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A COMPUTER PROGRAM FOR DETERMINING "HINSHELWOOD RATE MECHANISMS FROM NONISOTHERMAL PELLET DATA"

BY

JOSEPH J. ATKINS

A THESIS

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ABSTRACT

Methods of determining Hinshelwood rate correlations from non isothermal catalyst data was studied. It was determined for any chemical system involving a reacting gas mixture over a porous catalyst a node analysis could be used to determine chemical concentration and temperature variation through the pellet. Calculation performed with a spectra 360/Fortran 4 program defined the Hinshelwood equation from estimated surface rates. Then utilizing node analysis to determine concentration and temperature variance, transport and rate equations were integrated through the pellet to obtain a total pellet rate of reaction. For acceptance of Hinshelwood equations the calculated total rate must equal the measured total rate and the Hinshelwood constants must meet the Hinshelwood acceptance criteria. A sample problem employing Hydrogen and Oxygen catalyzed over platinum was used for checkout.

APPROVAL OF THESIS

A COMPUTER PROGRAM TO DETERMINE HINSHELWOOD MECHANISMS FROM NON ISOTHERMAL PELLET DATA

BY

JOSEPH J. ATKINS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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NEWARK, NEW JERSEY

JUNE, 1969

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NOMENCLATURE LIST

AR or S	Mean transport area and AR is mean area between nodes
C_A or CS	Concentration of components A through S
DEA or DES	Diffusivities of components A through S
DR or ΔX	Distance between nodes
E	Pellet effectiveness
F	Feed rate
ΔH	Heat of reaction
L.	Total number of adsorption sites
K_1 and K_2	Forward and reverse rate constants
KE	Equilibrium constant
K_1 to K_5	Hinshelwood constants
k or cK	Thermal conductivity
N	Node number
PA or PS	Partial pressure of components A through S
POT	Potential term in Hinshelwood equation
RA	Diffusion rate
R(N)	Node rate reduced to meet equation and diffusion limits
r_T	Total pellet reaction rate
r	Reaction rate
R	Pellet radius
X, X^1	(X) conversion X^1 amount of component adsorbed on catalyst
ZD	Multiplier for adjusting surface rate estimate
	Number of adsorption sites used by a component
	Density

I

INTRODUCTION

A topic of significant interest in the field of catalyst research is the application of computer techniques to determine Langmuir Hinshelwood Rate Mechanisms as applied to the design of catalytic reactors. Hinshelwood Rate Mechanisms are defined by the rate equation which best fits experimental reactor data. The rate forms are all based on the assumption that one reaction step controls the reaction rate and that a linear Langmuir isotherm for adsorption of reactant is descriptive of the chemical reaction being studied.

A comprehensive review of the available literature in this area and the work done by previous investigators revealed that Hinshelwood rate equations determined to date have been primarily based upon experimental data using fine particle catalyst. This was apparently because the influence of temperature and concentration variation associated with fine particles is small thus minimizing errors in the results. In commercial chemical production plants, however, catalysts are generally in pellet form and such catalyst structures do encounter significant variations in temperature and chemical concentration.

From these considerations, the question arose whether the Hinshelwood rate equations based upon the fine particle catalyst data were valid for other pellet geometry, catalyst properties and flow conditions.

It was hypothesized that the errors introduced by the change in geometry might be reduced if the pellet data could, by some method, be analyzed directly to determine the catalytic mechanisms. The object of the work undertaken therefore, was to establish a means of determining Hinshelwood equations directly from pellet data.

The method developed estimated Hinshelwood rate equations from reactor pellet data. The process encompassed estimating surface rates, and then integration of the transport equations through the pellet to arrive at a total rate which agreed with catalyst total rates determined experimentally.

Node analysis was selected for integration of the transport equations. A computer program was assembled and sample problems examined via this form of analysis. One such sample encompassed several computer runs for Hydrogen-Oxygen Catalysis over platinum summarized at the end of this discussion. Discussion of program input and nomenclature is presented in the Appendix.

