L)=MWS/D5/VBREF
      KH2(L)=AH2*DEXP(EH2(J)/R/TK(L))*DENS(L)/DEN
      KH2(L)=5.415275
      KP(L)=AP*DEXP(EP(J)/R/TK(L))*DENS(L)/DEN
      KRE(L)=AR*DEXP(ER(J)/R/TK(L))*DENS(L)/DEN
      A(L)=1.+KP(L)*(CR1+CP1)
  220 B(L)=KRE(L)-KP(L)
      IF (ARX.NE.-1.0) GO TO 230
      ARX=(A(ZZ)**2*DLOG(CR1/CRZZ)+B(ZZ)**2*(CR1**2-CRZZ**2)/2.+2.*A(ZZ)



     **B(ZZ)*(CR1-CRZZ))*ALHSV(ZZ)*VR*DENS(ZZ)*(1.+KH2(ZZ)*S(ZZ))/WT/DEX
     *P(-ERX(N)/R/TK(ZZ))/KH2(ZZ)/KRE(ZZ)/S(ZZ)/100.
      ARX=0.1D+15
      WRITE(KW,*)ARX
      L=0
  230 L=L+1
      CSTORE=0.0
      E=1.0
      MAX=100
      MAX=300
      MAXE=10
      KOWNT=0
  235 A(L)=1.+KP(L)*(CR1+CP1)
      B(L)=KRE(L)*E-KP(L)
      KOUNT=0
      KOWNT=KOWNT+1
      CG1=CR1
      DEL=CR1/10.
      IF (KOWNT.GE.MAXE) GO TO 285
  238 KRX(L)=ARX*DEXP(-ERX(J)/R/TK(L))
      KRX(L)=0.85111
      KRDKP(L)=KRE(L)/KP(L)
      KRDKP(L)=1.535154
      CF1=CR1+(CP1+CR1)*DLOG(CR1/CG1)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
C
C
C
C              ********************************************************
C              *                                                      *
C              * CALCULATE OUTLET CONCENTRATION  CR=FCN(CR)           *
C              *                                                      *
C              * CG1-4=ESTIMATED VALUES (0<CG<CR1)                    *
C              * CF1-4=CALCULATED VALUES CF=FCN(CG)                   *
C              *                                                      *
C              * CG IS ADJUSTED BY DECREASING INCREMENTS UNTIL THE    *
C              * INCREMENT IS LESS THAN 0.001% OF THE VALUE OF CG     *
C              *                                                      *
C              ********************************************************
C
  240 KOUNT=KOUNT+1
  242 CG2=CG1-DEL
      IF (CG2.GE.DABS(DEL)) GO TO 245
      DEL=DEL/10.
      GO TO 242
  245 CF2=CR1+(CP1+CR1)*DLOG(CR1/CG2)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      IF (L.GT.5) GO TO 249
      IF (L.LT.4) GO TO 249
      TERM1=DLOG(CR1/CG2)*A(L)/B(L)/2.
      TERM2=(CR1**2-CG2**2)*B(L)/A(L)/4.
      TERM3=CR1
      TERM4=KRX(L)*KH2(L)*KRE(L)*WT*E*S(L)*100./ALHSV(L)/VR/DENS(L)/(1.+
     *KH2(L)*S(L))/2./A(L)/B(L)
      TERM5=TERM1+TERM2+TERM3-TERM4
  249 IF (KOUNT.GE.MAX) GO TO 285
  250 IF (CF2.LE.CR1.AND.CF2.GE.0.0) GO TO 285
      IF (CF1*CF2.GT.0.0) GO TO 252
```

```
      DEL=-DEL/10.
      CG1=CG2
      CF1=CF2
      GO TO 240
  262 CG1=CG2
      CF1=CF2
      GO TO 240
  265 DEL=DEL/10.
  270 CG3=CG2-DEL
      CG4=CG2+DEL
      IF (CG3.LE.0.0) CG3=0.000001
      IF (CG4.LE.0.0) CG4=0.000001
      CF3=CR1+(CP1+CR1)*DLOG(CR1/CG3)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      CF4=CR1+(CP1+CR1)*DLOG(CR1/CG4)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      IF (DABS(CG2-CF3).LT.DABS(CG2-CF4)) GO TO 275
      DEL=-DEL
  275 CG1=CG2
      CG2=CG1-DEL
      IF (CG2.LE.0.0) CG2=0.000001
      KOUNT=KOUNT+1
      CF1=CR1+(CP1+CR1)*DLOG(CR1/CG1)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      CF2=CR1+(CP1+CR1)*DLOG(CR1/CG2)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      IF (L.GT.5) GO TO 279
      IF (L.LT.4) GO TO 279
      TERM1=DLOG(CR1/CG2)*A(L)/B(L)/2.
      TERM2=(CR1**2-CG2**2)*B(L)/A(L)/4.
      TERM3=CR1
      TERM4=KRX(L)*KH2(L)*KRE(L)*WT*E*S(L)*100./ALHSV(L)/VR/DENS(L)/(1.+
     *KH2(L)*S(L))/2./A(L)/B(L)
      TERM5=TERM1+TERM2+TERM3-TERM4
  279 IF (KOUNT.GE.MAX) GO TO 285
      IF ((CG1-CF1)*(CG2-CF2).LT.0.0) GO TO 280
      GO TO 270
  280 DEL=-DEL/10.
      IF (DABS(DEL/CG2).LT.0.00001) GO TO 285
      IF (DABS(DEL).LE.0.000001) GO TO 285
      GO TO 270
C
C
C
C                 ********************************
C                 *                              *
C                 * CALCULATE EFFECTIVENESS FACTOR *
C                 *                              *
C                 ********************************
C
  285 TR=TK(L)/TC
      IF (TR.LT.0.99) GO TO 288
      WRITE(KW,287)TR
  287 FORMAT(/////10X,'THE REDUCED TEMPERATURE =',F5.1,3X,'IS ABOVE THE
     *ACCEPTABLE MAXIMUM IN THE VISCOSITY CALCULATION.',////)
  288 O=TC**(1./6.)/MWB**0.5/PC**(2./3.)


      VO1=0.015174-.02135*TR+.0075*TR*TR
      VO2=.042552-.07674*TR+.0340*TR*TR
      VIS(L)=(VO1+W*VO2)/O
      K1=(1.+(3.*VB/VA)**(2./3.))*KNUM
      DAB(L)=K1*TK(L)/VIS(L)/VA**(1./3.)
      DEFF(L)=VF*DAB(L)/TOR*(1.-SIZ/PRAD)**4.
      KOB=DLOG(CR1/CG2)*ALHSV(L)
      H=CRAD*(KOB/DEFF(L)/3600.)**0.5
      E1(L)=3./H/H*(H*((DEXP(H)+DEXP(-H))/(DEXP(H)-DEXP(-H)))-1.)
      IF (INPUT.NE.1) GO TO 70
      IF (DABS(CG2-CSTORE)/CG2.LT.0.000002) GO TO 290
      CSTORE=CG2
      E=E1(L)
      GO TO 235
  290 IF (KOWNT.LE.MAXE) GO TO 295
      WRITE(KW,237)KOWNT,L,J,K
  237 FORMAT(   /,5X,'THE MAXIMUM NO. OF',I4,1X,'ITERATIONS HAS BEEN REA
     *CHED IN THE EFFECTIVENESS FACTOR CALCULATION',/5X,'FOR DATA POINT'
     *,I3,1X,'IN E-SET NO.',I3,1X,'AND K-RATIO NO.',I3,/)
  295 IF (KOUNT.LE.MAX) GO TO 299
      WRITE(KW,250)KOUNT,L,J,K
  250 FORMAT(   /,5X,'THE MAXIMUM NO. OF',I4,1X,'ITERATIONS HAS BEEN REA
     *CHED IN THE OUTLET CONCENTRATION CALCULATION',/5X,'FOR DATA POINT'
     *,I3,1X,'IN E-SET NO.',I3,1X,'AND K-RATIO NO.',I3,/)
  299 NM=((J-1)*M+K)
      CR(NM,L)=CG2
      IF (L.LT.NPTS) GO TO 230
C
C
C
C                 ********************************
C                 *                              *
C                 * WRITE KINETIC MODEL INFORMATION *
C                 *                              *
C                 ********************************
C
      WRITE(KW,*)KRX(1),KH2(1),KRE(1),KP(1)
      WRITE(KW,310)ERX(J)/1000.,EH2(J)/1000.,EP(J)/1000.,ER(J)/1000.,RP(
     *K),RR(K), KH2REF*DEXP(-S1/625.-S2)*DEN/MWH2
  310 FORMAT(1H1      //5X,'THIS PROGRAM GENERATES A SET OF OUTLET REACT
     *ANT CONCENTRATIONS GIVEN TEMPERATURE, PRESSURE,',//5X,'LHSV, AND I
     *NLET REACTANT CONCENTRATIONS GIVEN AN INTEGRATED RATE EQUATION AND
     * ITS RATE CONSTANTS.',//5X,'IT THEN FITS A KINETIC MODEL EQUATION
     *TO THIS SET OF HYPOTHETICALLY GENERATED DATA.',
     *//////5X,'FOR THIS CASE :',///5X,                      'REACTION A
     *CTIVATION ENERGY  =',F6.2,1X,'KCAL/GMOLE',/5X,'HYDROGEN HEAT OF AD
     *SORPTION =',F6.2,1X,'KCAL/GMOLE',/5X,'PRODUCT HEAT OF ADSORPTION
     *=' ,F6.2,1X,'KCAL/GMOLE',/5X,'REACTANT HEAT OF ADSORPTION =',F6.2,
     *1X,'KCAL/GMOLE',//5X,'ADSORPTION RATE CONSTANT RATIO   K-H2 (1/MOL
     *E% H2) : K-PRODUCT (1/MOLE% H2S)     ) :',F6.1,/38X,'K-H2 (1/MOLE%
     * H2) : K-REACTANT (1/MOLE% DBT)     ) :', F6.1,/5X,'FOR A REFERENCE
     * VALUE FOR K-H2 = ',1PD9.3,1X,'1/PSI  AT 625K.',//5X,'WT% IS THE W
     *EIGHT PERCENT OF ELEMENTAL SULFUR IN THE BULK FLUID.',/////)
  311 IF (INPUT.EQ.1) GO TO 314
      WRITE(KW,312)
  312 FORMAT(1H1//5X,'THIS PROGRAM FITS AN INTRINSIC KINETIC RATE MODEL
     *TO A SET OF EXPERIMENTAL DBT HDS DATA.',////5X,'WT% IS THE WEIGHT
     *PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.',///)
  314 WRITE(KW,315)CRAD*20.,PRAD*2.,VF,TOR
  315 FORMAT(///5X,'CATALYST PROPERTIES ARE :',//8X,'PARTICLE DIAMETER =
```

```
     *',F5.2,1X,'(MM)',/8X,'AVERAGE PORE DIAMETER =',F6.1,1X,'(ANGSTROMS
     *)',/8X,'VOID FRACTION =',F6.3,/8X,'TORTUOSITY FACTOR =',F6.2,////)
C
C
C
C           ***********************************
C           *                                 *
C           * WRITE GENERATED DATA FOR THIS SET *
C           *                                 *
C           ***********************************
C
      WRITE(KW,320)
  320 FORMAT(8X,'RUN',5X,'TEMP',6X,'PRESS',6X,'LHSV',6X,'H2 SOLUBILITY',
     *5X,'EFF DIFF',6X,'EFF FACTOR',5X,'IN  CONC.',6X,'FIN  CONC.',/18X,
     *'(F)',7X,'(PSI)',5X,'(1/HR)',11X,'(WT%)',7X,'(SQ CM/SEC)',22X,'(WT
     *%)',10X,'(WT%)',/)
      DO 350 L=1,NPTS
  330 C2(L)=CR(NM,L)
      WRITE(KW,340)L,T(L)-460.,P(L),ALHSV(L),S(L),DEFF(L),E1(L),CR1,C2(L
     *)
  340 FORMAT(5X,I5,F10.1,F11.1,F10.2,5X,5E15.5)
  350 CONTINUE
      CALL STEPT (EXFIT)
      DEV=0.0
      DEV1=0.0
      XD=0.5
      XC=0.5
      DO 405 JJ=1,NPTS
  403 XD1=1.-OEXP(-Y(JJ)*XD)
      XC1=1.-OEXP(-FIT(JJ)*XC)
      IF (DABS(XD1-XD)/XD1.LT.0.00001) GO TO 404
      XD=XD1
      XC=XC1
      GO TO 403
  404 C2D(JJ)=C1(JJ)*(1.-XD)
      C2C(JJ)=C1(JJ)*(1.-XC)
      DEV=DEV+DABS(C2C(JJ)-C2D(JJ))/NPTS
      DEV1=DEV1+DABS(C2C(JJ)-C2D(JJ))/NPTS/C2D(JJ)*100.
  405 CONTINUE
      WRITE(KW,501)X(1),X(2),X(3),X(1)/X(2)/X(3)
  501 FORMAT(1H1,/////5X,'INTRINSIC MODEL PARAMETERS',///5X,'FITTED BY
     *Y = (1/X)LN(1/(1-X))',//5X,'X(1) = K(KH)(KR/KP) = ',E10.4,//5X,'X(
     *2) = KH = ',E10.4,3X,'1/WT%',//5X,'X(3) = KR/KP = ',E10.4,//5X,'K
     *= ',E10.4,3X,'WT%/HR')
      WRITE(KW,550)DEV,DEV1
  550 FORMAT(////5X,'MEAN DEVIATION = ',F7.5,//5X,'AVERAGE PERCENT ERROR
     * = ',F7.5,////)
      IF (INPUT.NE.1) GO TO 999
      IF (KK.LT.NTEMP) GO TO 74
      IF (K.LT.M) GO TO 73
      IF (J.LT.N) GO TO 72
  999 STOP
      END
C
C
C
C     ****************************
C     *                          *
C     * END DATA GENERATION LOOPS *
C     *                          *



C     ****************************
C
C
C
C
C
C     **************************
C     *                        *
C     * DATA FITTING SUBROUTINE *
C     *                        *
C     **************************
C
      SUBROUTINE EXFIT (FITM)
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 KRXN,KHYD,KRCT,KPRD
      DOUBLE PRECISION X,FIT,OEXP,DEXP,ARG,FITM,FF
      DIMENSION FITM(300)
      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(27),P(27),ALHSV(27),C1(27),TERM(27),T1(10),P1(10)
     *,ALHSV1(10),E1(27),DAB(27),DEFF(27),S(27),VIS(27),TEMP(10),C2(27),
     *DENS(27),DEV,CP1,WT,VR,HI,TK(27),X1(27),DEV1,DEV2,C2C(27),C2D(27)
      OEXP(ARG)=DEXP(ARG)
      R=1.9872
      FOBJ=0.
      DO 380 J=1,NPTS
      YSIG(J)=1.
      FF=S(J)*E1(J)*WT*100.*X(1)/ALHSV(J)/C1(J)/VR/DENS(J)/(CP1/C1(J)+1.
     *)/X1(J)/(1.+X(2)*S(J))+(1.-X(3)*E1(J))/(CP1/C1(J)+1.)
      FITM(J)=FF
      FOBJ=FOBJ+(FF-Y(J)/YSIG(J))**2
  380 CONTINUE
      RETURN
      END

$ENTRY
```

```
THIS PROGRAM FITS AN INTRINSIC KINETIC RATE MODEL TO A SET OF EXPERIMENTAL DBT HDS DATA.


WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.



CATALYST PROPERTIES ARE :

   PARTICLE DIAMETER : 0.21 (MM)
   AVERAGE PORE DIAMETER :  28.0 (ANGSTROMS)
   VOID FRACTION : 0.500
   TORTUOSITY FACTOR : 2.50


   RUN     TEMP       PRESS      LHSV        H2 SOLUBILITY     EFF DIFF       EFF FACTOR      IN. CONC      FIN. CONC.
            (F)       (PSI)     (1/HR)           (WT%)       (SQ CM/SEC)                       (WT%)          (WT%)

    1      545.0      250.0      1.00        0.33515D-01    0.37868D-06    0.99730D 00    0.24300D 01    0.14700D 01
    2      545.0      250.0      3.00        0.33515D-01    0.37868D-06    0.99678D 00    0.24300D 01    0.19900D 01
    3      545.0      250.0      6.00        0.33515D-01    0.37868D-06    0.99655D 00    0.24300D 01    0.21900D 01
    4      545.0      250.0      9.00        0.33515D-01    0.37868D-06    0.99650D 00    0.24300D 01    0.22600D 01
    5      545.0      350.0      1.00        0.46921D-01    0.37868D-06    0.99686D 00    0.24300D 01    0.13800D 01
    6      545.0      350.0      3.00        0.46921D-01    0.37868D-06    0.99621D 00    0.24300D 01    0.19200D 01
    7      545.0      350.0      6.00        0.46921D-01    0.37868D-06    0.99591D 00    0.24300D 01    0.21400D 01
    8      545.0      350.0      9.00        0.46921D-01    0.37868D-06    0.99586D 00    0.24300D 01    0.22300D 01
    9      545.0      450.0      1.00        0.60327D-01    0.37868D-06    0.99656D 00    0.24300D 01    0 12800D 01
   10      545.0      450.0      3.00        0.60327D-01    0.37868D-06    0.99579D 00    0.24300D 01    0.18700D 01
   11      545.0      450.0      6.00        0.60327D-01    0.37868D-06    0.99546D 00    0.24300D 01    0.21100D 01
   12      545.0      450.0      9.00        0.60327D-01    0.37868D-06    0.99521D 00    0.24300D 01    0.22000D 01









MARQ....   BEGIN NONLINEAR LEAST SQUARES SOLUTION

MASK    :        0              0              0

X       :    0.000000D 00   0.000000D 00   0.000000D 00

XMAX    :    0.100000D 31   0.100000D 31   0.100000D 31

XMIN    :   -0.100000D 31  -0.100000D 31  -0.100000D 31

DELMN   :    0.10000D-07    0.10000D-07    0.10000D-07

NV :   3       NPTS :     12       LPDMA :    300       LPDMB :  20       NTRAC : 0       METHD :  1       KALCP :  0

KORDF : 1      NFLAT : 1       NFMAX :    1000      MAXIT :   50       MXSUB :  25

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

PHI (THE SUM OF SQUARES) : 0.38337110D 00                                                        LAMBDA : 0.10000D 01

********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....       QSAV(  2,  2) :  0.00000000D 00        ITERATION    1

RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.          RANK :   2         ORDER OF MATRIX :   3        ITERATION    1

CONVERGED WHEN THE STEP BECAME SMALL.
  15 ITERATIONS         NF :   92          PHI : 0.24031218D-03          FMGN : 0.10000D 01        LAMBDA : 0.27068D 02
         NORM OF SCALED GRADIENT VECTOR : 0.27282D-09
                X :    0.53201880D 00  0.18825460D 02  0.34951880D 00

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

            1     0.12722780E 01    0.12671741D 01     0.51048D-02     0.10000D 01         0.51048D-02
            2     0.11032000E 01    0.10991916D 01     0 40093D-02     0 10000D 01         0.40093D-02
            3     0 10528950E 01    0.10618847D 01    -0.89892D-02     0.10000D 01        -0.89892D-02
            4     0.10367010E 01    0.10377476D 01    -0.10464D-02     0.10000D 01        -0.10464D-02
            5     0.13181190E 01    0.13207825D 01    -0.26634D-02     0.10000D 01        -0.26634D-02
            6     0.11224020E 01    0.11195011D 01     0.29011D-02     0.10000D 01         0.29011D-02
            7     0.10648880E 01    0.10630365D 01     0.18515D-02     0.10000D 01         0.18515D-02
            8     0.10435590E 01    0.10493295D 01    -0.57705D-02     0.10000D 01        -0.57705D-02
            9     0.13545260E 01    0.13571775D 01    -0.26515D-02     0.10000D 01        -0.26515D-02
           10     0.11366870E 01    0.11345072D 01     0.21801D-02     0.10000D 01         0.21801D-02
           11     0.10722610E 01    0.10741638D 01    -0.19020D-02     0.10000D 01        -0.19020D-02
           12     0.10505390E 01    0.10435652D 01     0.69738D-02     0.10000D 01         0.69738D-02

NUMBER OF DEGREES OF FREEDOM :  0.90000D 01

R.M.S. SCALED DEVIATION OF DATA FROM FIT : 0.51672D-02

MAXIMUM SCALED DEVIATION : 0.89892D-02
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```
SUBROUTINE MOERR.