II

DISCUSSION OF ANALYSIS

A. Catalyst Reactions

A review of reaction rate controls indicated that a catalyst will not make a reaction proceed between chemical species that would not proceed in its absence, but it can increase reaction rates. The catalyst property promoting reaction rate is conjectured (5) to be chemisorption of gas or liquid on the catalyst surface producing an activated complex. The gas to catalyst complex is unstable and requires less energy for reaction to occur than is needed for reaction of the gas as without a catalyst. The change in the path of the chemical reaction sequence along with the accompanying decrease in energy requirement per step leads to greater chance of chemical reaction upon gas to catalyst contact. Interest in catalysts therefore, relates to the effect they have on the reaction rate. For purposes of analysis, one transport or reaction step is assumed to control. If the chemist is to determine a representative rate equation for catalyst data, he needs to know which of the following mechanisms is controlling.

Types of Rate Controlling Mechanisms

1. Mass transfer from the mainstream to and from the solid surface.
2. Diffusion of chemical species into and out of the catalyst pore structure.
3. Activated adsorption of reactants and desorption of products.
4. Speed of reaction of the adsorbed species on the catalyst.

For establishing a method of determining Hinshelwood mechanism from porous catalyst data, it is of major importance that the effect of each controlling mechanism or catalyst reaction be obtained. Then in the process of integrating the rates through the pellet, all factors will be accounted for providing the means for defining both the rate controlling step and estimating total pellet reaction rate. The representative rate equation should be based upon rates defined by reaction kinetics, unaltered by transport phenomena. Each of the four rate steps or mechanisms mentioned are considered in brief as follows.

1. Main stream to pellet transport. The Type 1 rate control -main stream to pellet- limits the rate of reaction by failure of reactant to diffuse rapidly enough to the pellet surface to feed the reaction. This results from film formation over the catalyst, decreasing the diffusion rate of the reactant. If the main stream flow over the surfaces is high, films are swept away. Careful control of reactor flow conditions will make these effects negligible and minimize their influence on catalytic reaction rate. The influence of the variation of surface concentrations produced during transport of reactant from the main stream to the pellet is small as long as pellet pore diffusion effects observed are small. If variation caused by pore diffusion should be large, then surface concentration should be adjusted to account for effect of transport from the main stream.

2. Pellet diffusion. The Type 2 rate control -pellet diffusion- is incurred by chemical diffusion limiting the flow into the catalyst pores. The diffusion effect upon reaction rate is analytically deter-

minable by integrating the mass transport equations through the porous material. Reaction rates may be estimated from the concentration versus pellet location relationship. If diffusion limits are severe, the reaction rate may further be limited by the inability of the species to penetrate the pore structure or for the product to escape fast enough, preventing the feeding of the reaction.

For development of the analytical approach (8) integration of transport equations is accomplished in the following manner. It is assumed that the catalyst is in the shape of a sphere and that the diffusion of the reactant "A" of partial pressure P is diffusing through a thin spherical shell of thickness ΔR. The difference between the amount of reactant diffusing into the shell, Na/in, and the amount exiting from the shell, Na/out, equals the amount depleted by the reaction in the shell.

$$Na/in - Na/out = \rho S \bar{r} \Delta R \qquad (1)$$

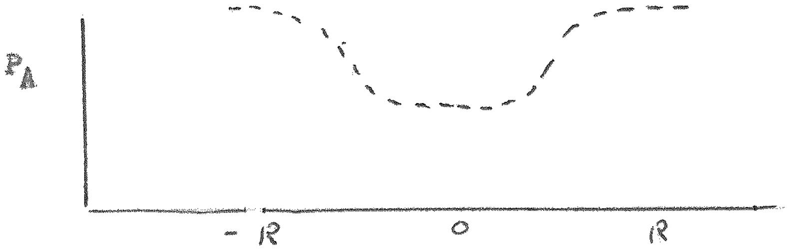
The mass flux is equal to the product of the effective diffusivity for porous catalyst (D_A) and the concentration or partial pressure drop (dp/dr) across the shell. Substitution for NA gives us the following result:

$$\begin{aligned} D_A \, \partial P_A / \partial R / in - D_A \, \partial P_A / \partial R / out &= \rho S \bar{\bar{r}} \Delta R \\ \partial / \partial R \, (D_A \, P_A / \partial R) - \rho S \bar{\bar{r}} &= 0 \end{aligned} \qquad (2)$$

The above equation may be solved if rate r is first order with respect to partial pressure of "A" (KPA). The equation is then of the form as follows:

$$\partial / \partial r \, (\; P_A / \partial \, r) - \left(\frac{\rho S K_1}{D_A} \right) P_A = 0 \qquad (3)$$

The term $\frac{PSK}{D}$ has been arbitrarily set equal to the square of the Theile modulus $\widehat{hp}^2$. Integration of the differential equation provides the partial pressure curve through the pellet as a function of radius.