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

  1     0.1000000D 01

  2   -0.9921821D 00  0.1000000D 01

  3   -0.9756327D 00  0.9832032D 00  0.1000000D 01


NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =     9

EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =     9  PLUS OR MINUS 0.42426D 01

ACTUAL VALUE OF PHI = 0.24031D-03

RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.51673D-02


MAXIMUM VARIANCE INFLATION FACTOR = 0.99405D 02

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

            1          0        0.53201658D 00      0.30871D 01      0.15952D-01

            2          0        0.18925464D 02      0.19009D 03      0.98224D 00

            3          0        0.34851684D 00      0.13414D 01      0.69315D-02


LOWER TRIANGLE OF THE CORRELATION MATRIX....

            K ....     1             2             3

        MASK(K)....    0             0             0

   J    MASK(J)

   1       0        0.10000D 01

   2       0        0.88940D 00  0.10000D 01

   3       0        0.59508D 00  0.17537D 00  0.10000D 01





    INTRINSIC MODEL PARAMETERS

    FITTED BY  Y = (1/X)LN(1/(1-X))

    X(1) = K(KH)(KR/KP) = 0.5320D 00

    X(2) = KH = 0.1893D 02    1/WT%

    X(3) = KR/KP = 0.3485D 00

    K = 0.8043D-01   WT%/HR


    MEAN DEVIATION = 0.01413

    AVERAGE PERCENT ERROR = 0.71387


STATEMENTS EXECUTED=   32402

CORE USAGE       OBJECT CODE=   61856 BYTES,ARRAY AREA=   89856 BYTES,TOTAL AREA AVAILABLE=  174080  BYTES

DIAGNOSTICS        NUMBER OF ERRORS=       0, NUMBER OF WARNINGS=       0, NUMBER OF EXTENSIONS=      18

COMPILE TIME=     0.46 SEC,EXECUTION TIME=     0.38 SEC,     17.35.29    SUNDAY        24 JUL 83    WATFIV - MAR 1980 V2L0

        C$STOP
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THIS PROGRAM FITS AN INTRINSIC KINETIC RATE MODEL TO A SET OF EXPERIMENTAL DBT HDS DATA


WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.



CATALYST PROPERTIES ARE :

   PARTICLE DIAMETER : 0.21 (MM)
   AVERAGE PORE DIAMETER :  28.0 (ANGSTROMS)
   VOID FRACTION : 0.500
   TORTUOSITY FACTOR : 2.50


   RUN     TEMP      PRESS      LHSV        H2 SOLUBILITY    EFF DIFF       EFF FACTOR      IN. CONC.      FIN. CONC.
            (F)      (PSI)     (1/HR)           (WT%)      (SQ CM/SEC)                       (WT%)           (WT%)

    1     572.0      250.0      1.00       0.34659D-01    0.42406D-06    0.99530D 00    0.24300D 01    0.81000D 00
    2     572.0      250.0      3.00       0.34659D-01    0.42406D-06    0.99521D 00    0.24300D 01    0.17400D 01
    3     572.0      250.0      6.00       0.34659D-01    0.42406D-06    0.99526D 00    0.24300D 01    0.20600D 01
    4     572.0      250.0      9.00       0.34659D-01    0.42406D-06    0.99513D 00    0.24300D 01    0.21700D 01
    5     572.0      350.0      1.00       0.48522D-01    0.42406D-06    0.99413D 00    0.24300D 01    0.71000D 00
    6     572.0      350.0      3.00       0.48522D-01    0.42406D-06    0.99402D 00    0.24300D 01    0.16000D 01
    7     572.0      350.0      6.00       0.48522D-01    0.42406D-06    0.99399D 00    0.24300D 01    0.18700D 01
    8     572.0      350.0      9.00       0.48522D-01    0.42406D-06    0.99393D 00    0.24300D 01    0.21100D 01
    9     572.0      350.0     12.00       0.48522D-01    0.42406D-06    0.99404D 00    0.24300D 01    0.21800D 01
   10     572.0      450.0      1.00       0.62386D-01    0.42406D-06    0.99317D 00    0.24300D 01    0.58000D 00
   11     572.0      450.0      3.00       0.62386D-01    0.42406D-06    0.99310D 00    0.24300D 01    0.15000D 01
   12     572.0      450.0      6.00       0.62386D-01    0.42406D-06    0.99296D 00    0.24300D 01    0.19000D 01
   13     572.0      450.0      9.00       0.62386D-01    0.42406D-06    0.99291D 00    0.24300D 01    0.20600D 01
   14     572.0      450.0     12.00       0.62386D-01    0.42406D-06    0.99300D 00    0.24300D 01    0.21500D 01
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MARQ....  BEGIN NONLINEAR LEAST SQUARES SOLUTION

MASK    :        0              0              0

X       :   0.000000D 00   0.000000D 00   0.000000D 00

XMAX    :   0.100000D 31   0.100000D 31   0.100000D 31

XMIN    :  -0.100000D 31  -0.100000D 31  -0.100000D 31

DELMN   :   0.100000D-07   0.100000D-07   0.100000D-07

NV :   3      NPTS :     14      LPDMA :    300      LPDMB :  20      NTRAC : 0      METHD :  1       KALCP :  0

KORDF : 1      NFLAT : 1      NFMAX :    1000      MAXIT :    50     MXSUB :  25

CRIT : 0.70711D 00        RELDF : 0.10000D-07       RELMN : 0.100000D-07

PHI (THE SUM OF SQUARES) : 0.18544408D 01                                                 LAMBDA : 0.100000D 01

********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....  .    QSAV(  2,  2) :  0.00000000D 00          ITERATION    1

RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.          RANK :   2        ORDER OF MATRIX :   3          ITERATION    1

CONVERGENCE ACHIEVED UNDER THE NFLAT OPTION.

  19 ITERATIONS          NF :  116          PHI : 0.78687323D-03           FMGN : 0.10000D 01          LAMBDA : 0.89881D 02

        NORM OF SCALED GRADIENT VECTOR : 0.25329D-09

              X :   0.1680122D 01  0.1136383D 02  0.9354837D 00


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

              1      0.15702300E 01     0.15711830D 01     -0.95254D-03      0.10000D 01       -0.95254D-03
              2      0.11762810E 01     0.11720248D 01      0.42571D-02      0.10000D 01        0.42571D-02
              3      0.10846640E 01     0.10975024D 01     -0.12838D-01      0.10000D 01       -0.12838D-01
              4      0.10576480E 01     0.10447513D 01      0.12897D-01      0.10000D 01        0.12897D-01
              5      0.17382700E 01     0.17380389D 01      0.23115D-03      0.10000D 01        0.23115D-03
              6      0.12234530E 01     0.12222051D 01      0.12484D-02      0.10000D 01        0.12484D-02
              7      0.11085860E 01     0.11094897D 01     -0.90386D-03      0.10000D 01       -0.90386D-03
              8      0.10722810E 01     0.10661901D 01      0.60717D-02      0.10000D 01        0.60717D-02
              9      0.10528960E 01     0.10661974D 01     -0.13302D-01      0.10000D 01       -0.13302D-01
             10      0.18817630E 01     0.18793528D 01      0.24106D-02      0.10000D 01        0.24106D-02
             11      0.12605320E 01     0.12700431D 01     -0.95108D-02      0.10000D 01       -0.95108D-02
             12      0.11280570E 01     0.11229726D 01      0.50849D-02      0.10000D 01        0.50849D-02
             13      0.10848640E 01     0.10755880D 01      0.92766D-02      0.10000D 01        0.92766D-02
             14      0.10624680E 01     0.10668255D 01     -0.41855D-02      0.10000D 01       -0.41855D-02

NUMBER OF DEGREES OF FREEDOM :  0.11000D 02

R.M.S. SCALED DEVIATION OF DATA FROM FIT : 0.84577D-02
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MAXIMUM SCALED DEVIATION = 0.13302D-01


SUBROUTINE MOERR.

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

  1    0.10000000 01

  2   -0.8694334D 00  0.1000000D 01

  3   -0.8758311D 00  0.8608114D 00  0.10000000 01


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 = 0.78687D-03

RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.84578D-02


MAXIMUM VARIANCE INFLATION FACTOR = 0.78275D 02

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

          1          0        0.16601215D 01      0.32462D 01     0.27456D-01

          2          0        0.11353632D 02      0.48318D 02     0.40867D 00

          3          0        0.93546371D 00      0.12442D 01     0.10523D-01


LOWER TRIANGLE OF THE CORRELATION MATRIX....

           K ....      1            2            3

      MASK(K)....      0            0            0

  J   MASK(J)

  1      0        0.10000D 01

  2      0        0.85585D 00  0.10000D 01

  3      0        0.62831D 00  0.14861D 00  0.10000D 01






   INTRINSIC MODEL PARAMETERS

   FITTED BY  Y = (1/X)LN(1/(1-X))

   X(1) = K(KH)(KR/KP) = 0.1660D 01

   X(2) = KH = 0.1135D 02   1/WT%

   X(3) = KR/KP = 0.9355D 00

   K = 0.1563D 00   WT%/HR


   MEAN DEVIATION = 0.02162

   AVERAGE PERCENT ERROR = 1.06811


STATEMENTS EXECUTED=   40145

CORE USAGE       OBJECT CODE=   61666 BYTES,ARRAY AREA=   69856 BYTES,TOTAL AREA AVAILABLE=  174080  BYTES

DIAGNOSTICS        NUMBER OF ERRORS=       0, NUMBER OF WARNINGS=       0, NUMBER OF EXTENSIONS=      18

COMPILE TIME=     0.46 SEC,EXECUTION TIME=     0.47 SEC,     17.36.47    SUNDAY       24 JUL 83    WATFIV - MAR 1980 V2L0

        C$STOP
```

```
THIS PROGRAM FITS AN INTRINSIC KINETIC RATE MODEL TO A SET OF EXPERIMENTAL DBT HDS DATA.


WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.



CATALYST PROPERTIES ARE :

   PARTICLE DIAMETER = 0.21 (MM)
   AVERAGE PORE DIAMETER =  28.0 (ANGSTROMS)
   VOID FRACTION = 0.500
   TORTUOSITY FACTOR = 2.50


   RUN     TEMP       PRESS      LHSV       H2 SOLUBILITY     EFF DIFF        EFF FACTOR      IN. CONC.       FIN. CONC.
            (F)       (PSI)     (1/HR)          (WT%)       (SQ CM/SEC)                      (WT%)           (WT%)

    1     590.0      250.0       1.00      0.35409D-01     0.45808D-06     0.99147D 00     0.24300D 01     0.35000D 00
    2     590.0      250.0       3.00      0.35409D-01     0.45808D-06     0.99223D 00     0.24300D 01     0 13500D 01
    3     590.0      250.0       6.00      0.35409D-01     0.45808D-06     0.99250D 00     0.24300D 01     0.18300D 01
    4     590.0      250.0       9.00      0.35409D-01     0.45808D-06     0.99266D 00     0 24300D 01     0.20200D 01
    5     590.0      250.0      12.00      0.35409D-01     0.45808D-06     0.99253D 00     0.24300D 01     0.21100D 01
    6     590.0      250.0      15.00      0.35409D-01     0.45808D-06     0.99282D 00     0.24300D 01     0.21800D 01
    7     590.0      350.0       1.00      0.49572D-01     0.45808D-06     0.98882D 00     0.24300D 01     0 19000D 00
    8     590.0      350.0       3.00      0.49572D-01     0.45808D-06     0.98991D 00     0.24300D 01     0.11300D 01
    9     590.0      350.0       6.00      0.49572D-01     0 45808D-06     0 99027D 00     0.24300D 01     0.16800D 01
   10     590.0      350.0       9.00      0.49572D-01     0.45808D-06     0.99047D 00     0.24300D 01     0.18100D 01
   11     590.0      350.0      12.00      0.49572D-01     0.45808D-06     0.99051D 00     0.24300D 01     0.20300D 01
   12     590.0      350.0      15.00      0.49572D-01     0.45808D-06     0.99059D 00     0.24300D 01     0.21100D 01
   13     590.0      450.0       3.00      0.63736D-01     0.45808D-06     0.98793D 00     0.24300D 01     0.87000D 00
   14     590.0      450.0       6.00      0.63736D-01     0.45808D-06     0.98851D 00     0.24300D 01     0.15700D 01
   15     590.0      450.0       9.00      0.63736D-01     0.45808D-06     0.98859D 00     0.24300D 01     0.18200D 01
   16     590.0      450.0      12.00      0.63735D-01     0.45808D-06     0.98869D 00     0.24300D 01     0.19600D 01
   17     590.0      450.0      15.00      0.63736D-01     0.45808D-06     0.98881D 00     0.24300D 01     0.20500D 01





MARQ....   BEGIN NONLINEAR LEAST SQUARES SOLUTION

MASK    =          0             0             0

X       =   0.00000D 00   0.00000D 00   0.00000D 00

XMAX    =   0.10000D 31   0.10000D 31   0.10000D 31

XMIN    =  -0.10000D 31  -0.10000D 31  -0.10000D 31

DELMN   =   0.10000D-07   0.10000D-07   0.10000D-07

NV =    3      NPTS =     17      LPDMA =    300      LPDMB =   20      NTRAC = 0      METHD =   1      KALCP =  0

KORDF = 1      NFLAT = 1       NFMAX =    1000      MAXIT =   50      MXSUB =   25

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

PHI (THE SUM OF SQUARES) = 0.54860081D 01
                                                                                                  LAMBDA = 0.10000D 01

********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....       QSAV(  2,  2) =  0.00000000D 00           ITERATION    1

RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.            RANK =   2        ORDER OF MATRIX =  -3          ITERATION    1

CONVERGENCE ACHIEVED UNDER THE NFLAT OPTION.

  14 ITERATIONS          NF =   80          PHI = 0.21159358D-02             FMGN = 0.10000D 01         LAMBDA = 0.10105D-03

        NORM OF SCALED GRADIENT VECTOR = 0.11058D-08

              X =   0.3582173D 01  0.8178506D 01  0.1396840D 01


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

       1      0.22637700E 01    0.22615308D 01      0.22392D-02     0.10000D 01          0.22392D-02
       2      0.13225190E 01    0.13142754D 01      0.82439D-02     0.10000D 01          0.82439D-02
       3      0.11484790E 01    0.11442887D 01      0.41907D-02     0.10000D 01          0.41907D-02
       4      0.10952400E 01    0.11069736D 01     -0.11733D-01     0.10000D 01         -0.11733D-01
       5      0.10722810E 01    0.10486446D 01      0.23637D-01     0.10000D 01          0.23637D-01
       6      0.10552640E 01    0.10830894D 01     -0.27825D-01     0.10000D 01         -0.27825D-01
       7      0.27548000E 01    0.27572271D 01     -0.24270D-02     0.10000D 01         -0.24270D-02
       8      0.14312200E 01    0 14273859D 01      0.38341D-02     0.10000D 01          0.38341D-02
       9      0.11958750E 01    0.11862758D 01      0.95998D-02     0.10000D 01          0.95998D-02
      10      0.11252200E 01    0.11259358D 01     -0.71535D-03     0.10000D 01         -0.71535D-03
      11      0.10926210E 01    0.10882024D 01      0.44194D-02     0.10000D 01          0.44194D-02
      12      0.10722810E 01    0.10882179D 01     -0.15956D-01     0.10000D 01         -0.15956D-01
      13      0.15284870E 01    0.15309008D 01     -0.24138D-02     0.10000D 01         -0.24138D-02
      14      0.12342570E 01    0.12421878D 01     -0.79301D-02     0.10000D 01         -0.79301D-02
      15      0.11514790E 01    0 11448440D 01      0.66358D-02     0.10000D 01          0.66358D-02
      16      0.11113200E 01    0.11040808D 01      0.72397D-02     0.10000D 01          0.72397D-02
      17      0.10874330E 01    0.10884580D 01     -0.10252D-02     0.10000D 01         -0.10252D-02

NUMBER OF DEGREES OF FREEDOM =  0.14000D 02
```

```
R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.12294D-01

MAXIMUM SCALED DEVIATION = 0.27825D-01

SUBROUTINE MOERR.

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

  1    0.1000000D 01

  2   -0.8871855D 00  0.1000000D 01

  3   -0.9556309D 00  0.8581448D 00  0.1000000D 01

NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    14

EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =    14  PLUS OR MINUS 0.52915D 01

ACTUAL VALUE OF PHI = 0.21159D-02

RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.12294D-01

MAXIMUM VARIANCE INFLATION FACTOR = 0.48598D 02

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

             1          0        0.35821734D 01      0.34005D 01    0.41805D-01

             2          0        0.81765058D 01      0.24838D 02    0.30537D 00

             3          0        0.13968401D 01      0.96285D 00    0.11837D-01

LOWER TRIANGLE OF THE CORRELATION MATRIX....

              K ....      1              2              3

        MASK(K)....       0              0              0

   J    MASK(J)

   1       0        0.10000D 01

   2       0        0.82852D 00  0.10000D 01

   3       0        0.43606D 00 -0.11986D 00  0.10000D 01




     INTRINSIC MODEL PARAMETERS

     FITTED BY   Y = (1/X)LN(1/(1-X))

     X(1) = K(KH)(KR/KP) = 0.3582D 01

     X(2) = KH = 0.8177D 01    1/WT%

     X(3) = KR/KP = 0.1397D 01

     K = 0.3136D 00    WT%/HR


     MEAN DEVIATION = 0.02857

     AVERAGE PERCENT ERROR = 1.50215


STATEMENTS EXECUTED=    32475

CORE USAGE        OBJECT CODE=    51656 BYTES,ARRAY AREA=    68856 BYTES,TOTAL AREA AVAILABLE=  174080  BYTES

DIAGNOSTICS         NUMBER OF ERRORS=        0, NUMBER OF WARNINGS=        0, NUMBER OF EXTENSIONS=       16

COMPILE TIME=     0.45 SEC,EXECUTION TIME=      0.41 SEC,       17.43.26     SUNDAY        24 JUL 83    WATFIV - MAR 1980 V2L0

         C$STOP
```

```
THIS PROGRAM FITS AN INTRINSIC KINETIC RATE MODEL TO A SET OF EXPERIMENTAL DBT HDS DATA.


WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.



CATALYST PROPERTIES ARE :

   PARTICLE DIAMETER : 0.21 (MM)
   AVERAGE PORE DIAMETER :  28.0 (ANGSTROMS)
   VOID FRACTION : 0.500
   TORTUOSITY FACTOR : 2.60


   RUN      TEMP       PRESS      LHSV       H2 SOLUBILITY     EFF DIFF       EFF FACTOR      IN. CONC.       FIN. CONC.
            (F)        (PSI)     (1/HR)         (WT%)        (SQ CM/SEC)                       (WT%)           (WT%)

    1      617.0       250.0      3.00       0.36515D-01    0.51574D-06    0.98488D 00    0.24300D 01    0.68000D 00
    2      617.0       250.0      6.00       0.36515D-01    0.51574D-06    0.98580D 00    0.24300D 01    0.13200D 01
    3      617.0       250.0      9.00       0.36515D-01    0.51574D-06    0.98627D 00    0.24300D 01    0.16400D 01
    4      617.0       250.0     12.00       0.36515D-01    0.51574D-06    0.98628D 00    0.24300D 01    0.18100D 01
    5      617.0       250.0     15.00       0.36515D-01    0.51574D-06    0.98658D 00    0.24300D 01    0.19300D 01
    6      617.0       350.0      3.00       0.51121D-01    0.51574D-06    0.97921D 00    0.24300D 01    0.40000D 00
    7      617.0       350.0      6.00       0.51121D-01    0.51574D-06    0.98104D 00    0.24300D 01    0.10700D 01
    8      617.0       350.0      9.00       0.51121D-01    0.51574D-06    0.98160D 00    0.24300D 01    0.14300D 01
    9      617.0       350.0     12.00       0.51121D-01    0.51574D-06    0.98208D 00    0.24300D 01    0.16800D 01
   10      617.0       350.0     15.00       0.51121D-01    0.51574D-06    0.98231D 00    0.24300D 01    0.17900D 01
   11      617.0       450.0      3.00       0.65727D-01    0.51574D-06    0.97484D 00    0.24300D 01    0.27000D 00
   12      617.0       450.0      6.00       0.65727D-01    0.51574D-06    0.97688D 00    0.24300D 01    0.68000D 00
   13      617.0       450.0      9.00       0.65727D-01    0.51574D-06    0.97782D 00    0.24300D 01    0.12700D 01
   14      617.0       450.0     12.00       0.65727D-01    0.51574D-06    0.97810D 00    0.24300D 01    0.15100D 01
   15      617.0       450.0     15.00       0.65727D-01    0.51574D-06    0.97841D 00    0.24300D 01    0.16700D 01
```

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

MASK   :         0            0            0

X      :   0.00000D 00  0.00000D 00  0.00000D 00

XMAX   :   0.10000D 31  0.10000D 31  0.10000D 31

XMIN   :  -0.10000D 31 -0.10000D 31 -0.10000D 31

DELMN  :   0.10000D-07  0.10000D-07  0.10000D-07

NV :   3      NPTS :    15      LPDMA :   300      LPDMB :  20      NTRAC : 0      METHD :   1       KALCP :  0

KORDF : 1       NFLAT : 1       NFMAX :   1000      MAXIT :   50      MXSUB :  25

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

PHI (THE SUM OF SQUARES) : 0.52831752D 01                                                     LAMBDA : 0.10000D 01

********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(  2,  2) :  0.00000000 00          ITERATION    1

RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.          RANK :   2        ORDER OF MATRIX :   3          ITERATION    1

CONVERGED WHEN THE STEP BECAME SMALL.
  15 ITERATIONS         NF :   63           PHI : 0.17811584D-02           FMGN : 0.10000D 01          LAMBDA : 0.61752D-08
        NORM OF SCALED GRADIENT VECTOR : 0.26515D-09
              X :   0.7075603D 01  0.5416278D 01  0.1635164D 01


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

           1      0.17894220E 01     0.18028763D 01     -0.13454D-01      0.10000D 01           -0.13454D-01
           2      0.13358720E 01     0.13338818D 01      0.19910D-02      0.10000D 01            0.19910D-02
           3      0.12094470E 01     0.12171841D 01     -0.77163D-02      0.10000D 01           -0.77163D-02
           4      0.11545010E 01     0.11403773D 01      0.14125D-01      0.10000D 01            0.14125D-01
           5      0.11198040E 01     0.11271603D 01     -0.75762D-02      0.10000D 01           -0.75762D-02
           6      0.21596860E 01     0.21321586D 01      0.27527D-01      0.10000D 01            0.27527D-01
           7      0.14655510E 01     0.14644877D 01      0.10741D-02      0.10000D 01            0.10741D-02
           8      0.12884260E 01     0.12807299D 01      0.76965D-02      0.10000D 01            0.76965D-02
           9      0.12060140E 01     0.12120766D 01     -0.60620D-02      0.10000D 01           -0.60620D-02
          10      0.11806120E 01     0.11891224D 01     -0.85103D-02      0.10000D 01           -0.85103D-02
          11      0.24716770E 01     0.24867723D 01     -0.15095D-01      0.10000D 01           -0.15095D-01
          12      0.15923930E 01     0.15846457D 01      0.77471D-02      0.10000D 01            0.77471D-02
          13      0.13592790E 01     0.13574277D 01      0.18519D-02      0.10000D 01            0.18519D-02
          14      0.12566830E 01     0.12565638D 01      0.11953D-03      0.10000D 01            0.11953D-03
          15      0.11992290E 01     0.12011081D 01     -0.18789D-02      0.10000D 01           -0.18789D-02

NUMBER OF DEGREES OF FREEDOM :  0.12000D 02

R.M.S. SCALED DEVIATION OF DATA FROM FIT : 0.12183D-01
```

```
MAXIMUM SCALED DEVIATION = 0.27527D-01


SUBROUTINE MOERR.

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

  1     0.1000000D 01

  2    -0.9841795D 00  0.1000000D 01

  3    -0.9810801D 00  0.8539284D 00  0.1000000D 01


NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    12

EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =    12  PLUS OR MINUS 0.48990D 01

ACTUAL VALUE OF PHI = 0.17812D-02

RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.12183D-01


MAXIMUM VARIANCE INFLATION FACTOR = 0.86450D 02

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

           1         0        0.70758028D 01      0.85148D 01       0.10374D 00

           2         0        0.54152757D 01      0.18873D 02       0.22993D 00

           3         0        0.15351538D 01      0.14444D 01       0.17598D-01


LOWER TRIANGLE OF THE CORRELATION MATRIX....

           K ....     1             2             3

      MASK(K)....     0             0             0

  J   MASK(J)

  1       0       0.10000D 01

  2       0       0.83150D 00   0.10000D 01

  3       0       0.78487D 00   0.33907D 00   0.10000D 01





    INTRINSIC MODEL PARAMETERS

    FITTED BY  Y = (1/X)LN(1/(1-X))

    X(1) = K(KH)(KR/KP) = 0.7076D 01

    X(2) = KH = 0.5415D 01    1/WT%

    X(3) = KR/KP = 0.1535D 01

    K = 0.8511D 00    WT%/HR


    MEAN DEVIATION = 0.01460

    AVERAGE PERCENT ERROR = 1.27922


STATEMENTS EXECUTED=    28256

CORE USAGE       OBJECT CODE=   61888 BYTES,ARRAY AREA=   59856 BYTES,TOTAL AREA AVAILABLE=  174080  BYTES

DIAGNOSTICS        NUMBER OF ERRORS=       0, NUMBER OF WARNINGS=       0, NUMBER OF EXTENSIONS=      18

COMPILE TIME=   . 0.45 SEC,EXECUTION TIME=     0.35 SEC,     17.30.22    SUNDAY       24 JUL 83    WATFIV - MAR 1980 V2L0

        C$STOP
```

```
THIS PROGRAM FITS AN INTRINSIC KINETIC RATE MODEL TO A SET OF EXPERIMENTAL DBT HDS DATA.


WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.



CATALYST PROPERTIES ARE :

   PARTICLE DIAMETER : 0.21 (MM)
   AVERAGE PORE DIAMETER :  28.0 (ANGSTROMS)
   VOID FRACTION : 0.500
   TORTUOSITY FACTOR : 2.50


   RUN      TEMP      PRESS      LHSV       H2 SOLUBILITY     EFF DIFF       EFF FACTOR      IN. CONC.      FIN. CONC.
            (F)       (PSI)     (1/HR)         (WT%)       (SQ CM/SEC)                       (WT%)          (WT%)

    1      662.0      250.0      6.00      0.383100D-01   0.633770D-06   0.974840D 00   0.243000D 01   0.630000D 00
    2      662.0      250.0      9.00      0.383100D-01   0.633770D-06   0.977250D 00   0.243000D 01   0.108000D 01
    3      662.0      250.0     12.00      0.383100D-01   0.633770D-06   0.978260D 00   0.243000D 01   0.136000D 01
    4      662.0      250.0     15.00      0.383100D-01   0.633770D-06   0.978930D 00   0.243000D 01   0.155000D 01
    5      662.0      350.0      6.00      0.536350D-01   0.633770D-06   0.963420D 00   0.243000D 01   0.330000D 00
    6      662.0      350.0      9.00      0.536350D-01   0.633770D-06   0.967500D 00   0.243000D 01   0.750000D 00
    7      662.0      350.0     12.00      0.536350D-01   0.633770D-06   0.969330D 00   0.243000D 01   0.106000D 01
    8      662.0      350.0     15.00      0.536350D-01   0.633770D-06   0.970680D 00   0.243000D 01   0.129000D 01
    9      662.0      450.0      6.00      0.689590D-01   0.633770D-06   0.952050D 00   0.243000D 01   0.170000D 00
   10      662.0      450.0      9.00      0.689590D-01   0.633770D-06   0.957870D 00   0.243000D 01   0.520000D 00
   11      662.0      450.0     12.00      0.689590D-01   0.633770D-06   0.960790D 00   0.243000D 01   0.830000D 00
   12      662.0      450.0     15.00      0.689590D-01   0.633770D-06   0.962480D 00   0.243000D 01   0.107000D 01
```

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

MASK    :        0             0             0

X       :   0.000000D 00  0.000000D 00  0.000000D 00

XMAX    :   0.100000D 31  0.100000D 31  0.100000D 31

XMIN    :  -0.100000D 31 -0.100000D 31 -0.100000D 31

DELMN   :   0.10000D-07   0.10000D-07   0.10000D-07

NV :    3       NPTS :     12       LPDMA :    300       LPDMB :  20       NTRAC : 0       METHD :  1       KALCP :  0

KBRDF : 1       NFLAT : 1       NFMAX :    1000       MAXIT :   50       MXSUB :  25

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

                                                                                               LAMBDA : 0.10000D 01
PHI (THE SUM OF SQUARES) : 0.85888053D 01

********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....       QSAV(  2,  2) :  0.00000000D 00           ITERATION     1

RANK-DEFICIENT NORMAL EQUATIONS IN MARQ.          RANK :    2        ORDER OF MATRIX :    3           ITERATION     1

CONVERGED WHEN THE STEP BECAME SMALL.
  17 ITERATIONS        NF :    99          PHI : 0.80043864D-03          FMGN : 0.10000D 01          LAMBDA : 0.55555D-01
        NORM OF SCALED GRADIENT VECTOR : 0.90077D-10
                X :   0.1680347D 02   0.2805538D 01   0.2435582D 01

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

          1      0.18224010E 01      0.18213904D 01      0.10107D-02      0.10000D 01          0.10107D-02
          2      0.14596730E 01      0.14674653D 01     -0.77925D-02      0.10000D 01         -0.77925D-02
          3      0.13181190E 01      0.13147640D 01      0.33551D-02      0.10000D 01          0.33551D-02
          4      0.12416080E 01      0.12413638D 01      0.24486D-03      0.10000D 01          0.24486D-03
          5      0.23102970E 01      0.23106446D 01     -0.34659D-03      0.10000D 01         -0.34659D-03
          6      0.17003820E 01      0.17040912D 01     -0.37089D-02      0.10000D 01         -0.37089D-02
          7      0.14715190E 01      0.14592283D 01      0.12291D-01      0.10000D 01          0.12291D-01
          8      0.13498200E 01      0.13508700D 01     -0.10498D-02      0.10000D 01         -0.10498D-02
          9      0.28599240E 01      0.28527301D 01      0.71942D-02      0.10000D 01          0.71942D-02
         10      0.19615790E 01      0.19778141D 01     -0.16235D-01      0.10000D 01         -0.16235D-01
         11      0.15314720E 01      0.15330495D 01     -0.15789D-02      0.10000D 01         -0.15789D-02
         12      0.14655810E 01      0.14569854D 01      0.85955D-02      0.10000D 01          0.85955D-02

NUMBER OF DEGREES OF FREEDOM :  0.90000D 01

R.M.S. SCALED DEVIATION OF DATA FROM FIT : 0.81675D-02

MAXIMUM SCALED DEVIATION : 0.16235D-01
```

```
SUBROUTINE MOERR.
OSAV (PT*P, SCALED, WHERE P IS THE JACOBIAN)....
  1    0.10000000D 01
  2   -0.93074330D 00  0.10000000D 01
  3   -0.89914750D 00  0.95484280D 00  0.10000000D 01

NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =     9
EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =     9  PLUS OR MINUS 0.42426D 01
ACTUAL VALUE OF PHI = 0.60044D-03
RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.81679D-02

MAXIMUM VARIANCE INFLATION FACTOR = 0.14948D 03

APPROXIMATE STANDARD ERRORS....
                                                                      RESCALED
            J       MASK(J)          X(J)               ERROR           ERROR
            1          0        0.18803471D 02      0.19105D 02      0.15605D 00
            2          0        0.28055381D 01      0.11472D 02      0.93707D-01
            3          0        0.24365820D 01      0.23870D 01      0.19578D-01

LOWER TRIANGLE OF THE CORRELATION MATRIX....
              K ....      1             2             3
        MASK(K)....       0             0             0
  J     MASK(J)
  1        0        0.100000 01
  2        0        0.930700 00  0.100000 01
  3        0        0.908070 00  0.951700 00  0.100000 01




    INTRINSIC MODEL PARAMETERS

    FITTED BY  Y = (1/X)LN(1/(1-X))
    X(1) = K(KH)(KR/KP) = 0.1880D 02
    X(2) = KH = 0.2806D 01    1/WT%
    X(3) = KR/KP = 0.2438D 01
    K = 0.2648D 01    WT%/HR


    MEAN DEVIATION = 0.00629
    AVERAGE PERCENT ERROR = 0.74809


STATEMENTS EXECUTED=    27886
CORE USAGE        OBJECT CODE=    61856 BYTES,ARRAY AREA=    99886 BYTES,TOTAL AREA AVAILABLE=  174080   BYTES
DIAGNOSTICS         NUMBER OF ERRORS=        0, NUMBER OF WARNINGS=        0, NUMBER OF EXTENSIONS=       18
COMPILE TIME=     0.46 SEC,EXECUTION TIME=      0.33 SEC,      17.46.53     SUNDAY        24 JUL 83     WATFIV - MAR 1980 V2L0

        C$STOP
```

APPENDIX G

LISTING OF PARAMETER SENSITIVITY PROGRAM AND SAMPLE DATA FIT CALCULATION RESULTS

```
$JOB
C     ******************************************************************
C     *                                                                *
C     *  PARAMETER SENSITIVITY CALCULATIONS                            *
C     *                                                                *
C     *  DATA GENERATED FROM INTRINSIC DIBENZOTHIOPHENE HDS MODEL      *
C     *                                                                *
C     *  FIT TO N-TH ORDER GLOBAL MODEL                                *
C     *                                                                *
C     *  OPERATING CONDITIONS FROM ESPINO                              *
C     *                                                                *
C     ******************************************************************
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGER ZZ
      REAL*8 KRX,KH2,KP,KRE,KH2REF,K1,H,KOB,KNUM
      REAL*8 KRDKP
      DIMENSION KRX(27),KH2(27),KRDKP(27),C2(27)
      EXTERNAL EXFIT
      DOUBLE PRECISION X,FIT
      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,MXSUE,MXUPD
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
      COMMON /CSTOR/ T(27),P(27),ALHSV(27),C1(27),TERM(27),T1(10),P1(10)
     *,ALHSV1(10),E1(27),DAB(27),DEFF(27),S(27),VIS(27),TEMP(10),
     *DENS(27),TK(27),C2C(27),C2D(27),DEV,DEV1,DEV2,CP1,WT,VR,ORDER,
     *Z,CM!N,HI,NDAT
      QEXP(ARG)=DEXP(ARG)
      CALL STSET
C
C
C
C
C     ***********************
C     *                     *
C     * MARQUARDT VARIABLES *
C     *                     *
C     ***********************
C
C
      FL=1.
      KR=5
      KW=6
      MATRX=1
      NFMAX=4000
      MAXIT=400
      METHD=1
      NTRAC=0
      NV=4
      XMIN(1)=0.0
      XMIN(2)=0.0
      XMIN(3)=0.0
      XMAX(4)=0.9999
      X(4)=0.5
      MASK(3)=1
      X(3)=0.0



      X(2)=3.0D+04
      X(1)=1.0D+10
      X1=X(1)
      X2=X(2)
      X3=X(3)
      X4=X(4)
C
C
C     ***********************************
C     *                                 *
C     *  MODEL CONSTANTS AND VARIABLES  *
C     *                                 *
C     ***********************************
C
C
      AH2=1.1848D-07
      ARDP=1.3178D+07
      ARX=8.1278D+13
      CP1=0.0
      CRAD=0.0105
      CRZZ=0.5
      CR1=2.43
      EH2=20934.7
      ERDP=-18971.8
      ERX=38408.7
      EOLD=0.5
      MWB=132.206
      MWH2=2.016
      MWP=34.08
      MWR=184.27
      MWS=32.064
C
      NL=1
      NL=5
      NP=5
      NP=1
      NT=1
      NT=5
      NPTS=NT*NP*NL
      ORDER=0.0
      PC=34.7
      PRAD=14.0
      R=1.9872
      S1=716.0
      S2=12.24
      SI2=10.0
      TC=719.0
      TOR=2.5
      TREF=625.0
      TREFL=293.0
      VA=182.0
      VB=147.0
      VBREF=135.87
      VF=0.6
      VR=15.0
      W=0.303
      WT=6.0
      ZZ=1
C
C     ******************************************************************
```

```
C     *                                                              *
C     *  DATA MAY BE GENERATED IN TWO MANNERS:                       *
C     *      1 SUPPLY ALL PRE-EXPONENTIAL AND EXPONENTIAL CONSTANTS  *
C     *      2 SUPPLY EXPONENTIAL CONSTANTS AND RATIOS OF EQUILIBRIUM *
C     *        CONSTANTS AT A SPECIFIED REFERENCE TEMPERATURE        *
C     *                                                              *
C     ****************************************************************
C
C
      HI=1
      KNUM=17.5D-8
      IF (VA/VB.GE.2.5) KNUM=8.2D-8
      IF (VA/VB.LE.1.0) KNUM=25.2D-8
C
C
C
C     **************************************
C     *                                    *
C     * READ TEMPERATURES, PRESSURES, LHSVS *
C     *                                    *
C     **************************************
C
   90 DO 110 K=1,NT
      READ(KR,100)T1(K)
  100 FORMAT(7X,F10.5)
      T1(K)=T1(K)+460.
  110 CONTINUE
      DO 130 K=1,NP
      READ(KR,120)P1(K)
  120 FORMAT(7X,F10.5)
  130 CONTINUE
      DO 150 K=1,NL
      READ(KR,140)ALHSV1(K)
  140 FORMAT(7X,F10.5)
  150 CONTINUE
C
C
C
C             *********************************************
C             *                                           *
C             * COMBINE TEMP, PRESS, LHSV TO FORM DATA SET *
C             *                                           *
C             *********************************************
C
      LT=1
      LP=1
      LL=1
      KNTT=0
      KNTP=0
      DO 210 L=1,NPTS
      KNTT=KNTT+1
      KNTP=KNTP+1
      T(L)=T1(LT)
      P(L)=P1(LP)
      ALHSV(L)=ALHSV1(LL)
      IF (KNTT.NE.NP*NL) GO TO 180
      KNTT=0
      LT=LT+1
  180 IF (LP.NE.NP) GO TO 190
      IF (KNTP.EQ.NL) LP=0



  190 IF (KNTP.NE.NL) GO TO 200
      KNTP=0
      LP=LP+1
  200 IF (LL.EQ.NL) LL=0
      LL=LL+1
  210 CONTINUE
C
C
C
C             ******************************************
C             *                                        *
C             * START EQUILIBRIUM CONSTANT CALCULATIONS *
C             *                                        *
C             * PRE-EXPONENTIAL CONSTANTS              *
C             * ARX-REACTION                           *
C             * AH2-HYDROGEN                           *
C             * AP -PRODUCT                            *
C             * AR -REACTANT                           *
C             *                                        *
C             * EQUILIBRIUM CONSTANTS                  *
C             *                                        *
C             * KRX-REACTION                           *
C             * KH2-HYDROGEN ADSORPTION                *
C             * KP -PRODUCT ADSORPTION                 *
C             * KR -REACTANT ADSORPTION                *
C             *                                        *
C             ******************************************
C
      DO 220 L=1,NPTS
      TK(L)=T(L)/1.8
      S(L)=DEXP(-S1/TK(L)-S2)*P(L)*100.
      TR=TK(L)/TC
      D1=.33583-.33853*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D2=.29807-.09045*TR-.04842*TR*TR
      TR=TREFL/TC
      D3=.33583-.33853*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D4=.29807-.09045*TR-.04842*TR*TR
      D5=D1*(1.-W*D2)/D3/(1.-W*D4)
      DENS(L)=MWB/D5/VBREF
      KH2(L)=AH2*DEXP(EH2/R/TK(L))
      KRX(L)=ARX*DEXP(-ERX/R/TK(L))
  220 KRDKP(L)=ARDP*DEXP(ERDP/R/TK(L))
C
C
C
C             ***************************************************
C             *                                                 *
C             * CALCULATE OUTLET CONCENTRATION  CR=FCN(CR)      *
C             *                                                 *
C             * CG1-4=ESTIMATED VALUES (0<CG<CR1)               *
C             * CF1-4=CALCULATED VALUES CF=FCN(CG)              *
C             *                                                 *
C             * CG IS ADJUSTED BY DECREASING INCREMENTS UNTIL THE *
C             * INCREMENT IS LESS THAN 0.001% OF THE VALUE OF CG *
C             *                                                 *
C             ***************************************************
C
      L=0
```