For estimating the rate of reaction in single pellets, the transport equations have been solved using first order rate approximation of the data. When the total pellet rate is determined, it is divided by the rate for the same volume of catalyst unaffected by diffusion, obtaining a pellet effectiveness ($\mathcal{E}$). Effectiveness is plotted against Theile modulus for first order reactions, thus rates can be determined from these effectiveness plots for any given values of the modulus.

Estimating pellet rates becomes more complex if the rate equation is not a first order approximation. Since all Hinshelwood rate equations are more complex, it is the latter case in which we have the greatest interest.

An example problem illustrates methods of solving for pellet concentrations and rates. Analysis of carbon and carbon dioxide catalysis was performed by Austin and Walker (8). The reaction of carbon dioxide to form carbon monoxide is written as follows:

$$C + CO_2 \rightarrow 2CO$$

Small amounts of carbon monoxide inhibit this reaction. Thus, diffusion of the carbon monoxide out as well as carbon dioxide into the catalyst must be considered. It was ascertained beforehand that a Hinshelwood rate equation represented the rate data:

$$r = KP_A \,/\, (1 + K_2 * P_A + K_3 * P_B) \tag{4}$$

Considering the mass transport equation for carbon dioxide P_A and carbon monoxide P_B, we obtain transport equations for CO_2 and CO:

1.) carbon dioxide (CO_2)

$$\partial/\partial R\,(D_A\,\partial P_A\,/\partial R) - \rho S\left[K_1 * P_A/(1 + K_2 * P_A + K_3 * P_B\right] = 0 \tag{5}$$

2.) carbon monoxide (CO)

$$\frac{\partial}{\partial r}\,(D_B\,\partial P_B/\partial r) - 2\rho S\left[K_1 * P_A/(1 + K_2 * P_A + K_3 * P_B\right] = 0 \tag{6}$$

Multiplying equation (1) by $(\frac{\rho_A}{2})$ and equation (2) by ρ_A and subtracting 3 from 1 we get the following:

$$\partial/\partial r\,(D_A\,\partial P_A/\partial R) = -\tfrac{1}{2}\,\partial/\partial R\left[D_B\,\partial P_B/\partial R\right] \tag{7}$$

Integration occurs in two steps, and in each case R is the independent variable.

Step 1 Integration Yields the following:

$$D_A\ \partial P_A/\partial R = -\tfrac{1}{2}\,D_B\ \partial P_B/\partial R + C \tag{8}$$

Solving for C we note the condition at pellet center where mass flux is zero.

$$R = 0 \qquad \partial P_A/\partial R = 0 \qquad \partial P_B/\partial R = 0$$

Step 2 Setting C = 0

$$D \, \partial P_A / \partial R = -1/2 \, D_B \, \partial P_B / \partial R \tag{10}$$

Again integrating the partial pressures with respect to R we get the following:

$$D_A P_A = -1/2 \, D_B P_B + C \tag{11}$$

We make use of the second boundary condition that the partial pressures at the pellet surface are the stream conditions.

$$R = R \qquad P_A = P_{AO} \qquad P_B = P_{BO} \tag{12}$$

$$C = D_A P_{AO} + 1/2 \, D_B P_{BO}$$

Substituting and refining the equation, we get the following:

$$P_B = 2 \, D_A / D_B \, (P_{AO} - P_A) + P_{BO} \tag{13}$$

The authors integrated the equation assuming P_{BO} of carbon monoxide is zero at the surface and substituting back into the initial transport equation containing partial pressure (P_A) as a function of radius.

$$\partial / \partial R (D_A \, \partial P_A / \partial R) - \rho S (K_1 * P_A / (1 + K_2 * P_A + K_3 * D_A / D_B (P_A - P_{AO})) = 0 \tag{14}$$

It is worthy of note that the transport equations for diffusion of each chemical specie are interelated by the chemical mass balance. Also, the conditions of known surface concentrations and zero diffusion rate at pellet center are influential in node analysis. Node analyses are described (3) as used in determining termperatures of materials at specific locations called nodes.