```
  230 L=L+1
      CSTORE=0.0
      E=1.0
      MAX=600
      MAXE=50
      KOWNT=0
  235 KOWNT=KOWNT+1
      CG1=CR1
      DEL=CR1/10.
      IF (KOWNT.GE.MAXE) GO TO 285
  236 CF1=CR1+(CP1+CR1)*DLOG(CR1/CG1)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      KOUNT=0
  240 KOUNT=KOUNT+1
  242 CG2=CG1-DEL
      IF (CG2.GE.DABS(DEL)) GO TO 245
      DEL=DEL/10.
      GO TO 242
  245 CF2=CR1+(CP1+CR1)*DLOG(CR1/CG2)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
  248 IF (KOUNT.GE.MAX) GO TO 285
  260 IF (CF2.LE.CR1.AND.CF2.GE.0.0) GO TO 265
      IF(DABS(CG2-CF2).LT.DABS(CG1-CF1)) GO TO 261
      DEL=-DEL/10.
  261 CG1=CG2
      CF1=CF2
      GO TO 240
  265 DEL=DEL/10.
  270 CG3=CG2-DEL
      CG4=CG2+DEL
      IF (CG3.LE.0.0) CG3=0.000001
      IF (CG4.LE.0.0) CG4=0.000001
      CF3=CR1+(CP1+CR1)*DLOG(CR1/CG3)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      CF4=CR1+(CP1+CR1)*DLOG(CR1/CG4)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      IF (DABS(CG2-CF3).LT.DABS(CG2-CF4)) GO TO 275
      DEL=-DEL
  275 CG1=CG2
      CG2=CG1-DEL
      IF (CG2.LE.0.0) CG2=0.000001
      KOUNT=KOUNT+1
      CF1=CR1+(CP1+CR1)*DLOG(CR1/CG1)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      CF2=CR1+(CP1+CR1)*DLOG(CR1/CG2)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
  279 IF (KOUNT.GE.MAX) GO TO 285
  282 IF ((CG1-CF1)*(CG2-CF2).LT.0.0) GO TO 280
      GO TO 270
  280 DEL=-DEL/10.
      IF (DABS(DEL/CG2).LT.0.1D-06) GO TO 285
      IF (DABS(DEL).LE.0.1D-15) GO TO 285
      GO TO 270
C



C
C
C                   *********************************
C                   *                               *
C                   * CALCULATE EFFECTIVENESS FACTOR *
C                   *                               *
C                   *********************************
C
  285 TR=TK(L)/TC
      IF (TR.LT.0.99) GO TO 289
      WRITE(KW,287)TR
  287 FORMAT(/////10X,'THE REDUCED TEMPERATURE =',F6.1,3X,'IS ABOVE THE
     *ACCEPTABLE MAXIMUM IN THE VISCOSITY CALCULATION.',////)
  289 O=TC**(1./6.)/MWB**0.5/PC**(2./3.)
      VO1=0.015174-.02135*TR+.0075*TR*TR
      VO2=.042552-.07674*TR+.0340*TR*TR
      VIS(L)=(VO1+W*VO2)/O
      K1=(1.+(3.*VB/VA)**(2./3.))*KNUM
      DAB(L)=K1*TK(L)/VIS(L)/VA**(1./3.)
      DEFF(L)=VF*DAB(L)/TOR*(1.-SIZ/PRAD)**4.
      KOB=DLOG(CR1/CG2)*ALHSV(L)
      H=CRAD*(KOB/DEFF(L)/3600.)**0.5
      E1(L)=3./H/H*(H*((DEXP(H)+DEXP(-H))/(DEXP(H)-DEXP(-H)))-1.)
      IF (DABS(E-E1(L))/E1(L).LT.0.000002) GO TO 290
      IF (DABS(EOLD-E1(L))/E1(L).LT.0.000002) GO TO 290
      CSTORE=CG2
      EOLD=E
      E=E1(L)
      GO TO 235
  290 IF (KOWNT.LT.MAXE) GO TO 295
      WRITE(KW,239)MAXE,L
  239 FORMAT(//5X,'THE MAXIMUM NUMBER OF',I5,2X,'ITERATIONS HAS BEEN',
     *' REACHED IN THE EFFECTIVENESS FACTOR CALCULATION FOR POINT',I3)
  295 IF (KOUNT.LT.MAX) GO TO 299
      WRITE(KW,250)MAX,L
  250 FORMAT(//5X,'THE MAXIMUM NUMBER OF',I5,2X,'ITERATIONS HAS BEEN',
     *' REACHED IN THE OUTLET CONC. CALCULATION LOOP FOR POINT',I3)
  299 C2(L)=CG2
      IF (L.LT.NPTS) GO TO 230
C .
C
C                   **********************************
C                   *                                *
C                   * WRITE KINETIC MODEL INFORMATION *
C                   *                                *
C                   **********************************
C
      WRITE(KW,310)
  310 FORMAT(1H1        //5X,'THIS PROGRAM GENERATES A SET OF OUTLET REACT
     *ANT CONCENTRATIONS GIVEN TEMPERATURE, PRESSURE,',//5X,'LHSV, AND I
     *NLET REACTANT CONCENTRATIONS GIVEN AN INTEGRATED RATE EQUATION AND
     * ITS RATE CONSTANTS ',//5X,' IT THEN FITS AN N-TH ORDER GLOBAL MOD
     *EL EQUATION TO THIS SET OF HYPOTHETICALLY GENERATED DATA.')
      IF (HI.EQ.1) GO TO 313
  309 WRITE(KW,311)
  311 FORMAT(//////5X,'FOR THIS CASE  '///5X,                  'REACTION A
     *CTIVATION ENERGY   =',F6.2,1X,'KCAL/GMOLE',/5X,'HYDROGEN HEAT OF AD
     *SORPTION =',F6.2,1X,'KCAL/GMOLE',/5X,'PRODUCT HEAT OF ADSORPTION
     *=' ,F6.2,1X,'KCAL/GMOLE',/5X,'REACTANT HEAT OF ADSORPTION =',F6.2,
     *1X,'KCAL/GMOLE',//5X,'ADSORPTION RATE CONSTANT RATIO   K-H2 (1/MOL
```

```
     *E% H2) : K-PRODUCT (1/MOLE% H2S)      1 :',F6.1,/38X,'K-H2 (1/MOLE%
     * H2) : K-REACTANT (1/MOLE% DBT)     1 :', F6.1,/5X,'FOR A REFERENCE
     * VALUE FOR K-H2 = ',1PD9.3,1X,'1/PSI  AT 625K.',//5X,'WT% IS THE W
     *EIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK ELUID.',/////)
  313 WRITE(KW,312)ERX/1000.,EH2/1000.,ERDP/1000
  312 FORMAT(/////5X,'FOR THIS CASE :',//5X,'REACTION ACTIVATION ENERGY
     *=',E12.6,3X,'KCAL/GMOLE',/5X,'HYDROGEN HEAT OF ADSORPTION =',E12.6
     *,3X,'KCAL/GMOLE',/5X,'REACTANT-PRODUCT HEAT OF ADSORPTION DIFFEREN
     *CE =',E12.6,///5X,'WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN T
     *HE BULK FLUID.',///)
  314 WRITE(KW,315)CRAD=20.,PRAD=2.,VF,TOR
  315 FORMAT(///5X,'CATALYST PROPERTIES ARE :',//8X,'PARTICLE DIAMETER =
     *',F5.2,1X,'(MM)',/8X,'AVERAGE PORE DIAMETER =',F6 1,1X,'(ANGSTROMS
     *)',/8X,'VOID FRACTION =',F6.3,/8X,'TORTUOSITY FACTOR =',F5.2,////)
C
C
C
C              ************************************
C              *                                  *
C              * WRITE GENERATED DATA FOR THIS SET *
C              *                                  *
C              ************************************
C
      WRITE(KW,320)
  320 FORMAT(8X,'RUN',5X,'TEMP',6X,'PRESS',6X,'LHSV',8X,'H2 SOLUBILITY',
     *5X,'EFF DIFF',6X,'EFF FACTOR',5X,'IN. CONC.',6X,'FIN. CONC.',/18X,
     *'(F)',7X,'(PSI)',5X,'(1/HR)',11X,'(WT%)',7X,'(SQ CM/SEC)',22X,'(WT
     *%)',10X,'(WT%)',/)
      DO 350 L=1,NPTS
  330 Y(L)=C2(L)
      C2D(L)=Y(L)
      C1(L)=CR1
      WRITE(KW,340)L,T(L)-460.,P(L),ALHSV(L),S(L),DEFF(L),E1(L),C1(L),Y(
     *L)
  340 FORMAT(5X,I5,F10.1,F11.1,F10.2,5X,5E15.5)
  350 CONTINUE
      CMIN=0.01
      CMIN=0.1D-06
      NDAT=NPTS
      DO 600 J=1,NDAT
  600 IF (C2D(J).LT.CMIN) NPTS=NPTS-1
  400 CALL STEPT (EXFIT)
      DEV=0.0
      DEV1=0.0
      SOS=0.0
      DO 405 JJ=1,NPTS
  404 DEV=DEV+DABS(C2C(JJ)-C2D(JJ))/NPTS
      DEV1=DEV1+DABS(C2C(JJ)-C2D(JJ))/NPTS/C2D(JJ)*100.
      SOS=SOS+(C2C(JJ)-C2D(JJ))**2
  405 CONTINUE
      WRITE(KW,500)
  500 FORMAT(1H1,/////5X,'N-TH ORDER GLOBAL MODEL PARAMETERS',/)
      WRITE(KW,510)X(1),X(2),X(4)
  510 FORMAT(//5X,'AP**M = ',E10.4,3X,'WT%**(1-N)/HR',//5X,'E = ',E10.4,
     *3X,'CAL/GMOLE',//5X,'N = ',E10.4)
      WRITE(KW,520)DEV,DEV1,FOBJ,SOS
  520 FORMAT(////5X,'MEAN DEVIATION = ',E10.4,//5X,'AVG. PERCENT ERROR =
     * ',E10.4,//5X,'FOBJ = ',E10.4,//5X,'SUM OF SQUARES = ',E10.4,////)
      IF (ORDER.EQ.1.0) GO TO 999
      IF (X(4).LT.0.9998) GO TO 999



      IF (X(4).GT.1.0002) GO TO 999
      IF (X(4).GE.1.0001.AND.X(4).LE.1.0002) GO TO 995
  901 FLAMB=1.
      XMAX(4)=.1D31
      XMIN(4)=1.0001
      X(1)=X1
      X(2)=X2
      X(3)=X3
      X(4)=1.21
      X(4)=1.5
      FLAMB=1.0
      GO TO 400
  995 ORDER=1.0
      NV=3
      FLAMB=1.0
      GO TO 400
  999 STOP
      END
C
C
C
C     ***************************
C     *                         *
C     * END DATA GENERATION LOOPS *
C     *                         *
C     ***************************
C
C
C
C
C     *************************
C     *                       *
C     * DATA FITTING SUBROUTINE *
C     *                       *
C     *************************
C

      SUBROUTINE EXFIT (FITM)
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 KRXN,KHYD,KRCT,KPRO
      DOUBLE PRECISION X,FIT,QEXP,DEXP,ARG,FITM,FF
      DIMENSION FITM(300)
      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(27),P(27),ALHSV(27),C1(27),TERM(27),T1(10),P1(10)
     *,ALHSV1(10),E1(27),DAB(27),DEFF(27),S(27),VIS(27),TEMP(10),
     *DENS(27),TK(27),C2C(27),C2D(27),DEV,DEV1,DEV2,CP1,WT,VR,ORDER,
     *2,CMIN,HI,NDAT
      QEXP(ARG)=DEXP(ARG)
      K=0
      R=1.9872
      FOBJ=0.
      DO 380 J=1,NPTS
  480 K=K+1
      IF (K.GT.NDAT) GO TO 380
      IF (C2D(K).LT.CMIN) GO TO 480
      Y(J)=0.0
      Y(J)=C2D(K)
```

```
               YSIG(J)=Y(J)
               YSIG(J)=1.
               C2D(J)=C2D(K)
               IF (ORDER.EQ.1.0) GO TO 500
               TERM(J)=(C1(K)**(1.-X(4))-X(1)*DEXP(-X(2)/R/TK(K))*P(K)**X(3)
              **(1.-X(4))/ALHSV(K))
               IF (TERM(J).LT.0.0) TERM(J)=0.0
               FF=TERM(J)**(1./(1.-X(4)))
               GO TO 501
         500   FF=C1(K)/DEXP(X(1)*DEXP(-X(2)/R/TK(K))*P(K)**X(3)/ALHSV(K))
         501   FITM(J)=FF
               C2C(J)=FF
         504   FOBJ=FOBJ+((FF-Y(J))/YSIG(J))**2
         380   CONTINUE
               RETURN
               END

      $ENTRY
```

```
THIS PROGRAM GENERATES A SET OF OUTLET REACTANT CONCENTRATIONS GIVEN TEMPERATURE, PRESSURE,

LHSV, AND INLET REACTANT CONCENTRATIONS GIVEN AN INTEGRATED RATE EQUATION AND ITS RATE CONSTANTS.

 IT THEN FITS AN N-TH ORDER GLOBAL MODEL EQUATION TO THIS SET OF HYPOTHETICALLY GENERATED DATA.



FOR THIS CASE :

REACTION ACTIVATION ENERGY =0.384087D 02   KCAL/GMOLE
HYDROGEN HEAT OF ADSORPTION =0.209347D 02   KCAL/GMOLE
REACTANT-PRODUCT HEAT OF ADSORPTION DIFFERENCE =************


WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.



CATALYST PROPERTIES ARE :

   PARTICLE DIAMETER = 0.21 (MM)
   AVERAGE PORE DIAMETER =  28.0 (ANGSTROMS)
   VOID FRACTION = 0.500
   TORTUOSITY FACTOR = 2.50


   RUN    TEMP      PRESS     LHSV       H2 SOLUBILITY     EFF DIFF        EFF FACTOR      IN. CONC.      FIN. CONC.
           (F)      (PSI)    (1/HR)         (WT%)        (SQ CM/SEC)                       (WT%)          (WT%)

    1    450.0     1000.0     1.00      0.11726D 00     0.25943D-06    0.99974D 00    0.24300D 01    0.23499D 01
    2    450.0     1000.0     3.00      0.11726D 00     0.25943D-06    0.99971D 00    0.24300D 01    0.24001D 01
    3    450.0     1000.0     6.00      0.11726D 00     0.25943D-06    0.99970D 00    0.24300D 01    0.24145D 01
    4    450.0     1000.0     9.00      0.11726D 00     0.25943D-06    0.99970D 00    0.24300D 01    0.24196D 01
    5    450.0     1000.0    12.00      0.11726D 00     0.25943D-06    0.99969D 00    0.24300D 01    0.24221D 01
    6    500.0     1000.0     1.00      0.12624D 00     0.31546D-06    0.99868D 00    0.24300D 01    0.19820D 01
    7    500.0     1000.0     3.00      0.12624D 00     0.31546D-06    0.99845D 00    0.24300D 01    0.22436D 01
    8    500.0     1000.0     6.00      0.12624D 00     0.31546D-06    0.99836D 00    0.24300D 01    0.23295D 01
    9    500.0     1000.0     9.00      0.12624D 00     0.31546D-06    0.99833D 00    0.24300D 01    0.23610D 01
   10    500.0     1000.0    12.00      0.12624D 00     0.31546D-06    0.99831D 00    0.24300D 01    0.23775D 01
   11    550.0     1000.0     1.00      0.13491D 00     0.38662D-06    0.99452D 00    0.24300D 01    0.85408D 00
   12    550.0     1000.0     3.00      0.13491D 00     0.38662D-06    0.99369D 00    0.24300D 01    0.16258D 01
   13    550.0     1000.0     6.00      0.13491D 00     0.38662D-06    0.99331D 00    0.24300D 01    0.19632D 01
   14    550.0     1000.0     9.00      0.13491D 00     0.38662D-06    0.99314D 00    0.24300D 01    0.21005D 01
   15    550.0     1000.0    12.00      0.13491D 00     0.38662D-06    0.99305D 00    0.24300D 01    0.21752D 01
   16    600.0     1000.0     1.00      0.14328D 00     0.47845D-06    0.97517D 00    0.24300D 01    0.58347D-02
   17    600.0     1000.0     3.00      0.14328D 00     0.47845D-06    0.97622D 00    0.24300D 01    0.35515D 00
   18    600.0     1000.0     6.00      0.14328D 00     0.47845D-06    0.97694D 00    0.24300D 01    0.95767D 00
   19    600.0     1000.0     9.00      0.14328D 00     0.47845D-06    0.97727D 00    0.24300D 01    0.13182D 01
   20    600.0     1000.0    12.00      0.14328D 00     0.47845D-06    0.97746D 00    0.24300D 01    0.15419D 01
   21    650.0     1000.0     1.00      0.15135D 00     0.59920D-06    0.90097D 00    0.24300D 01    0.50448D-14
```