The Austin-Walker example considers two chemical components. If these analyses are extended to consider a reaction of the type $(A + B \rightarrow R + S)$, the four chemical species require four mass transport equations. Temperature variation through the catalyst provides a fifth.

Because of the large number of partial differential equations involved, a node analysis was selected for determination of Hinshelwood rate equations for non-isothermal pellet data.

3. Adsorption and desorption. The Type 3 rate control - adsorption and desorption - occurs when the speed of reaction is limited by the rate of adsorption and desorption of chemical species. It is noted (4) that the concentration (X) of chemical species adsorbed on a solid surface is related to the partial pressure of "A" in the main stream. This relation is defined as the Langmuir Isotherm.

$$X = a\,(P_A)^n \tag{15}$$

For adsorption rates or condensation on the catalyst surface, rate is assumed proportional to the partial pressure of "A". This is based upon kinetic theory of gases where the reaction is controlled by the number of molecular collisions molecule "A" makes with the catalyst surface. Rate of adsorption = $K_1\ P_A\ (1 - \sigma)$. Here σ is the surface covered with reactant or product, and a linear isotherm $(n = 1)$ has been assumed. Desorption on the other hand is a function of the product of a constant and the concentration of the adsorbed product.

The desorption rate is defined as follows:

$$\text{Rate of Desorption} = K_2 \sigma$$

At equilibrium condensation rate equals evaporation rate.

$$K_1 P_A (1 - \sigma') = K_2 \sigma'$$

$$\sigma = K_1 * P_A / (K_2 + K_1 * P_A) \qquad (16)$$

Further development involved study of more than one chemical species vying for the same site. Parameters σ and σ' are the coverage of metal surface by species A and B, respectively. Then $(1 - \sigma - \sigma')$ is the uncovered catalyst surface.

$$\text{Condensing rate of } A = K_1 (1 - \sigma - \sigma') P_A \qquad (17)$$

$$\text{Evaporation rate} = K_2 \sigma \qquad (18)$$

A similar equation for species B can also be defined.

$$K_1' P_B (1 - \sigma - \sigma') = K' \sigma'$$

The catalyst surface coverage of component B, (σ') may now be obtained from the two equations for species A and B if we assume that the slow step is the adsorbing of "A". Thus surface coverage of "A" σ, is negligible and influences the reaction very little. Solving the above equations for σ' we obtain the following:

$$\sigma' = K_1 P_B \left[\frac{1}{K_2' + K_1' P_B} \right] \qquad (19)$$

The rate of reaction of "A" is the product of the free surface $(1 - \sigma')$ and the specific rate of adsorption of "A" per unit free surface, or the rate of reaction of A proportional to a constant times partial pressure of species "A" upon the free adsorption sites ($\sigma = 0$).

$$r = KP_A (1 - \sigma ')$$

$$r = K K_2' (\frac{1}{K_2' + K_1' P_B}) P_A \qquad (20)$$

This is the form of one Hinshelwood equation. Other equations may be determined by assuming adsorption of B or desorption of products R and S control.

4. Surface reaction. The Type 4 rate control surface reaction is associated with the speed of the reaction on the catalyst surface. Concentrations of the chemisorbed reactant are controlled by the adsorption equilibrium between fluid and solid while the surface rate is a function of the surface adsorbed reactants and vacant site locations. In the case of a monomolecular reaction (5).

$$A \rightarrow R$$

The chemical reaction is defined by the following equation:

$$r = K_1 (P_A - P_B/KE) \qquad (21)$$

If the reaction rate is controlling, the adsorption steps are assumed to be in equilibrium between condensation and evaporation of reactants and products. Surface concentrations of A and R can then be determined from Langmuir isotherm considerations. It is noted for specie "A" in the previous section, the following equation was defined.