```
22     650.0    1000.0     3.00        0.15135D 00   0.59920D-06   0.90679D 00   0.24300D 01   0.58376D-04
23     650.0    1000.0     6.00        0.15135D 00   0.59920D-06   0.91587D 00   0.24300D 01   0.22702D-01
24     650.0    1000.0     9.00        0.15135D 00   0.59920D-06   0.92404D 00   0.24300D 01   0.15128D 00
25     650.0    1000.0    12.00        0.15135D 00   0.59920D-06   0.93010D 00   0.24300D 01   0.36413D 00
```

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

MASK   =       0             0             1             0

X      =   0.10000D 11  0.30000D 05  0.00000D 00  0.50000D 00

XMAX   =   0.10000D 31  0.10000D 31  0.10000D 31  0.99990D 00

XMIN   =   0.00000D 00  0.00000D 00  0.00000D 00 -0.10000D 31

DELMN  =   0.10000D 03  0.30000D-03  0.00000D 00  0.50000D-08

NV =   4      NPTS =    24      LPDMA =   300      LPDMB =  20      NTRAC = 0      METHO =  1      KALCP =  0

KORDF = 1      NFLAT = 1      NFMAX =   4000      MAXIT =  400      MXSUB =  25

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

PHI (THE SUM OF SQUARES) = 0.37228198D 02                                                 LAMBDA = 0.10000D 01

********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(  2,  1) =  0.10000000D 01          ITERATION    1
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(  3,  1) =  0.10000000D 01          ITERATION    1
********  POSSIBLY DANGEROUS VALUE OF COEFFICIENT....      QSAV(  3,  2) =  0.10000000D 01          ITERATION    1

CONSTRAINT VIOLATED BY X(  4).   VALUE RESET TO  0.99989998D 00 USING CUTSTEP FACTOR =  0 17873D 00    ITER.    2

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION    3

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION    4

CONSTRAINT VIOLATED BY X(  4).   VALUE RESET TO  0.99989998D 00 USING CUTSTEP FACTOR =  0.64196D 00    ITER.   27

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   28

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   28

FIX  X(  4] =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   29

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   30

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   30

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   31

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   32

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   33

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   34

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   35

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   36

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   37

FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   38
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FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   39
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   40
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   41
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   42
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   43
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   44
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   45
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   46
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   47
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   47
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   48
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   49
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   50
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   51
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   52
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   53
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   53
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   53
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   53
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   53
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   54
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   54
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   54
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   55
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   56
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   56
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   56
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   56
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   57
FIX  X(  4) =  0.99990D 00 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                    ITERATION   58


CONVERGED WHEN THE STEP BECAME SMALL.
  58 ITERATIONS        NF =  340         PHI = 0.44886544D-01          FMGN = 0.10000D 01        LAMBDA = 0.12833D 05
        NORM OF SCALED GRADIENT VECTOR = 0.98916D-05
              X =   0.7442968D 14  0.3543814D 05  0.0000000D 00  0.9990000D 00

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

            1     0.23499340E 01     0.23448697D 01     0.50648D-02     0.10000D 01          0.50648D-02
            2     0.24001210E 01     0.24012855D 01    -0.11638D-02     0.10000D 01         -0.11638D-02
            3     0.24145390E 01     0.24156002D 01    -0.10609D-02     0.10000D 01         -0.10609D-02
            4     0.24195660E 01     0.24203908D 01    -0.82460D-03     0.10000D 01         -0.82460D-03
            5     0.24221250E 01     0.24227888D 01    -0.66376D-03     0.10000D 01         -0.66376D-03
            6     0.18819750E 01     0.18424892D 01     0.39486D-01     0.10000D 01          0.39486D-01
            7     0.22436280E 01     0.22552291D 01    -0.11601D-01     0.10000D 01         -0.11601D-01
            8     0.23294580E 01     0.23409844D 01    -0.11526D-01     0.10000D 01         -0.11526D-01
            9     0.23610350E 01     0.23702881D 01    -0.92527D-02     0.10000D 01         -0.92527D-02
           10     0.23774960E 01     0.23850772D 01    -0.75804D-02     0.10000D 01         -0.75804D-02
           11     0.85408040E 00     0.75252228D 00     0.10156D 00     0.10000D 01          0.10156D 00
           12     0.16258390E 01     0.16440586D 01    -0.18219D-01     0.10000D 01         -0.18219D-01
           13     0.19631610E 01     0.19987692D 01    -0.35608D-01     0.10000D 01         -0.35608D-01
           14     0.21004660E 01     0.21332613D 01    -0.32795D-01     0.10000D 01         -0.32795D-01
           15     0.21752200E 01     0.22038635D 01    -0.28643D-01     0.10000D 01         -0.28643D-01
           16     0.58346680E-02     0.12750103D-01    -0.69154D-02     0.10000D 01         -0.69154D-02
           17     0.35514670E 00     0.42238498D 00    -0.67238D-01     0.10000D 01         -0.67238D-01
           18     0.95766690E 00     0.10131506D 01    -0.55484D-01     0.10000D 01         -0.55484D-01
           19     0.13182420E 01     0.13561940D 01    -0.37952D-01     0.10000D 01         -0.37952D-01
           20     0.15419260E 01     0.15690773D 01    -0.27151D-01     0.10000D 01         -0.27151D-01
           21     0.66376460E-04     0.28753210D-08     0.66374D-04     0.10000D 01          0.66374D-04
           22     0.22702300E-01     0.25822900D-02     0.20120D-01     0.10000D 01          0.20120D-01
           23     0.15127890E 00     0.79261122D-01     0.72018D-01     0.10000D 01          0.72018D-01
           24     0.36412790E 00     0.24810307D 00     0.11602D 00     0.10000D 01          0.11602D 00

NUMBER OF DEGREES OF FREEDOM =  0.21000D 02

R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.46130D-01

MAXIMUM SCALED DEVIATION = 0.11602D 00

SUBROUTINE MOERR

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

   1     0.1000000D 01

   2    -0.9993942D 00   0.1000000D 01

   3     0.7610400D 00  -0.7732414D 00   0.1000000D 01
```

```
NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    21

EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SORT(2*N.D.F.) =    21  PLUS OR MINUS 0.64807D 01

ACTUAL VALUE OF PHI = 0.44687D-01

RESCALING FACTOR = SORT(PHI/N.D.F.) = 0.46129D-01


MAXIMUM VARIANCE INFLATION FACTOR = 0.12046D 04

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

           1         0       0.74429691D 14     0.11860D 16     0.54710D 14

           2         0       0.35436138D 05     0.18733D 05     0.86414D 03

           3         1       0.00000000D 00     0.00000D 00     0.00000D 00

           4         0       0.99989998D 00     0.16465D 01     0.75950D-01


LOWER TRIANGLE OF THE CORRELATION MATRIX....

             K ....    1             2             3             4

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

  J     MASK(J)

  1        0       0.10000D 01

  2        0       0.99897D 00  0.10000D 01

  3        1       0.00000D 00  0.00000D 00  0.00000D 00

  4        0       0.53167D 00  0.56088D 00  0.00000D 00  0.10000D 01
```

```
N-TH ORDER GLOBAL MODEL PARAMETERS


AP**M = 0.7443D 14   WT%**(1-N)/HR

E = 0.3544D 05   CAL/GMOLE

N = 0.9999D 00


MEAN DEVIATION = 0.2950D-01

AVG. PERCENT ERROR = 0.1824D 02

FOBJ = 0.4469D-01

SUM OF SOUARES = 0.4469D-01
```

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

MASK   :        0              0              1              0

X      :   0.100000D 11   0.300000D 05   0.000000D 00   0.150000D 01

XMAX   :   0.100000D 31   0.100000D 31   0.100000D 31   0.100000D 31

XMIN   :   0.000000D 00   0.000000D 00   0.000000D 00   0.10001D 01

DELMN  :   0.100000D 03   0.30000D-03    0.000000D 00   0.50000D-08

NV :   4      NPTS :    24      LPDMA :   300      LPDMB :  20      NTRAC : 0      METHD :  1      KALCP :  0

KORDF : 1      NFLAT : 1      NFMAX :   4000      MAXIT :  400      MXSUB :  25

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

PHI (THE SUM OF SQUARES) : 0.32102702D 02                                                LAMBDA : 0.100000D 01


CONSTRAINT VIOLATED BY X(  4).   VALUE RESET TO  0.10001001D 01 USING CUTSTEP FACTOR :  0.71984D 00    ITER.      3

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    4

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    5

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    6

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    6

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    7

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    8

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    8

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION    9

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   10

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   10

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   11

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   12

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   12

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   13

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   14

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   14

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   15



FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   16

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   17

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   18

FIX  X(  4) :  0.10001D 01 TEMPORARILY, TO AVOID VIOLATING A CONSTRAINT.                          ITERATION   19

CONVERGENCE ACHIEVED UNDER THE NFLAT OPTION.
  58 ITERATIONS          NF :  334           PHI : 0.28107132D-01           FMGN : 0.100000D 01         LAMBDA : 0.10395D 03
         NORM OF SCALED GRADIENT VECTOR : 0.53081D-08
               X :   0.2240597D 15  0.3680201D 05  0.0000000D 00  0.1210068D 01

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

            1     0.23499340E 01    0.23507170D 01    -0.78245D-03     0.100000D 01     -0.78245D-03
            2     0.24001210E 01    0.24032180D 01    -0.30963D-02     0.100000D 01     -0.30963D-02
            3     0.24145390E 01    0.24165643D 01    -0.20249D-02     0.100000D 01     -0.20249D-02
            4     0.24195660E 01    0.24210329D 01    -0.14668D-02     0.100000D 01     -0.14668D-02
            5     0.24221250E 01    0.24232710D 01    -0.11452D-02     0.100000D 01     -0.11452D-02
            6     0.19819750E 01    0.19516882D 01     0.30287D-01     0.100000D 01      0.30287D-01
            7     0.22436280E 01    0.22562377D 01    -0.12609D-01     0.100000D 01     -0.12609D-01
            8     0.23294580E 01    0.23411693D 01    -0.11711D-01     0.100000D 01     -0.11711D-01
            9     0.23610350E 01    0.23703362D 01    -0.93008D-02     0.100000D 01     -0.93008D-02
           10     0.23774960E 01    0.23850844D 01    -0.75877D-02     0.100000D 01     -0.75877D-02
           11     0.85408040E 00    0.79993305D 00     0.54147D-01     0.100000D 01      0.54147D-01
           12     0.16258390E 01    0.16290578D 01    -0.32185D-02     0.100000D 01     -0.32185D-02
           13     0.19631610E 01    0.19812913D 01    -0.18130D-01     0.100000D 01     -0.18130D-01
           14     0.21004660E 01    0.21187542D 01    -0.18287D-01     0.100000D 01     -0.18287D-01
           15     0.21752200E 01    0.21918060D 01    -0.16586D-01     0.100000D 01     -0.16586D-01
           16     0.58346680E-02    0.51488285D-01    -0.45654D-01     0.100000D 01     -0.45654D-01
           17     0.35514670E 00    0.46441180D 00    -0.10927D 00     0.100000D 01     -0.10927D 00
           18     0.95766690E 00    0.98896263D 00    -0.31296D-01     0.100000D 01     -0.31296D-01
           19     0.13182420E 01    0.13101141D 01     0.81280D-02     0.100000D 01      0.81280D-02
           20     0.15419260E 01    0.15177153D 01     0.24211D-01     0.100000D 01      0.24211D-01
           21     0.66376460E-04    0.42948730D-03    -0.36311D-03     0.100000D 01     -0.36311D-03
           22     0.22702300E-01    0.20963057D-01     0.17392D-02     0.100000D 01      0.17392D-02
           23     0.15127890E 00    0.12763088D 00     0.23648D-01     0.100000D 01      0.23648D-01
           24     0.36412790E 00    0.28267751D 00     0.81450D-01     0.100000D 01      0.81450D-01

NUMBER OF DEGREES OF FREEDOM :  0.21000D 02

R.M.S  SCALED DEVIATION OF DATA FROM FIT : 0.38586D-01

MAXIMUM SCALED DEVIATION : 0.10927D 00


SUBROUTINE MOERR

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

   1     0.1000000D 01
```

```
  2    -0.9893938D 00   0.1000000D 01

  3     0.7528815D 00  -0.7654432D 00   0.1000000D 01


NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    21

EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =    21  PLUS OR MINUS 0.64807D 01

ACTUAL VALUE OF PHI = 0.28107D-01

RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.36585D-01


MAXIMUM VARIANCE INFLATION FACTOR = 0.12209D 04


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

            1          0        0.22405973D 15      0.38333D 16      0.14024D 15

            2          0        0.36802010D 05      0.20083D 05      0.73511D 03

            3          1        0.00000000D 00      0.00000D 00      0.00000D 00

            4          0        0.12100680D 01      0.17028D 01      0.62287D-01


LOWER TRIANGLE OF THE CORRELATION MATRIX....

             K ....     1             2             3             4

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

  J     MASK(J)

  1        0.       0.10000D 01

  2        0        0.99801D 00  0.10000D 01

  3        1        0.00000D 00  0.00000D 00  0.00000D 00

  4        0        0.54132D 00  0.56941D 00  0.00000D 00  0.10000D 01







     N-TH ORDER GLOBAL MODEL PARAMETERS


     AP**M = 0.2241D 15   WT%**(1-N)/HR

     E = 0.3680D 05   CAL/GMOLE

     N = 0.1210D 01


     MEAN DEVIATION = 0.2151D-01

     AVG. PERCENT ERROR = 0.5934D 02

     FOBJ = 0.2811D-01

     SUM OF SQUARES = 0.2811D-01



STATEMENTS EXECUTED=  563816

CORE USAGE        OBJECT CODE=   57568 BYTES,ARRAY AREA=   66984 BYTES,TOTAL AREA AVAILABLE=  174080  BYTES

DIAGNOSTICS         NUMBER OF ERRORS=        0, NUMBER OF WARNINGS=        0, NUMBER OF EXTENSIONS=       16

COMPILE TIME=     0.41 SEC,EXECUTION TIME=     6.75 SEC,      23.32.31     MONDAY        25 JUL 83     WATFIV - MAR 1980 V2L0

        C$STOP
```

APPENDIX H

DIBENZOTHIOPHENE HYDRODESULFURIZATION PROCESS MODEL FIT TO NON-ISOTHERMAL DATA

```
$JOB
C     ***********************************************************
C     *                                                         *
C     *  DIBENZOTHIOPHENE HDS PROCESS MODEL                     *
C     *                                                         *
C     *  DATA FROM ESPINO                                       *
C     *                                                         *
C     *  FIT TO NON-ISOTHERMAL DATA                             *
C     *                                                         *
C     *  ALL KINETIC PARAMETERS FIXED AT THE VALUES OBTAINED FROM *
C     *  LINEAR FITS OF THEIR ARRHENIUS PLOTS DETERMINED FROM   *
C     *  ISOTHERMAL CALCULATIONS                                *
C     *                                                         *
C     ***********************************************************
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGER ZZ
      REAL*8 KRX,KH2,KP,KRE,KH2REF,K1,H,KOB,KNUM
      REAL*8 KRDKP
      DIMENSION KRX(70),KH2(70),KRDKP(70),C2(70)
      EXTERNAL EXFIT
      DOUBLE PRECISION X,FIT
      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,MXSUE,MXUPD
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
      COMMON /CSTOR/ T(70),P(70),ALHSV(70),C1(70),TERM(70),T1(10),P1(10)
     *,ALHSV1(10),E1(70),DAB(70),DEFF(70),S(70),VIS(70),TEMP(10),
     *DENS(70),DEV,CP1,WT,VR,HI,TK(70),        DEV1,DEV2,C2C(70),C2D(70),
     *ORDER,Z,CMIN,NDAT
      QEXP(ARG)=DEXP(ARG)
      CALL STSET
C
C
C
C
C     **********************
C     *                    *
C     * MARQUARDT VARIABLES *
C     *                    *
C     **********************
C
C
      HI=0
      FL=1.
      KR=5
      KW=6
      MATRX=1
      NFMAX=5000
      MAXIT=400
      MAXIT=1
      METHD=1
      NTRAC=0
      NV=6
      XMIN(3)=8.1D13
      XMAX(3)=8.2D13
      MASK(1)=1


      MASK(2)=1
      MASK(4)=1
      MASK(5)=1
      MASK(6)=1
      X(1)=1.1848D-7
      X(2)=20934.7
      X(3)=8.1276D13
      X(4)=38408.7
      X(5)=1.3178D7
      X(6)=-18971.8
      X1=X(1)
      X2=X(2)
      X3=X(3)
      X4=X(4)
C
C
C     **********************************
C     *                                *
C     *  MODEL CONSTANTS AND VARIABLES *
C     *                                *
C     **********************************
C
      AH2=1.1848D-07
      ARDP=1.3178D+07
      ARX=8.1276D+13
      CP1=0.0
      CRAD=0.0105
      CR22=0.5
      CR1=2.43
      EH2=20934.7
      ERDP=-18971.8
      ERX=38408.7
      EOLD=0.5
      MWB=132.205
      MWH2=2.016
      MWP=34.08
      MWR=184.27
      MWS=32.064
C
      NL=1
      NL=5
      NP=6
      NP=1
      NT=1
      NT=5
      NPTS=NT*NP*NL
      ORDER=0.0
      PC=34.7
      PRAD=14.0
      R=1.9872
      S1=716.0
      S2=12.24
      SI2=10.5
      TC=719.0
      TOR=2.5
      TREF=625.0
      TREFL=293.0
      VA=182.0
      VB=147.0
      VBREF=135.87
```

```
      VF=0.5
      VR=15.0
      W=0.303
      WT=6.0
      ZZ=1
C
C     ***************************************************************
C     *                                                             *
C     *   INPUT=1   IF DATA IS TO BE HYPOTHETICALLY GENERATED       *
C     *   INPUT=2   IF DATA IS TO BE SUPPLIED                       *
C     *                                                             *
C     *   DATA MAY BE GENERATED IN TWO MANNERS:                     *
C     *       1 SUPPLY ALL PRE-EXPONENTIAL AND EXPONENTIAL CONSTANTS *
C     *       2 SUPPLY EXPONENTIAL CONSTANTS AND RATIOS OF EQUILIBRIUM *
C     *         CONSTANTS AT A SPECIFIED REFERENCE TEMPERATURE      *
C     *                                                             *
C     ***************************************************************
C
C
      KNUM=17.5D-8
      IF (VA/VB.GE.2.5) KNUM=8.2D-8
      IF (VA/VB.LE.1.0) KNUM=25.2D-8
C
      READ(KR,10)NPTS
   10 FORMAT(I5)
      DO 30 K=1,NPTS
      READ(KR,20)T(K),P(K),ALHSV(K),C1(K),Y(K)
   20 FORMAT(7X,5F10.5)
      C2(K)=Y(K)
   30 T(K)=T(K)+460.
      IF (HI.EQ.0) GO TO 555
C
C
C     ***************************************
C     *                                     *
C     * READ TEMPERATURES, PRESSURES, LHSVS *
C     *                                     *
C     ***************************************
C
   90 DO 110 K=1,NT
      READ(KR,100)T1(K)
  100 FORMAT(7X,F10.5)
      T1(K)=T1(K)+460.
  110 CONTINUE
      DO 130 K=1,NP
      READ(KR,120)P1(K)
  120 FORMAT(7X,F10.5)
  130 CONTINUE
      DO 150 K=1,NL
      READ(KR,140)ALHSV1(K)
  140 FORMAT(7X,F10.5)
  150 CONTINUE
C
C
C
C             *******************************************
C             *                                         *
C             * COMBINE TEMP, PRESS, LHSV TO FORM DATA SET *
C             *                                         *
C             *******************************************


C
      LT=1
      LP=1
      LL=1
      KNTT=0
      KNTP=0
      DO 210 L=1,NPTS
      KNTT=KNTT+1
      KNTP=KNTP+1
      T(L)=T1(LT)
      P(L)=P1(LP)
      ALHSV(L)=ALHSV1(LL)
      IF (KNTT.NE.NP*NL) GO TO 180
      KNTT=0
      LT=LT+1
  180 IF (LP.NE.NP) GO TO 190
      IF (KNTP.EQ.NL) LP=0
  190 IF (KNTP.NE.NL) GO TO 200
      KNTP=0
      LP=LP+1
  200 IF (LL.EQ.NL) LL=0
      LL=LL+1
  210 CONTINUE
C
C
C
C             *******************************************
C             *                                         *
C             * START EQUILIBRIUM CONSTANT CALCULATIONS *
C             *                                         *
C             * PRE-EXPONENTIAL CONSTANTS               *
C             * ARX-REACTION                            *
C             * AH2-HYDROGEN                            *
C             * AP -PRODUCT                             *
C             * AR -REACTANT                            *
C             *                                         *
C             * EQUILIBRIUM CONSTANTS                   *
C             *                                         *
C             * KRX-REACTION                            *
C             * KH2-HYDROGEN ADSORPTION                 *
C             * KP -PRODUCT ADSORPTION                  *
C             * KR -REACTANT ADSORPTION                 *
C             *                                         *
C             *******************************************
C
  555 DO 220 L=1,NPTS
      TK(L)=T(L)/1.8
      S(L)=DEXP(-S1/TK(L)-S2)*P(L)*100
      TR=TK(L)/TC
      D1=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D2=.29607-.09045*TR-.04842*TR*TR
      TR=TREFL/TC
      D3=.33593-.33953*TR+1.51941*(TR**2)-2.02512*(TR**3)+1.11422*(TR**4
     *)
      D4=.29607-.09045*TR-.04842*TR*TR
      D5=D1*(1.-W*D2)/D3/(1.-W*D4)
      DENS(L)=MWB/D5/VBREF
      KH2(L)=AH2*DEXP(EH2/R/TK(L))
      KRX(L)=ARX*DEXP(-ERX/R/TK(L))
```

```
  220 KRDKP(L)=ARDP*DEXP(ERDP/R/TK(L))
      IF (HI.EQ.0) GO TO 284
C
C
C
C             *****************************************************
C             *                                                   *
C             * CALCULATE OUTLET CONCENTRATION  CR=FCN(CR)        *
C             *                                                   *
C             * CG1-4=ESTIMATED VALUES (0<CG<CR1)                 *
C             * CF1-4=CALCULATED VALUES CF=FCN(CG)                *
C             *                                                   *
C             * CG IS ADJUSTED BY DECREASING INCREMENTS UNTIL THE *
C             * INCREMENT IS LESS THAN 0.001% OF THE VALUE OF CG  *
C             *                                                   *
C             *****************************************************
C
      L=0
  230 L=L+1
      CSTORE=0.0
      E=1.0
      MAX=600
      MAXE=50
      KOWNT=0
  235 KOWNT=KOWNT+1
      CG1=CR1
      DEL=CR1/10.
      IF (KOWNT.GE.MAXE) GO TO 285
  236 CF1=CR1+(CP1+CR1)*DLOG(CR1/CG1)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      KOUNT=0
  240 KOUNT=KOUNT+1
  242 CG2=CG1-DEL
      IF (CG2.GE.DABS(DEL)) GO TO 245
      DEL=DEL/10.
      GO TO 242
  245 CF2=CR1+(CP1+CR1)*DLOG(CR1/CG2)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
  249 IF (KOUNT.GE.MAX) GO TO 285
  260 IF (CF2.LE.CR1.AND.CF2.GE.0.0) GO TO 265
      IF(DABS(CG2-CF2).LT.DABS(CG1-CF1)) GO TO 261
      DEL=-DEL/10.
  261 CG1=CG2
      CF1=CF2
      GO TO 240
  265 DEL=DEL/10.
  270 CG3=CG2-DEL
      CG4=CG2+DEL
      IF (CG3.LE.0.0) CG3=0.000001
      IF (CG4.LE.0.0) CG4=0.000001
      CF3=CR1+(CP1+CR1)*DLOG(CR1/CG3)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      CF4=CR1+(CP1+CR1)*DLOG(CR1/CG4)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      IF (DABS(CG2-CF3).LT.DABS(CG2-CF4)) GO TO 275
      DEL=-DEL



  275 CG1=CG2
      CG2=CG1-DEL
      IF (CG2.LE.0.0) CG2=0.000001
      KOUNT=KOUNT+1
      CF1=CR1+(CP1+CR1)*DLOG(CR1/CG1)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
      CF2=CR1+(CP1+CR1)*DLOG(CR1/CG2)/(KRDKP(L)*E-1.)-WT*S(L)*E*100.*
     *KRX(L)*KH2(L)*KRDKP(L)/ALHSV(L)/VR/DENS(L)/(1.+KH2(L)*S(L))/
     *(KRDKP(L)*E-1.)
  279 IF (KOUNT.GE.MAX) GO TO 285
  282 IF ((CG1-CF1)*(CG2-CF2).LT.0.0) GO TO 280
      GO TO 270
  280 DEL=-DEL/10.
      IF (DABS(DEL/CG2).LT.0.1D-06) GO TO 285
      IF (DABS(DEL).LE.0.1D-15) GO TO 285
      GO TO 270
C
C
C
C             ********************************
C             *                              *
C             * CALCULATE EFFECTIVENESS FACTOR *
C             *                              *
C             ********************************
C
  285 TR=TK(L)/TC
  284 DO 286 L=1,NPTS
      TR=TK(L)/TC
      CG2=Y(L)
      IF (TR.LT.0.99) GO TO 289
      WRITE(KW,287)TR
  287 FORMAT(/////10X,'THE REDUCED TEMPERATURE =',F5.1,3X,'IS ABOVE THE
     *ACCEPTABLE MAXIMUM IN THE VISCOSITY CALCULATION.',////)
  289 O=TC**(1./6.)/MWB**0.5/PC**(2./3.)
      VO1=0.015174-.02135*TR+.0075*TR*TR
      VO2=.042552-.07674*TR+.0340*TR*TR
      VIS(L)=(VO1+W*VO2)/O
      K1=(1.+(3.*VB/VA)**(2./3.))*KNUM
      DAB(L)=K1*TK(L)/VIS(L)/VA**(1./3.)
      DEFF(L)=VF*DAB(L)/TOR*(1.-SIZ/PRAD)**4.
      KOB=DLOG(CR1/CG2)*ALHSV(L)
      H=CRAD*(KOB/DEFF(L)/3600.)**0.5
      E1(L)=3./H/H*(H*((DEXP(H)+DEXP(-H))/(DEXP(H)-DEXP(-H)))-1.)
  286 CONTINUE
      IF (HI.EQ.0) GO TO 311
      IF (DABS(E-E1(L))/E1(L).LT.0.000002) GO TO 290
      IF (DABS(EOLD-E1(L))/E1(L).LT.0.000002) GO TO 290
      CSTORE=CG2
      EOLD=E
      E=E1(L)
      GO TO 235
  290 IF (KOWNT.LT.MAXE) GO TO 295
      WRITE(KW,239)MAXE,L
  239 FORMAT(//5X,'THE MAXIMUM NUMBER OF',I5,2X,'ITERATIONS HAS BEEN',
     *' REACHED IN THE EFFECTIVENESS FACTOR CALCULATION FOR POINT',I3)
  295 IF (KOUNT.LT.MAX) GO TO 299
      WRITE(KW,250)MAX,L
  250 FORMAT(//5X,'THE MAXIMUM NUMBER OF',I5,2X,'ITERATIONS HAS BEEN',
     *' REACHED IN THE OUTLET CONC. CALCULATION LOOP FOR POINT',I3)
```

```
  289 C2(L)=CC2
      IF (L.LT.NPTS) GO TO 230
C
C
C
C              ********************************
C              *                              *
C              * WRITE KINETIC MODEL INFORMATION *
C              *                              *
C              ********************************
C
      WRITE(KW,310)ERX,EH2,ERDP
  310 FORMAT(1H1       //5X,'THIS PROGRAM GENERATES A SET OF OUTLET REACT
     *ANT CONCENTRATIONS GIVEN TEMPERATURE, PRESSURE,',//5X,'LHSV, AND I
     *NLET REACTANT CONCENTRATIONS GIVEN AN INTEGRATED RATE EQUATION AND
     * ITS RATE CONSTANTS ',//5X,'IT THEN FITS A KINETIC MODEL EQUATION
     *TO THIS SET OF HYPOTHETICALLY GENERATED DATA.',
     *//////5X,'FOR THIS CASE :',///5X,                   'REACTION A
     *CTIVATION ENERGY  =',F6.2,1X,'KCAL/GMOLE',/5X,'HYDROGEN HEAT OF AD
     *SORPTION =',F6.2,1X,'KCAL/GMOLE',/5X,'PRODUCT HEAT OF ADSORPTION
     *=' ,F6.2,1X,'KCAL/GMOLE',/5X,'REACTANT HEAT OF ADSORPTION =',F8.2,
     *1X,'KCAL/GMOLE',//5X,'ADSORPTION RATE CONSTANT RATIO   K-H2 (1/MOL
     *E% H2) : K-PRODUCT (1/MOLE% H2S)      1 :',F6.1,/38X,'K-H2 (1/MOLE%
     * H2) : K-REACTANT (1/MOLE% DBT)     1 :', F5.1,/5X,'FOR A REFERENCE
     * VALUE FOR K-H2 = ',1PD9.3,1X,'1/PSI  AT 625K.',//5X,'WT% IS THE W
     *EIGHT PERCENT OF ELEMENTAL SULFUR IN THE BULK FLUID.',/////)
  311 WRITE(KW,312)
  312 FORMAT(1H1,/////5X,'THIS PROGRAM SHOWS THE ABILITY OF THE DIBENZOT
     *HIOPHENE HDS MODEL TO FIT NON-ISOTHERMAL DATA.',//5X,'THE VALUES O
     *F THE MODEL PARAMETERS ARE FIXED AT THOSE VALUES OBTAINED FROM LIN
     *EAR FITS',//5X,'TO THE ARRHENIUS PLOTS OF K,KH, AND KR/KP.',//5X,'
     *THESE ARRHENIUS PLOTS WERE DETERMINED BY THE ISOTHERMAL CALCULATIO
     *N OF THE THREE KINETIC PARAMETERS.',///5X,'WT% IS THE WEIGHT PERCE
     *NT DIBENZOTHIOPHENE IN THE BULK FLUID.')
  314 WRITE(KW,315)CRAD=20.,PRAD=2.,VF,TOR
  315 FORMAT(///5X,'CATALYST PROPERTIES ARE :',//8X,'PARTICLE DIAMETER =
     *',F5.2,1X,'(MM)',/8X,'AVERAGE PORE DIAMETER =',F6.1,1X,'(ANGSTROMS
     *)',/8X,'VOID FRACTION =',F6.3,/8X,'TORTUOSITY FACTOR =',F5.2,////)
C
C
C
C              ***********************************
C              *                                 *
C              * WRITE GENERATED DATA FOR THIS SET *
C              *                                 *
C              ***********************************
C
      WRITE(KW,320)
  320 FORMAT(8X,'RUN',5X,'TEMP',6X,'PRESS',6X,'LHSV',8X,'H2 SOLUBILITY',
     *5X,'EFF DIFF',6X,'EFF FACTOR',5X,'IN. CONC.',6X,'FIN. CONC.',/16X,
     *'(F)',7X,'(PSI)',5X,'(1/HR)',11X,'(WT%)',7X,'(SQ CM/SEC)',22X,'(WT
     *%)',10X,'(WT%)',/)
      DO 350 L=1,NPTS
  330 Y(L)=C2(L)
      C2D(L)=Y(L)
      C1(L)=CR1
      WRITE(KW,340)L,T(L)-460.,P(L),ALHSV(L),S(L),DEFF(L),E1(L),C1(L),Y(
     *L)
  340 FORMAT(5X,I5,F10.1,F11.1,F10.2,5X,5E15.5)
  350 CONTINUE



      CMIN=0.1D-06
      CMIN=0.0
      NDAT=NPTS
      DO 600 J=1,NDAT
  600 IF (C2D(J).LT.CMIN) NPTS=NPTS-1
  400 CALL STEPT (EXFIT)
      DEV=0.0
      DEV1=0.0
      SOS=0.0
      DO 405 JJ=1,NPTS
  404 DEV=DEV+DABS(C2C(JJ)-C2D(JJ))/NPTS
      DEV1=DEV1+DABS(C2C(JJ)-C2D(JJ))/NPTS/C2D(JJ)*100.
      SOS=SOS+(C2C(JJ)-C2D(JJ))**2
  405 CONTINUE
      WRITE(KW,500)
  500 FORMAT(1H1,/////5X,'DIBENZOTHIOPHENE HDS PROCESS MODEL FIT TO NON-
     *ISOTHERMAL DATA.')
      WRITE(KW,510)X(3),X(4),X(1),X(2),X(5),X(6),DEV,DEV1,FOBJ,SOS
  510 FORMAT(////5X,'THE KINETIC PARAMETERS WERE FIXED AT THE FOLLOWING
     *VALUES:',///5X,'K',5X,'A = ',E10.4,3X,'1/WT%',5X,'E = ',E10.4,3X,'
     *CAL/GMOLE',//5X,'K',5X,'AH = ',E10.4,3X,'1/WT%',5X,'EH = ',E10.4,3
     *X,'CAL/GMOLE',//5X,'KR/KP',5X,'AR/AP = ',E10.4,13X,'ER-EP = ',E11.
     *4,3X,'CAL/GMOLE',///5X,'THE RESULTING FIT:',//5X,'MEAN DEVIATION =
     * ',E12.6,//5X,'AVERAGE PERCENT ERROR = ',E12.6,//5X,'FOBJ = ',E12.
     *6,//5X,'SUM OF SQUARES = ',E12.6,//////////)
      IF (ORDER.EQ.1.0) GO TO 999
      IF (X(4).LT.0.9999) GO TO 999
      IF (X(4).GT.1.0001) GO TO 995
      IF (X(4).EQ. 1.0001) GO TO 995
  901 FLAMB=1.
      XMAX(4)= 1031
      XMIN(4)=1.0001
      X(1)=X1
      X(2)=X2
      X(3)=X3
      X(4)=1.5
      FLAMB=1.0
      GO TO 400
  995 ORDER=1.0
      NV=3
      FLAMB=1.0
      GO TO 400
  999 STOP
      END
C
C
C
C     ****************************
C     *                          *
C     * END DATA GENERATION LOOPS *
C     *                          *
C     ****************************
C
C
C
C
C     *************************
C     *                       *
C     * DATA FITTING SUBROUTINE *
C     *                       *
```

```
C       **************************
C

        SUBROUTINE EXFIT (FITM)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 KRXN,KHYD,KRCT,KPRD
        REAL*8 K2,K3,K4
        DOUBLE PRECISION X,FIT,OEXP,DEXP,ARG,FITM,FF
        DIMENSION FITM(300)
        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(70),P(70),ALHSV(70),C1(70),TERM(70),T1(10),P1(10)
       *,ALHSV1(10),E1(70),DAB(70),DEFF(70),S(70),VIS(70),TEMP(10),
       *DENS(70),DEV,CP1,WT,VR,HI,TK(70),          DEV1,DEV2,C2C(70),C2D(70),
       *ORDER,Z,CMIN,NDAT
        OEXP(ARG)=DEXP(ARG)
        K=0
        R=1.9872
        FOBJ=0.
        DO 380 J=1,NPTS
  490   K=K+1
        IF (K.GT.NDAT) GO TO 380
        IF (C2D(K).LT.CMIN) GO TO 490
        Y(J)=0.0
        Y(J)=C2D(K)
        YSIG(J)=Y(J)
        YSIG(J)=1.
        K2=X(1)*DEXP(X(2)/R/TK(J))
        K3=X(3)*DEXP(-X(4)/R/TK(J))
        K4=X(5)*DEXP(X(6)/R/TK(J))
        FF=C1(J)+(CP1+C1(J))/(K4*E1(J)-1.)*DLOG(C1(J)/C2D(J))-K2*K3*K4*WT*
       *100.*S(J)*E1(J)/ALHSV(J)/VR/DENS(J)/(1.+K2*S(J))/(K4*E1(J)-1.)
  501   FITM(J)=FF
        C2C(J)=FF
  504   FOBJ=FOBJ+((FF-Y(J))/YSIG(J))**2
  380   CONTINUE
        RETURN
        END

$ENTRY
```

```
THIS PROGRAM SHOWS THE ABILITY OF THE DIBENZOTHIOPHENE HDS MODEL TO FIT NON-ISOTHERMAL DATA.

THE VALUES OF THE MODEL PARAMETERS ARE FIXED AT THOSE VALUES OBTAINED FROM LINEAR FITS

TO THE ARRHENIUS PLOTS OF K,KH, AND KR/KP.

THESE ARRHENIUS PLOTS WERE DETERMINED BY THE ISOTHERMAL CALCULATION OF THE THREE KINETIC PARAMETERS.

WT% IS THE WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK FLUID.


CATALYST PROPERTIES ARE :

   PARTICLE DIAMETER = 0.21 (MM)
   AVERAGE PORE DIAMETER =  28.0 (ANGSTROMS)
   VOID FRACTION = 0.500
   TORTUOSITY FACTOR = 2.50


 RUN     TEMP       PRESS      LHSV        H2 SOLUBILITY     EFF DIFF       EFF FACTOR     IN. CONC.     FIN. CONC.
          (F)       (PSI)     (1/HR)           (WT%)       (SQ CM/SEC)                     (WT%)          (WT%)

   1    545.0      250.0       1.00        0.33515D-01    0.37868D-06    0.99730D 00    0 24300D 01    0.14700D 01
   2    545.0      250.0       3.00        0.33515D-01    0.37868D-06    0.99678D 00    0.24300D 01    0.19800D 01
   3    545.0      250.0       6.00        0.33515D-01    0.37868D-06    0.99665D 00    0.24300D 01    0.21900D 01
   4    545.0      250.0       9.00        0.33515D-01    0.37868D-06    0.99650D 00    0.24300D 01    0.22600D 01
   5    545.0      350.0       1.00        0.46921D-01    0.37868D-06    0.99688D 00    0.24300D 01    0.13600D 01
   6    545.0      350.0       3.00        0.46921D-01    0.37868D-06    0.99621D 00    0.24300D 01    0.19200D 01
   7    545.0      350.0       6.00        0.46921D-01    0.37868D-06    0.99591D 00    0.24300D 01    0.21400D 01
   8    545.0      350.0       9.00        0.46921D-01    0.37868D-06    0.99586D 00    0.24300D 01    0.22300D 01
   9    545.0      450.0       1.00        0.60327D-01    0.37868D-06    0.99656D 00    0.24300D 01    0.12800D 01
  10    545.0      450.0       3.00        0.60327D-01    0.37868D-06    0.99579D 00    0.24300D 01    0.18700D 01
  11    545.0      450.0       6.00        0.60327D-01    0.37868D-06    0.99546D 00    0.24300D 01    0.21100D 01
  12    545.0      450.0       9.00        0.60327D-01    0.37868D-06    0.99521D 00    0.24300D 01    0.22000D 01
  13    572.0      250.0       1.00        0.34659D-01    0.42406D-06    0.99530D 00    0.24300D 01    0.91000D 00
  14    572.0      250.0       3.00        0.34659D-01    0.42406D-06    0.99521D 00    0.24300D 01    0.17400D 01
  15    572.0      250.0       6.00        0.34659D-01    0.42406D-06    0.99526D 00    0.24300D 01    0.20600D 01
  16    572.0      250.0       9.00        0.34659D-01    0.42406D-06    0.99513D 00    0.24300D 01    0.21700D 01
  17    572.0      350.0       1.00        0.48522D-01    0.42406D-06    0.99413D 00    0.24300D 01    0.71000D 00
  18    572.0      350.0       3.00        0.48522D-01    0.42406D-06    0 99402D 00    0.24300D 01    0.16000D 01
  19    572.0      350.0       6.00        0.48522D-01    0.42406D-06    0.99359D 00    0 24300D 01    0 19700D 01
  20    572.0      350.0       9.00        0.48522D-01    0.42406D-06    0.99393D 00    0.24300D 01    0.21100D 01
  21    572.0      350.0      12.00        0 48522D-01    0.42406D-06    0 99404D 00    0.24300D 01    0.21900D 01
  22    572.0      450.0       1.00        0.62386D-01    0.42406D-06    0 99317D 00    0.24300D 01    0.58000D 00
  23    572.0      450.0       3.00        0.62386D-01    0.42406D-06    0.99310D 00    0.24300D 01    0.15000D 01
  24    572.0      450.0       6.00        0.62386D-01    0.42406D-06    0.99296D 00    0 24300D 01    0.19000D 01
  25    572 0      450.0       9.00        0.62386D-01    0.42406D-06    0.99291D 00    0 24300D 01    0.20600D 01
  26    572 0      450.0      12.00        0.62386D-01    0.42406D-06    0.99300D 00    0.24300D 01    0 21500D 01
  27    590.0      250.0       1.00        0.35409D-01    0.45808D-06    0.99147D 00    0.24300D 01    0.35000D 00
  28    590.0      250.0       3.00        0.35409D-01    0.45808D-06    0.99223D 00    0.24300D 01    0 13500D 01
  29    590.0      250.0       6.00        0.35409D-01    0.45808D-06    0.99260D 00    0.24300D 01    0.18300D 01
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30    590.0    250.0     9.00     0.354090D-01   0.458080D-06   0.99266D 00   0.243000D 01   0.202000D 01
31    590.0    250.0    12.00     0.354090D-01   0.458080D-06   0.99253D 00   0.243000D 01   0.211000D 01
32    590.0    250.0    15.00     0.354090D-01   0.458080D-06   0.99282D 00   0.243000D 01   0.218000D 01
33    590.0    350.0     1.00     0.495720D-01   0.458080D-06   0.98882D 00   0.243000D 01   0.190000D 00
34    590.0    350.0     3.00     0.495720D-01   0.458080D-06   0.98991D 00   0.243000D 01   0.113000D 01
35    590.0    350.0     6.00     0.495720D-01   0.458080D-06   0.99027D 00   0.243000D 01   0.168000D 01
36    590.0    350.0     9.00     0.495720D-01   0.458080D-06   0.99047D 00   0.243000D 01   0.191000D 01
37    590.0    350.0    12.00     0.495720D-01   0.458080D-06   0.99051D 00   0.243000D 01   0.203000D 01
38    590.0    350.0    15.00     0.495720D-01   0.458080D-06   0.99069D 00   0.243000D 01   0.211000D 01
39    590.0    450.0     3.00     0.637360D-01   0.458080D-06   0.98793D 00   0.243000D 01   0.970000D 00
40    590.0    450.0     6.00     0.637360D-01   0.458080D-06   0.98851D 00   0.243000D 01   0.157000D 01
41    590.0    450.0     9.00     0.637360D-01   0.458080D-06   0.98859D 00   0.243000D 01   0.182000D 01
42    590.0    450.0    12.00     0.637360D-01   0.458080D-06   0.98869D 00   0.243000D 01   0.198000D 01
43    590.0    450.0    15.00     0.637360D-01   0.458080D-06   0.98881D 00   0.243000D 01   0.205000D 01
44    617.0    250.0     3.00     0.365150D-01   0.515740D-06   0.98486D 00   0.243000D 01   0.660000D 00
45    617.0    250.0     6.00     0.365150D-01   0.515740D-06   0.98580D 00   0.243000D 01   0.132000D 01
46    617.0    250.0     9.00     0.365150D-01   0.515740D-06   0.98627D 00   0.243000D 01   0.164000D 01
47    617.0    250.0    12.00     0.365150D-01   0.515740D-06   0.98628D 00   0.243000D 01   0.181000D 01
48    617.0    250.0    15.00     0.365150D-01   0.515740D-06   0.98658D 00   0.243000D 01   0.193000D 01
49    617.0    350.0     3.00     0.511210D-01   0.515740D-06   0.97921D 00   0.243000D 01   0.400000D 00
50    617.0    350.0     6.00     0.511210D-01   0.515740D-06   0.98104D 00   0.243000D 01   0.107000D 01
51    617.0    350.0     9.00     0.511210D-01   0.515740D-06   0.98160D 00   0.243000D 01   0.143000D 01
52    617.0    350.0    12.00     0.511210D-01   0.515740D-06   0.98208D 00   0.243000D 01   0.165000D 01
53    617.0    350.0    15.00     0.511210D-01   0.515740D-06   0.98231D 00   0.243000D 01   0.179000D 01
54    617.0    450.0     3.00     0.657270D-01   0.515740D-06   0.97484D 00   0.243000D 01   0.270000D 00
55    617.0    450.0     6.00     0.657270D-01   0.515740D-06   0.97668D 00   0.243000D 01   0.880000D 00
56    617.0    450.0     9.00     0.657270D-01   0.515740D-06   0.97762D 00   0.243000D 01   0.127000D 01
57    617.0    450.0    12.00     0.657270D-01   0.515740D-06   0.97810D 00   0.243000D 01   0.151000D 01
58    617.0    450.0    15.00     0.657270D-01   0.515740D-06   0.97841D 00   0.243000D 01   0.167000D 01
59    662.0    250.0     6.00     0.383100D-01   0.633770D-06   0.97484D 00   0.243000D 01   0.630000D 00
60    662.0    250.0     9.00     0.383100D-01   0.633770D-06   0.97725D 00   0.243000D 01   0.108000D 01
61    662.0    250.0    12.00     0.383100D-01   0.633770D-06   0.97826D 00   0.243000D 01   0.136000D 01
62    662.0    250.0    15.00     0.383100D-01   0.633770D-06   0.97893D 00   0.243000D 01   0.155000D 01
63    662.0    350.0     6.00     0.536350D-01   0.633770D-06   0.96342D 00   0.243000D 01   0.330000D 00
64    662.0    350.0     9.00     0.536350D-01   0.633770D-06   0.96750D 00   0.243000D 01   0.750000D 00
65    662.0    350.0    12.00     0.536350D-01   0.633770D-06   0.96933D 00   0.243000D 01   0.106000D 01
66    662.0    350.0    15.00     0.536350D-01   0.633770D-06   0.97068D 00   0.243000D 01   0.129000D 01
67    662.0    450.0     6.00     0.689590D-01   0.633770D-06   0.95209D 00   0.243000D 01   0.170000D 00
68    662.0    450.0     9.00     0.689590D-01   0.633770D-06   0.95797D 00   0.243000D 01   0.520000D 00
69    662.0    450.0    12.00     0.689590D-01   0.633770D-06   0.96079D 00   0.243000D 01   0.830000D 00
70    662.0    450.0    15.00     0.689590D-01   0.633770D-06   0.96248D 00   0.243000D 01   0.107000D 01
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MARO....  BEGIN NONLINEAR LEAST SQUARES SOLUTION