$$C_A = \sigma = K * P_A/(1 + K * P_A) \qquad (22)$$

It is further noted that for equilibrium condition in a reaction, the equilibrium constant is defined as the ratio of the forward rate constant divided by the reverse rate constant.

$$K_1 (1 - \sigma) P_A = K_2 \sigma$$

$$K = K_1/K_2 = \sigma/(1 - \sigma) P_A \qquad (23)$$

If component "A" is in an admixture with several other components A, B and R adsorbed on active sites, adsorption equilibrium equations may be written for each component. Available free sites will equal to the total number of sites less those sites ($C_A \cdots C_R$) used by the components

$$C_L = (1 - \sigma) = L - (C_A + C_R) \qquad (24)$$

Concentrations C_A and C_R are defined by equation 22 where the concentration is the product of the equilibrium constant, the number of free sites, and the activity or partial pressure of the component ($C_A = K(1 - \sigma)P_A$). The concentration of free sites may then be defined as follows:

$$C_L = L-(K (1 - \sigma)P_A + K_R (1 - \sigma) P_B) \qquad (25)$$

Since C_L EQUALS $1 - \sigma$ we solve for C_L arriving at equation

$$C_L = L/(1 + K_A * P_A + K_R * P_R) \qquad (26)$$

The equilibrium concentration of "A" on the catalyst surface is obtained by substituting for C_L or $(1 - \sigma)$ in equation $C_A = K(1 - \sigma) P_A$.

$$C_A = K_A (L/(1 + K_A * P_A + K_R * P_R) P_A \qquad (27)$$

and for the product concentration C_R

$$C_R = K_R (L/(K_A * P_A + K_R * P_R) P_R \qquad (28)$$

Making substitutions for C_A and C_R in the rate equation we obtain

$$\bar{F} = K_1 \ (L/(K_A * P_A + K_R * P_R)) \ (K_A * P_A - \frac{K_R * P_R)}{KE} \qquad (29)$$

Additional equations have been derived assuming different surface rate steps controlling the bulk of which are known as Hinshelwood rate equations. A least square approximation of the rate constants is used to derive an equation representative of the rate versus concentration data. The equation best fitting the data is considered representative and because the equation is based upon a specific rate controlling step, the controlling mechanism is identified.

B. Hinshelwood Rate Equation Determination

The previous section discussed the control mechanisms and how the nature of these mechanisms affect the derivation of Hinshelwood equations. It was found that catalysis is composed of a sequence of reaction steps; and for analysis one step is assumed to control the overall rate. To pin point the controlling step the rate equation is determined for a reaction $A + B \longrightarrow R + S$ the general rate equation as defined in (9) is:

$$r = \frac{K \quad (P_A * P_B) - (P_R * P_S)/KE}{(1 + K_2' * P_A + K_3' * P_B + K_4' * P_R + K_5' * P_S)^n} \qquad (30)$$

The Hinshelwood rate constants are then K, K_2', K_3', K_4', and K_5'. To determine these constants from rate data the equation is rewritten with all the unknown constants to one side of the equation.

$$K_1 + K_2 * P_A + K_3 * P_B + K_4 * P_R + K_5 * P_S = \left[\frac{POT}{r}\right]^{1/n} \qquad (31)$$

Solution of these constants is accomplished via least square linear approximation. Recent studies show non linear analysis to be more accurate for rate correlation but, here it was not needed to demonstrate methods of estimating constants from pellet information. The linear least square analysis assumes various rate equations and solves for values of K_1, through K_5 using rate (r) and concentration data P_A, P_B, P_R, and P_S. As an example, let us consider the rate equation for adsorption of "A" controlling. Large equilibrium constant makes the second term of numerator negligible.

$$r = P_A * P_B /(1 + K_3' * P_B + K_4' * P_R + K_5' * P_S)^n \qquad (32)$$

Placing all rate constants on one side of the equation we obtain the rate for $(K_1 + K_3 * P_B + K_4 * P_R + K_5 * P_S) = K * P_A * P_B/r$. For the results of the least square analysis to be acceptable the terms K_1, K_3, K_4, and K_5 must all be positive or zero otherwise equilibrium constant (forward and reverse rate) must be of opposite sign and cannot be equal as required for equilibrium. And since P_A does not appear in the denominator the constant K_2 must be zero. In similar manner, a large number of reactions are tried until all constants are positive or zero. When all the constants meet these requirements, the equation is found acceptable. Of the acceptable equations, the equation which shows the least deviation of the calculated rate from the measured rate is generally selected.

C. Reactor Pellet Data Analysis

The rate data itself is of importance to the analysis. Since results of Hinshelwood analyses are sensitive to errors introduced by the data, it is desirable to measure rates in a reactor segment where little change in physical conditions occur and chemical changes are readily measured. The two principal types of reactors used to measure rates are the differential and integral reactors.

The differential reactor is of interest because chemical reaction is performed in short reactor sections where conditions of temperature and stream chemical composition can be held constant. The reacting mixture is cycled through the reactor and the change in chemical composition noted. The rate of reaction in this increment of volume is defined (5) by an equation relating the changes in feed composition ($F\Delta X$) to the rate of reaction (r) in the small increment of catalyst mass (Δw):

$$F * \Delta X = \overset{=}{r} * \Delta W \tag{33}$$

Integral data is obtained from reactors where temperature and concentration vary. To determine reactor size integration of the equation 31 provides a relation between reactor weight catalyst, the feed rate F, and the amount of reaction (ΔX) occurring in the reactor bed.

$$F/W = \int dX/r \tag{34}$$

Integral data is plotted in terms of conversion X versus W/F. Thus for a given conversion it is possible to take the value of W/F and size the reactor for a given feed rate. Rates are determined by taking the slope of the plot ($\Delta X/\Delta W/F$); this provides a result similar to differential rate equation 31.

D. Node Analyses

The approach to determining Hinshelwood mechanisms from non-isothermal pellet data employs a node analysis similar to that used in Southwell's Relaxation Method. In Southwell's method (3) for heat transfer, nodes are specified geometric locations distributed uniformly throughout the material. Temperature gradients are calculated from node to node based upon known boundary temperatures, known material thermal properties and known fact that the sum of the heat fluxes into each node must be zero for steady state temperature.

The heat fluxes are determined from node to node based upon the Fourier equation -

$$q = \frac{(KA)}{X} (T_{node\ 2} - T_{node\ 1}) = c' (T_{N2} - T_{N1}). \tag{35}$$

Heat fluxes into and out of the nodes are summed with positive values for heat flux in, and negative for heat flux out. The sums of the heat fluxes in terms of node temperatures are set equal to residuals R1 to RN. The object of the analyses is to make these residuals go to zero. To accomplish this a table is formed which indicates how large the changes are in residuals for a unit change in node temperature. By inspection, the largest residual is altered to go to zero by changing one of the temperatures. Changes in all of the residual terms are noted and residual terms adjusted. The next highest residual is examined and temperatures are changed to make it go to zero. This is repeated until all residual terms are zero or sufficiently close to zero to be considered negligible. The set of adjusted temperatures provides the desired temperature distribution through the material.

Node analysis for heat and mass flux into the catalyst required significant modification as undertaken in the ensuing investigation. Temperatures were found to be dependent upon the amount of reaction occurring in the nodes. Analysis assumed the outermost node exhibited pellet surface conditions. Surface rates were used to estimate rate equations. The sum of the reactions in all nodes was required to equal the total rate observed for the pellet. Node rates were limited to values less than that defined by diffusion rates and by the rate equation determined from the surface rate estimates.

1. <u>Concentration distribution in pellet</u>. With non-isothermal pellet data the achievement of steady state conditions required that mass flux into a node be zero. To simplify the computer program a spherical pellet was selected having four nodes, each node representing 1/4 of the pellet volume. Nodes in the spherical pellet were defined as the surfaces of a thin spheres located centrally in the node shells. It was assumed that the amount of reaction occurring in each shell could be represented at the node. For the purpose of calculation, the total rate of reaction in a pellet (r_t) equals the sum of the rates in all four nodes. This means that transport of reactants and products is controlled by the concentration gradient for each. Thus for a reaction of A + B = R + S, the concentration drop between nodes may be determined from a set of equations describing flow between node N-1 and N:

$$\begin{aligned} -RA(N) &= DEA * AR(N)/DR(N)\ \ C_A(N) - C_{AS} \\ -F*RA(N) &= DEB * AR(N)/DR(N)\ C_B(N) - C_{BS} \\ H*RA(N) &= DER * AR(N)/DR(N)\ C_R(N) - C_{RS} \\ Q*RA(N) &= DES * AR(N)/DR(N)\ C_S(N) - C_{SS} \end{aligned} \tag{36}$$

Here, the diffusion rate of each component is related to diffusion of species A or RA(N) times a coefficient determined by the mass balance from the reaction. Since product mass exiting equals reactant mass entering the node, the requirement that mass flux in equals mass flux out is satisfied.