MASK   :          1            1            0            1            1            1

X      :    0.11848D-06  0.20935D 05  0.81276D 14  0.38409D 05  0.13178D 08 -0.18972D 05

XMAX   :    0.10000D 31  0.10000D 31  0.82000D 14  0.10000D 31  0.10000D 31  0.10000D 31

XMIN   :   -0.10000D 31 -0.10000D 31  0.81000D 14 -0.10000D 31 -0.10000D 31 -0.10000D 31

DELMN  :    0.00000D 00  0.00000D 00  0.81276D 06  0.00000D 00  0.00000D 00  0.00000D 00

NV :   6      NPTS :    70      LPDMA :   300      LPDMB :  20      NTRAC : 0      METHD :  1      KALCP :  0

KORDF : 1       NFLAT : 1       NFMAX :   5000      MAXIT :     1      MXSUB :  25

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

PHI (THE SUM OF SQUARES) : 0.23728658D 04                                                 LAMBDA : 0.10000D 01


CONSTRAINT VIOLATED BY X(  3).   VALUE RESET TO  0.82000000D 14 USING CUTSTEP FACTOR :  0.15055D 00    ITER.    1

MAXIMUM NUMBER OF ITERATIONS REACHED IN MARO.       MAXIT :     1

   1 ITERATIONS          NF :    4           PHI : 0.20389130D 04            FMGN : 0.10000D 01        LAMBDA : 0.10000D 01

        NORM OF SCALED GRADIENT VECTOR : 0.42898D 02

                X :    0.11848000D-06  0.20934700D 05  0.82000000D 14  0.38408700D 05  0.13178000D 08 -0.18971800D 05


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

         1      0.14699990E 01      0.15549688D 01      -0.84969D-01       0.10000D 01          -0.84969D-01
         2      0.19899990E 01      0.19839616D 01       0.60382D-02       0.10000D 01           0.60382D-02
         3      0.21899990E 01      0.21872921D 01       0.27074D-02       0.10000D 01           0.27074D-02
         4      0.22599990E 01      0.22528750D 01       0.71242D-02       0.10000D 01           0.71242D-02
         5      0.13599990E 01      0.15098906D 01      -0.14989D 00       0.10000D 01          -0.14989D 00
         6      0.19199990E 01      0.19216247D 01      -0.16256D-02       0.10000D 01          -0.16256D-02
         7      0.21399990E 01      0.21312901D 01       0.87093D-02       0.10000D 01           0.87093D-02
         8      0.22299990E 01      0.22252811D 01       0.47185D-02       0.10000D 01           0.47185D-02
         9      0.12799990E 01      0.14699778D 01      -0.18998D 00       0.10000D 01          -0.18998D 00
        10      0.18699990E 01      0.18787618D 01      -0.87620D-02       0.10000D 01          -0.87620D-02
        11      0.21099990E 01      0.21054485D 01       0.45511D-02       0.10000D 01           0.45511D-02
        12      0.21999990E 01      0.21882957D 01       0.11704D-01       0.10000D 01           0.11704D-01
        13      0.90999990E 00      0.18692098D 01      -0.95921D 00       0.10000D 01          -0.95921D 00
        14      0.17399990E 01      0.21732939D 01      -0.43329D 00       0.10000D 01          -0.43329D 00
        15      0.20599990E 01      0.23208455D 01      -0.26085D 00       0.10000D 01          -0.26085D 00
        16      0.21699990E 01      0.23251247D 01      -0.15513D 00       0.10000D 01          -0.15513D 00
        17      0.70999990E 00      0.17698789D 01      -0.10599D 01       0.10000D 01          -0.10599D 01
        18      0.15999990E 01      0.21282302D 01      -0.52823D 00       0.10000D 01          -0.52823D 00
        19      0.19699990E 01      0.22694942D 01      -0.29949D 00       0.10000D 01          -0.29949D 00
        20      0.21099990E 01      0.23093341D 01      -0.19933D 00       0.10000D 01          -0.19933D 00
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  21     0.21899990E 01     0.23598335D 01     -0.16983D 00     0.10000D 01          -0.16983D 00
  22     0.57999990E 00     0.16881981D 01     -0.11082D 01     0.10000D 01          -0.11082D 01
  23     0.15000000E 01     0.21313842D 01     -0.63138D 00     0.10000D 01          -0.63138D 00
  24     0.18999990E 01     0.22300340D 01     -0.33003D 00     0.10000D 01          -0.33003D 00
  25     0.20599990E 01     0.22845121D 01     -0.22451D 00     0.10000D 01          -0.22451D 00
  26     0.21499990E 01     0.23362650D 01     -0.18627D 00     0.10000D 01          -0.18627D 00
  27     0.34999990E 00     0.20925300D 02     -0.20575D 02     0.10000D 01          -0.20576D 02
  28     0.13499990E 01     0.12983470D 01      0.51652D-01     0.10000D 01           0.51652D-01
  29     0.18299990E 01     0.63577810D 00      0.11942D 01     0.10000D 01           0.11942D 01
  30     0.20199990E 01     0.73816046D 00      0.12818D 01     0.10000D 01           0.12818D 01
  31     0.21099990E 01     0.14643794D 01      0.64562D 00     0.10000D 01           0.64562D 00
  32     0.21799990E 01     0.11501420D 01      0.10299D 01     0.10000D 01           0.10299D 01
  33     0.18999990E 00     0.39833325D 02     -0.39643D 02     0.10000D 01          -0.39643D 02
  34     0.11299990E 01     0.25385004D 01     -0.14085D 01     0.10000D 01          -0.14085D 01
  35     0.16799990E 01     0.62519112D 00      0.10548D 01     0.10000D 01           0.10548D 01
  36     0.19099990E 01     0.53529048D 00      0.13747D 01     0.10000D 01           0.13747D 01
  37     0.20299990E 01     0.91389941D 00      0.11161D 01     0.10000D 01           0.11161D 01
  38     0.21099990E 01     0.87466629D 00      0.12353D 01     0.10000D 01           0.12353D 01
  39     0.96999990E 00     0.42972245D 01     -0.33272D 01     0.10000D 01          -0.33272D 01
  40     0.15699990E 01    -0.34153739D-01      0.16042D 01     0.10000D 01           0.16042D 01
  41     0.18199990E 01     0.47322893D 00      0.13468D 01     0.10000D 01           0.13468D 01
  42     0.19599990E 01     0.69677167D 00      0.12632D 01     0.10000D 01           0.12632D 01
  43     0.20499990E 01     0.77259289D 00      0.12774D 01     0.10000D 01           0.12774D 01
  44     0.65999990E 00     0.15476466D 01     -0.88765D 00     0.10000D 01          -0.88765D 00
  45     0.13199990E 01     0.17959043D 01     -0.47590D 00     0.10000D 01          -0.47590D 00
  46     0.16399990E 01     0.19440162D 01     -0.30402D 00     0.10000D 01          -0.30402D 00
  47     0.18099990E 01     0.20639761D 01     -0.25398D 00     0.10000D 01          -0.25398D 00
  48     0.19299990E 01     0.21127600D 01     -0.18276D 00     0.10000D 01          -0.18276D 00
  49     0.39999990E 00     0.17240975D 01     -0.13241D 01     0.10000D 01          -0.13241D 01
  50     0.10699990E 01     0.16881350D 01     -0.61814D 00     0.10000D 01          -0.61814D 00
  51     0.14299990E 01     0.18570915D 01     -0.42709D 00     0.10000D 01          -0.42709D 00
  52     0.16499990E 01     0.19507184D 01     -0.30072D 00     0.10000D 01          -0.30072D 00
  53     0.17899990E 01     0.20277216D 01     -0.23772D 00     0.10000D 01          -0.23772D 00
  54     0.26999990E 00     0.16598078D 01     -0.13898D 01     0.10000D 01          -0.13898D 01
  55     0.87999990E 00     0.16443336D 01     -0.76433D 00     0.10000D 01          -0.76433D 00
  56     0.12699990E 01     0.17707100D 01     -0.50071D 00     0.10000D 01          -0.50071D 00
  57     0.15099990E 01     0.18836394D 01     -0.37364D 00     0.10000D 01          -0.37364D 00
  58     0.16699990E 01     0.19664525D 01     -0.29645D 00     0.10000D 01          -0.29645D 00
  59     0.62999990E 00     0.27069610D 00      0.35930D 00     0.10000D 01           0.35930D 00
  60     0.10799990E 01     0.87392057D 00      0.20608D 00     0.10000D 01           0.20608D 00
  61     0.13599990E 01     0.12267511D 01      0.13325D 00     0.10000D 01           0.13325D 00
  62     0.15499990E 01     0.14483232D 01      0.10168D 00     0.10000D 01           0.10168D 00
  63     0.32999990E 00    -0.24898178D 00      0.57898D 00     0.10000D 01           0.57898D 00
  64     0.75000000E 00     0.43574453D 00      0.31426D 00     0.10000D 01           0.31426D 00
  65     0.10599990E 01     0.86521817D 00      0.19478D 00     0.10000D 01           0.19478D 00
  66     0.12899990E 01     0.11379661D 01      0.15203D 00     0.10000D 01           0.15203D 00
  67     0.16999990E 00    -0.63835048D 00      0.80835D 00     0.10000D 01           0.80835D 00
  68     0.51999990E 00     0.66961255D-01      0.45304D 00     0.10000D 01           0.45304D 00
  69     0.82999990E 00     0.54658956D 00      0.28341D 00     0.10000D 01           0.28341D 00
  70     0.10689990E 01     0.87068336D 00      0.19831D 00     0.10000D 01           0.19831D 00

NUMBER OF DEGREES OF FREEDOM =  0.69000D 02

R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.54359D 01

MAXIMUM SCALED DEVIATION = 0.39643D 02



SUBROUTINE MOERR.

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

  1     0.1000000D 01


NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    69

EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =    69  PLUS OR MINUS 0.11747D 02

ACTUAL VALUE OF PHI = 0.20389D 04

RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.54359D 01


MAXIMUM VARIANCE INFLATION FACTOR = 0.10000D 01


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

          1          1       0.11848000D-06     0.00000D 00     0.00000D 00

          2          1       0.20934699D 05     0.00000D 00     0.00000D 00

          3          0       0.82000000D 14     0.17715D 12     0.96296D 12

          4          1       0.38408699D 05     0.00000D 00     0.00000D 00

          5          1       0.13178000D 08     0.00000D 00     0.00000D 00

          6          1      -0.16971801D 05     0.00000D 00     0.00000D 00


LOWER TRIANGLE OF THE CORRELATION MATRIX....

          K ....    1           2           3           4           5           6

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

  J  MASK(J)

  1     1      0.00000D 00

  2     1      0.00000D 00 0.00000D 00

  3     0      0.00000D 00 0.00000D 00 0.10000D 01

  4     1      0.00000D 00 0.00000D 00 0.00000D 00 0.00000D 00

  5     1      0.00000D 00 0.00000D 00 0.00000D 00 0.00000D 00 0.00000D 00

  6     1      0.00000D 00 0.00000D 00 0.00000D 00 0.00000D 00 0.00000D 00 0.00000D 00
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    DIBENZOTHIOPHENE HDS PROCESS MODEL FIT TO NON-ISOTHERMAL DATA.


    THE KINETIC PARAMETERS WERE FIXED AT THE FOLLOWING VALUES:

    K      A = 0.8200D 14    1/WT%      E = 0.3841D 05    CAL/GMOLE
    K      AH = 0.1185D-06    1/WT%      EH = 0.2093D 05    CAL/GMOLE
    KR/KP     AR/AP = 0.1318D 08              ER-EP = -0.1897D 05    CAL/GMOLE

    THE RESULTING FIT:
    MEAN DEVIATION = 0.140825D 01
    AVERAGE PERCENT ERROR = 0.442053D 03
    FOBJ = 0.203881D 04
    SUM OF SQUARES = 0.203881D 04




STATEMENTS EXECUTED=    11718
CORE USAGE        OBJECT CODE=   58472 BYTES,ARRAY AREA=   73176 BYTES,TOTAL AREA AVAILABLE=  174080  BYTES
DIAGNOSTICS        NUMBER OF ERRORS=        0, NUMBER OF WARNINGS=        0, NUMBER OF EXTENSIONS=       12
COMPILE TIME=      0.41 SEC,EXECUTION TIME=     0.24 SEC,       0.39.45     TUESDAY       26 JUL 83     WATFIV - MAR 1980 V2L0

         C$STOP
```

APPENDIX I

N-TH ORDER GLOBAL MODEL FIT TO NON-ISOTHERMAL DIBENZOTHIOPHENE HYDRODESULFURIZATION DATA

```
$JOB
C
C     ****************************
C     *                          *
C     *  N-TH ORDER GLOBAL MODEL *
C     *                          *
C     *  ESPINO DATA             *
C     *                          *
C     *  DIBENZOTHIOPHENE HDS    *
C     *                          *
C     *  NON-ISOTHERMAL FIT      *
C     *                          *
C     ****************************
C
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL EXFIT
      DOUBLE PRECISION X,FIT
      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,METHO,KALCP,KORDF,
     *MAXIT,LEQU,MXSUE,MXUPD
      COMMON /CDAT/ FIT(300),Y(300),YSIG(300),NPTS
      COMMON /CSTOR/ T(70),P(70),ALHSV(70),C1(70),X1(70)
      KR=5
      KW=6
      FL=1.
      CALL STSET
      MAXIT=200
      NV=4
      XMIN(1)=0.1D8
      XMAX(4)=0.9999
      X(1)=0.1698D10
      X(2)=0.5327D5
      X(3)=0.5794
      X(4)=1.5
      NTRAC=0
      WRITE(KW,40)
   40 FORMAT(1H1,/////5X,'WT% IS WEIGHT PERCENT DIBENZOTHIOPHENE IN THE
     *BULK LIQUID')
      WRITE(KW,50)
   50 FORMAT(/////10X,'TEMPERATURE',5X,'PRESSURE',9X,'LHSV',9X,'IN. CONC
     *.',6X,'FIN. CONC.',//14X,'(R)',10X,'(PSI)',10X,'(1/HR)',10X,'(WT%)
     *',10X,'(WT%)')
      READ(KR,100)NPTS
  100 FORMAT(I5)
      DO 110 K=1,NPTS
      READ(KR,120)T(K),P(K),ALHSV(K),C1(K),Y(K)
  120 FORMAT(7X,5F10.5)
  110 T(K)=T(K)+460.
      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))
      CALL STEPT (EXFIT)
      DEV=0.0
      PE=0.0
      SOS=0.0
      DO 130 L=1,NPTS
      DEV=DEV+DABS(FIT(L)-Y(L))/NPTS
      PE=PE+DABS(FIT(L)-Y(L))/NPTS/Y(L)*100.
  130 SOS=SOS+(FIT(L)-Y(L))**2



      WRITE(KW,135)
  135 FORMAT(1H1,/////5X,'N-TH ORDER GLOBAL MODEL PARAMETERS')
      WRITE(KW,140)X(1),X(2),X(3),X(4)
  140 FORMAT(///5X,'A = ',E10.4,3X,'WT%**(1-N)/PSI**M/HR',//5X,'E = ',
     *E10.4,3X,'BTU/LBMOLE',//5X,'M = ',E10.4,//5X,'N = ',E10.4)
      WRITE(KW,150)DEV,PE,FOBJ,SOS
  150 FORMAT(////5X,'MEAN DEVIATION = ',E10.4,//5X,'AVG. PERCENT ERROR =
     * ',E10.4,//5X,'FOBJ = ',E10.4,//5X,'SUM OF SQUARES = ',E10.4,////)
      STOP
      END

      SUBROUTINE EXFIT (FITM)
      IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION X,FIT,OEXP,DEXP,ARG,FITM,FF
      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(70),P(70),ALHSV(70),C1(70),X1(70)
      OEXP(ARG)=DEXP(ARG)
      FOBJ=0.
      R=1.987
      DO 200 J=1,NPTS
      YSIG(J)=1.0
      YSIG(J)=Y(J)
      TERM=(C1(J)**(1.-X(4))-X(1)*OEXP(-X(2)/R/T(J))*P(J)**X(3)*(1.-X(4)
     *)/ALHSV(J))
      IF (TERM.LT.0.0) TERM=0.0
      FF=TERM**(1./(1.-X(4)))
      FITM(J)=FF
  200 FOBJ=FOBJ+((FF-Y(J))/YSIG(J))**2
      RETURN
      END

$ENTRY
```

```
WT% IS WEIGHT PERCENT DIBENZOTHIOPHENE IN THE BULK LIQUID


      TEMPERATURE     PRESSURE        LHSV         IN. CONC.      FIN. CONC.

          (R)           (PSI)        (1/HR)          (WT%)          (WT%)

70

 1    0.10050D 04   0.25000D 03   0.10000D 01   0.24300D 01   0.14700D 01
 2    0.10050D 04   0.25000D 03   0.30000D 01   0.24300D 01   0.19800D 01
 3    0.10050D 04   0.25000D 03   0.60000D 01   0.24300D 01   0 21900D 01
 4    0.10050D 04   0.25000D 03   0.90000D 01   0.24300D 01   0.22600D 01
 5    0.10050D 04   0.35000D 03   0.10000D 01   0.24300D 01   0.13800D 01
 6    0.10050D 04   0.35000D 03   0.30000D 01   0.24300D 01   0.19200D 01
 7    0.10050D 04   0.35000D 03   0.60000D 01   0.24300D 01   0.21400D 01
 8    0.10050D 04   0.35000D 03   0.90000D 01   0.24300D 01   0.22300D 01
 9    0.10050D 04   0.45000D 03   0.10000D 01   0.24300D 01   0.12800D 01
10    0.10050D 04   0.45000D 03   0.30000D 01   0.24300D 01   0.18700D 01
11    0.10050D 04   0.45000D 03   0.60000D 01   0.24300D 01   0.21100D 01
12    0.10050D 04   0.45000D C3   0.90000D 01   0.24300D 01   0.22000D 01
13    0.10320D 04   0.25000D 03   0.10000D 01   0.24300D 01   0.81000D 00
14    0.10320D 04   0.25000D 03   0.30000D 01   0.24300D 01   0.17400D 01
15    0.10320D 04   0.25000D 03   0.60000D 01   0.24300D 01   0.20800D 01
16    0.10320D 04   0.25000D 03   0.90000D 01   0.24300D 01   0.21700D 01
17    0.10320D 04   0.35000D 03   0.10000D 01   0.24300D 01   0.71000D 00
18    0.10320D 04   0.35000D 03   0.30000D 01   0.24300D 01   0.18000D 01
19    0.10320D 04   0.35000D 03   0.60000D 01   0.24300D 01   0.19700D 01
20    0.10320D 04   0.35000D 03   0.90000D 01   0.24300D 01   0.21100D 01
21    0.10320D 04   0.35000D 03   0.12000D 02   0.24300D 01   0.21800D 01
22    0.10320D 04   0.45000D 03   0.10000D 01   0.24300D 01   0.58000D 00
23    0.10320D 04   0.45000D 03   0.30000D 01   0.24300D 01   0.15000D 01
24    0.10320D 04   0.45000D 03   0.60000D 01   0.24300D 01   0.19000D 01
25    0.10320D 04   0.45000D 03   0.90000D 01   0.24300D 01   0.20600D 01
26    0.10320D 04   0.45000D 03   0.12000D 02   0.24300D 01   0.21500D 01
27    0.10500D 04   0.25000D 03   0.10000D 01   0.24300D 01   0.35000D 00
28    0.10500D 04   0.25000D 03   0.30000D 01   0.24300D 01   0.13500D 01
29    0.10500D 04   0.25000D 03   0.60000D 01   0.24300D 01   0.18300D 01
30    0.10500D 04   0.25000D 03   0.90000D 01   0.24300D 01   0.20200D 01
31    0.10500D 04   0.25000D 03   0.12000D 02   0.24300D 01   0.21100D 01
32    0.10500D 04   0.25000D 03   0.15000D 02   0.24300D 01   0.21800D 01
33    0.10500D 04   0.35000D 03   0.10000D 01   0.24300D 01   0.19000D 00
34    0.10500D 04   0.35000D 03   0.30000D 01   0.24300D 01   0.11300D 01
35    0.10500D 04   0.35000D 03   0.60000D 01   0.24300D 01   0.16800D 01
36    0.10500D 04   0.35000D 03   0.90000D 01   0.24300D 01   0.19100D 01
37    0.10500D 04   0.35000D 03   0.12000D 02   0.24300D 01   0.20300D 01
38    0.10500D 04   0.35000D 03   0.15000D 02   0.24300D 01   0.21100D 01
39    0.10500D 04   0.45000D 03   0.30000D 01   0.24300D 01   0.97000D 00
40    0.10500D 04   0.45000D 03   0.60000D 01   0.24300D 01   0.15700D 01
41    0.10500D 04   0.45000D 03   0.90000D 01   0.24300D 01   0.18200D 01
42    0.10500D 04   0.45000D 03   0.12000D 02   0.24300D 01   0.19500D 01



43    0.10500D 04   0.45000D 03   0.15000D 02   0.24300D 01   0.20500D 01
44    0.10770D 04   0.25000D 03   0.3000CD 01   0.24300D 01   0.68000D 00
45    0.10770D 04   0.25000D 03   0.60000D 01   0.24300D 01   0.13200D 01
46    0.10770D 04   0.25000D 03   0.90000D 01   0.24300D 01   0.16400D 01
47    0.10770D 04   0.25000D 03   0.12000D 02   0.24300D 01   0.18100D 01
48    0.10770D 04   0.25000D 03   0.15000D 02   0.24300D 01   0.19300D 01
49    0.10770D 04   0.35000D 03   0.30000D 01   0.24300D 01   0.40000D 00
50    0.10770D 04   0.35000D 03   0.60000D 01   0.24300D 01   0.10700D 01
51    0.10770D 04   0.35000D 03   0.90000C 01   0.24300D 01   0.14300D 01
52    0.10770D 04   0.35000D 03   0.12000D 02   0.24300D 01   0.16500D 01
53    0.10770D 04   0.35000D 03   0.15000D 02   0.24300D 01   0.17900D 01
54    0.10770D 04   0.45000D 03   0.30000D 01   0.24300D 01   0.27000D 00
55    0.10770D 04   0.45000D 03   0.60000D 01   0.24300D 01   0.88000D 00
56    0.10770D 04   0.45000D 03   0.90000D 01   0.24300D 01   0.12700D 01
57    0.10770D 04   0.45000D 03   0.12000D 02   0.24300D 01   0.15100D 01
58    0.10770D 04   0.45000D 03   0.15000D 02   0.24300D 01   0.16700D 01
59    0.11220D 04   0.25000D 03   0.60000D 01   0.24300D 01   0.63000D 00
60    0.11220D 04   0.25000D 03   0.90000D 01   0.24300D 01   0.10600D 01
61    0.11220D 04   0.25000D 03   0.12000D 02   0.24300D 01   0.13800D 01
62    0.11220D 04   0.25000D 03   0.15000D 02   0.24300D 01   0.15500D 01
63    0.11220D 04   0.35000D 03   0.60000D 01   0.24300D 01   0.33000D 00
64    0.11220D 04   0.35000D 03   0.90000D 01   0.24300D 01   0.75000D 00
65    0.11220D 04   0.35000D 03   0.12000D 02   0.24300D 01   0.10600D 01
66    0.11220D 04   0.35000D 03   0.15000D 02   0.24300D 01   0.12800D 01
67    0.11220D 04   0.45000D 03   0.60000D 01   0.24300D 01   0.17000D 00
68    0.11220D 04   0.45000D 03   0.90000D 01   0.24300D 01   0.52000D 00
69    0.11220D 04   0.45000D 03   0.12000D 02   0.24300D 01   0.83000D 00
70    0.11220D 04   0.45000D 03   0.15000D 02   0.24300D 01   0.10700D 01
```

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

MASK    =        0              0              0              0

X       =   0.189800 10   0.532700 05   0.879400 00   0.999900 00

XMAX    =   0.100000 31   0.100000 31   0.100000 31   0.999900 00

XMIN    =   0.100000 06  -0.100000 31  -0.100000 31  -0.100000 31

DELMN   =   0.189800 02   0.532700-03   0.879400-08   0.150000-07

NV =    4       NPTS =      70       LPDMA =     300       LPDMB =   20       NTRAC = 0       METHD =   1       KALCP =   0

KBRDF = 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) = 0.10559885D 01                                                        LAMBDA = 0.10000D 01


CONVERGED WHEN THE STEP BECAME SMALL.
  10 ITERATIONS        NF =    52            PHI = 0.90808264D 00             FMGN = 0.10000D 01         LAMBDA = 0.10833D-08
        NORM OF SCALED GRADIENT VECTOR = 0.19975D-07
              X =   0.18787230 10  0.52713460 05  0.81966460 00  0.83538580 00

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

          1      0.14699990E 01      0.14196817D 01      0.50318D-01      0.14700D 01          0.34230D-01
          2      0.19899990E 01      0.20420817D 01     -0.52082D-01      0.19900D 01         -0.26172D-01
          3      0.21899990E 01      0.22289999D 01     -0.39000D-01      0.21900D 01         -0.17808D-01
          4      0.22599990E 01      0.22943946D 01     -0.34395D-01      0.22600D 01         -0.15219D-01
          5      0.13599990E 01      0.11844685D 01      0.17553D 00      0.13600D 01          0.12907D 00
          6      0.19199990E 01      0.19303045D 01     -0.10305D-01      0.19200D 01         -0.53674D-02
          7      0.21399990E 01      0.21681520D 01     -0.28153D-01      0.21400D 01         -0.13156D-01
          8      0.22299990E 01      0.22526760D 01     -0.22676D-01      0.22300D 01         -0.10169D-01
          9      0.12799990E 01      0.99227381D 00      0.28773D 00      0.12800D 01          0.22479D 00
         10      0.18699990E 01      0.18289979D 01      0.41002D-01      0.18700D 01          0.21926D-01
         11      0.21099990E 01      0.21116951D 01     -0.16954D-02      0.21100D 01         -0.80352D-03
         12      0.21999990E 01      0.22136718D 01     -0.13672D-01      0.22000D 01         -0.62145D-02
         13      0.90999990E 00      0.78968363D 00      0.12032D 00      0.91000D 00          0.13222D 00
         14      0.17399990E 01      0.17088772D 01      0.31123D-01      0.17400D 01          0.17887D-01
         15      0.20599990E 01      0.20429898D 01      0.17010D-01      0.20600D 01          0.82571D-02
         16      0.21699990E 01      0.21658053D 01      0.41938D-02      0.21700D 01          0.19325D-02
         17      0.70999990E 00      0.52651259D 00      0.18349D 00      0.71000D 00          0.25843D 00
         18      0.15999990E 01      0.15213887D 01      0.78611D-01      0.16000D 01          0.49132D-01
         19      0.19699990E 01      0.19314462D 01      0.38553D-01      0.19700D 01          0.19570D-01
         20      0.21099990E 01      0.20871059D 01      0.22894D-01      0.21100D 01          0.10850D-01
         21      0.21899990E 01      0.21687809D 01      0.21218D-01      0.21900D 01          0.96889D-02
         22      0.57999990E 00      0.34891391D 00      0.23109D 00      0.58000D 00          0.39842D 00
         23      0.15000000E 01      0.13596658D 01      0.14033D 00      0.15000D 01          0.93558D-01


         24      0.18999990E 01      0.18303391D 01      0.69660D-01      0.19000D 01          0.36663D-01
         25      0.20599990E 01      0.20146416D 01      0.45358D-01      0.20600D 01          0.22018D-01
         26      0.21499990E 01      0.21124511D 01      0.37549D-01      0.21500D 01          0.17464D-01
         27      0.34999990E 00      0.38230694D 00     -0.32307D-01      0.35000D 00         -0.92308D-01
         28      0.13499990E 01      0.13933724D 01     -0.43373D-01      0.13500D 01         -0.32128D-01
         29      0.18299990E 01      0.18518272D 01     -0.21827D-01      0.18300D 01         -0.11927D-01
         30      0.20199990E 01      0.20301363D 01     -0.10137D-01      0.20200D 01         -0.50182D-02
         31      0.21099990E 01      0.21245317D 01     -0.14532D-01      0.21100D 01         -0.68872D-02
         32      0.21799990E 01      0.21829084D 01     -0.29091D-02      0.21800D 01         -0.13344D-02
         33      0.18999990E 00      0.18450129D 00      0.54987D-02      0.19000D 00          0 28941D-01
         34      0.11299990E 01      0.11547548D 01     -0.24755D-01      0.11300D 01         -0 21907D-01
         35      0.16799990E 01      0.16943084D 01     -0.14309D-01      0.16800D 01         -0.85173D-02
         36      0.19099990E 01      0.19153007D 01     -0.53008D-02      0.19100D 01         -0.27753D-02
         37      0.20299990E 01      0.20345180D 01     -0.45182D-02      0.20300D 01         -0.22257D-02
         38      0.21099990E 01      0.21089779D 01      0.10218D-02      0.21100D 01          0.48424D-03
         39      0.96999990E 00      0.96087081D 00      0.91292D-02      0.97000D 00          0.94116D-02
         40      0.15699990E 01      0.15553289D 01      0.14671D-01      0.15700D 01          0.93445D-02
         41      0.18199990E 01      0.18113878D 01      0.86121D-02      0.18200D 01          0.47318D-02
         42      0.19599990E 01      0.19520610D 01      0.79380D-02      0.19600D 01          0.40500D-02
         43      0.20499990E 01      0.20407618D 01      0.92374D-02      0.20500D 01          0.45061D-02
         44      0.65999990E 00      0.81360088D 00     -0.15360D 00      0.66000D 00         -0.23273D 00
         45      0.13199990E 01      0.14411034D 01     -0.12110D 00      0.13200D 01         -0.91745D-01
         46      0.16399990E 01      0.17239367D 01     -0.83937D-01      0.16400D 01         -0.51181D-01
         47      0.18099990E 01      0.18818713D 01     -0.71872D-01      0.18100D 01         -0.39708D-01
         48      0.19299990E 01      0.19823034D 01     -0.52304D-01      0.19300D 01         -0.27101D-01
         49      0.39999990E 00      0.54908834D 00     -0.14909D 00      0.40000D 00         -0.37272D 00
         50      0.10699990E 01      0.12087842D 01     -0.13878D 00      0.10700D 01         -0.12971D 00
         51      0.14299990E 01      0.15384177D 01     -0.10842D 00      0.14300D 01         -0.75816D-01
         52      0.16499990E 01      0.17311441D 01     -0.81144D-01      0.16500D 01         -0.49178D-01
         53      0.17899990E 01      0.18554659D 01     -0.65466D-01      0.17900D 01         -0.36573D-01
         54      0.26999990E 00      0.36869470D 00     -0.98695D-01      0.27000D 00         -0.36554D 00
         55      0.87999990E 00      0.10181022D 01     -0.13810D 00      0.88000D 00         -0.15693D 00
         56      0.12699990E 01      0.13798588D 01     -0.10986D 00      0.12700D 01         -0.86503D-01
         57      0.15099990E 01      0.15975610D 01     -0.87562D-01      0.15100D 01         -0.57988D-01
         58      0.16699990E 01      0.17414354D 01     -0.71436D-01      0.16700D 01         -0.42776D-01
         59      0.62999990E 00      0.53158358D 00      0.98416D-01      0.63000D 00          0.15622D 00
         60      0.10799990E 01      0.92131797D 00      0.15868D 00      0.10800D 01          0.14693D 00
         61      0.13599990E 01      0.11917354D 01      0.16826D 00      0.13600D 01          0.12372D 00
         62      0.15499990E 01      0.13836847D 01      0.16631D 00      0.15500D 01          0.10730D 00
         63      0.32999990E 00      0.29919684D 00      0.30803D-01      0.33000D 00          0.93343D-01
         64      0.75000000E 00      0.65348575D 00      0.96514D-01      0.75000D 00          0.12869D 00
         65      0.10599990E 01      0.93282845D 00      0.12717D 00      0.10600D 01          0.11997D 00
         66      0.12899990E 01      0.11438554D 01      0.14614D 00      0.12900D 01          0.11329D 00
         67      0.16999990E 00      0.16405961D 00      0.59403D-02      0.17000D 00          0.34943D-01
         68      0.51999990E 00      0.46281893D 00      0.57181D-01      0.52000D 00          0.10996D 00
         69      0.82999990E 00      0.73234389D 00      0.97656D-01      0.83000D 00          0.11766D 00
         70      0.10699990E 01      0.94939878D 00      0.12060D 00      0.10700D 01          0.11271D 00

NUMBER OF DEGREES OF FREEDOM =   0.66000D 02

R.M.S. SCALED DEVIATION OF DATA FROM FIT = 0.11730D 00

MAXIMUM SCALED DEVIATION = 0.39842D 00


SUBROUTINE MOERR.

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

```
   1    0.1000000D 01
   2   -0.5984929D 00  0.1000000D 01
   3    0.8883237D 00 -0.8885110D 00  0.1000000D 01
   4    0.1419108D 00 -0.1478237D 00  0.1313249D 00  0.1000000D 01

NUMBER OF DEGREES OF FREEDOM (N.D.F.) = (NPTS-NACTV) =    66
EXPECTED VALUE OF PHI = N.D.F. PLUS OR MINUS SQRT(2*N.D.F.) =   66  PLUS OR MINUS 0.11489D 02
ACTUAL VALUE OF PHI = 0.90808D 00
RESCALING FACTOR = SQRT(PHI/N.D.F.) = 0.11730D 00

MAXIMUM VARIANCE INFLATION FACTOR = 0.23402D 04

APPROXIMATE STANDARD ERRORS....
                                                                 RESCALED
           J      MASK(J)        X(J)               ERROR          ERROR
           1         0      0.18767229D 10      0.10617D 11     0.12453D 10
           2         0      0.52713455D 05      0.82368D 04     0.96616D 03
           3         0      0.61866464D 00      0.57651D 00     0.67623D-01
           4         0      0.83535576D 00      0.38472D 00     0.45300D-01

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         0.90891D 00  0.10000D 01
 3       0        -0.75035D 00 -0.21487D 00  0.10000D 01
 4       0        -0.57715D-01  0.12739D 00  0.25103D 00  0.10000D 01




     N-TH ORDER GLOBAL MODEL PARAMETERS

     A = 0.1877D 10   WT%**(1-N)/PSI**M/HR
     E = 0.5271D 05   BTU/LBMOLE
     M = 0.6187D 00
     N = 0.8354D 00

     MEAN DEVIATION = 0.5906D-01
     AVE. PERCENT ERROR = 0.7158D 01
     FOBJ = 0.9081D 00
     SUM OF SQUARES = 0.9067D 00

STATEMENTS EXECUTED=   73778
CORE USAGE       OBJECT CODE=   43816 BYTES,ARRAY AREA=   85488 BYTES,TOTAL AREA AVAILABLE=  128024  BYTES
DIAGNOSTICS        NUMBER OF ERRORS=       0, NUMBER OF WARNINGS=       0, NUMBER OF EXTENSIONS=      10
COMPILE TIME=     0.28 SEC,EXECUTION TIME=     1.34 SEC,     16.09.58     TUESDAY      26 JUL 83    WATFIV - MAR 1980 V2L0

        C$STOP
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2

VITA

Thomas Mason Pendergast

Candidate for the Degree of

Master of Science

Thesis: MATHEMATICAL MODELING OF COAL LIQUID HYDROTREATMENT KINETICS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Terre Haute, Indiana, November 25, 1958, the son of Mr. and Mrs. James H. Pendergast.

Education: Graduated from Terre Haute North Vigo High School, Terre Haute, Indiana, in June, 1977; received Bachelor of Science degree in Chemical Engineering from Rose-Hulman Institute of Technology in 1981; completed requirements for the Master of Science degree at Oklahoma State University in December, 1983.

Professional Experience: Summer Engineer, DOW Chemical U.S.A., 1981; graduate teaching assistant, School of Chemical Engineering, Oklahoma State University, 1981; graduate research assistant, School of Chemical Engineering, Oklahoma State University, 1982-83.