Diffusion rates are controlled by a requirement to feed the reaction at the inside nodes. Reaction rates therefore influence the variation in concentrations observed. The solution for the concentration curve requires the solving of the above equations for $C_A(N)$, $C_B(N)$, $C_R(N)$, and $C_S(N)$ at each node N. Main stream concentrations are assumed known. The N in bracket refers to the node number and is written in this discussion in Matrix notation similar to the Fortran IV designation.

2. Temperature distribution. Temperature through the pellet is related to the heat released at each node from the reaction occurring there. The heat flux rate is based upon the heat generated in the inner nodes which must flow out to satisfy pellet steady state temperature conditions.

$$\sum_{n+1}^{4} R(N) * \Delta H = CK * AR(N)/DR(N) * (T_{N2} - T_{N1}) \qquad (37)$$

Temperatures for each node are obtained by summing and adding these to the experimentally determined surface temperature.

$$T_N = T_S + \Sigma \Delta T \qquad (38)$$

3. Rate determination. For the initial least square approximation of the surface rates all of the reaction is assumed placed in the surface node. The program solves (via least square analysis) for the rate

equation and constants which fit the data for high and low catalyst surface temperatures. If rates are calculated for each node using the least square equation, the total quantity reacted would be about four times the total mass experimentally observed to react in the pellet. Subsequent approximations alter the equation to reduce the calculated rates. Next considering the other extreme, if all the reacting mass diffuses as far as possible into the pellet, we find that the total reacting mass diffuses into the first two or three nodes, but because of diffusion restriction, the total pellet reaction flow may not reach the last node. These two conditions are represented by the curves in Figure 1.

Rate determination is accomplished by first assuming an initial rate distribution through the pellet. In this analysis we assume that the pellet total rate is disseminated to the interior nodes to the maximum allowable by diffusion. Then by decreasing the equation estimated rates at each node, the reacting mass in the inner nodes are moved to the outer ones until all nodes rates summed equal the total pellet rate.

Chemical concentration variance is estimated based on the following assumption critical to the argument presented: The amount of diffusion (quantity of mass) traveling from one node to the next is controlled by the rate of reaction occurring in the innermost nodes. If we take the center (Innermost) node, the amount diffusing into the node is the amount being reacted there. An equal mass must leave the node — in this case, the products of reaction. Product accumulation does not allow a steady state chemical composition in the node. In similar manner, the amount

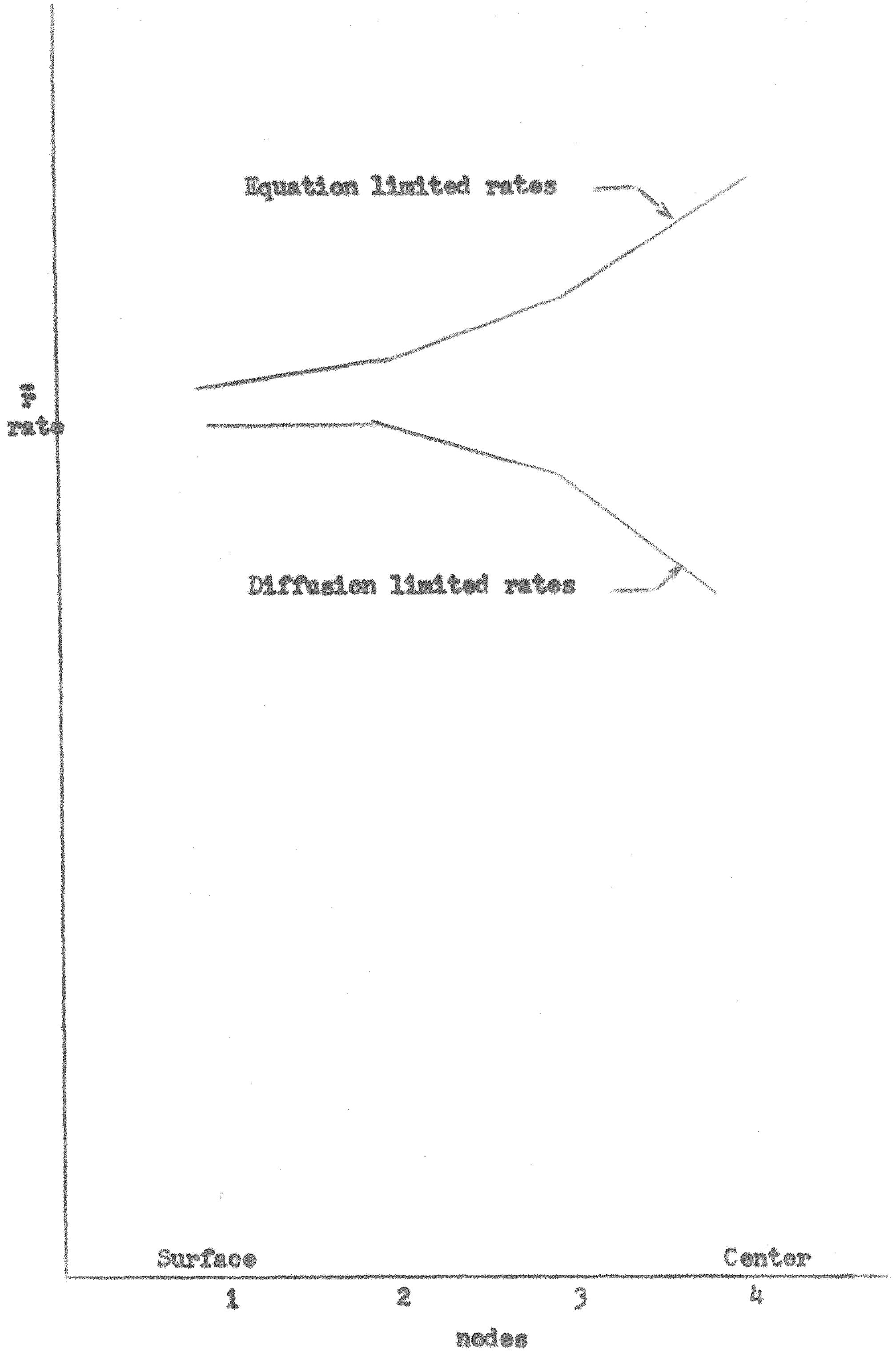


FIGURE 1

RATE VS NODE
(Based upon Diffusion Limits Least Square Approximation -
First Iteration)

of diffusion between second and third nodes can be estimated as equal to the quantity of reactant needed to feed the inner nodes three and four. The same holds true for diffusion between nodes one and two. For calculations of interior node concentrations, the surface node concentration must be known. Internal rates and resultant concentration gradients provide the driving force for flow of reactants into the inner nodes.

These concentrations and temperatures are subsequently used in the rate equation to calculate node rates. Estimates of node one rate (surface rate) are used to determine the Hinshelwood rate equation. Employing equation calculated interior node rates, a difference determined node one is estimated by subtracting the node two, three and four rates from the total pellet rate. If this node one rate is smaller than the rate used to define the equation, the equation rates are decreased by taking incrementally smaller surface rate estimates. To achieve this, a percentage cut of the last surface or node one estimate is used. This is done by using a multiplier term call ZD. The term ZD is decreased and then used to multiply all pellet last estimated node one rates.

$$\begin{aligned} ZD &= 0.8 * ZD \\ r(1) &= ZD * (\text{last node one estimate}) \end{aligned} \tag{39}$$

A least square approximation from the decreased pellet node one rates is calculated. Next, all rates used to define the Hinshelwood equation are compared with the difference determined rates. This process is continued until the surface node for pellets provides a ZD * (last node one estimate) product incrementally less than the difference determined node one rate yielding a rate versus node curve as shown in Figure 2.

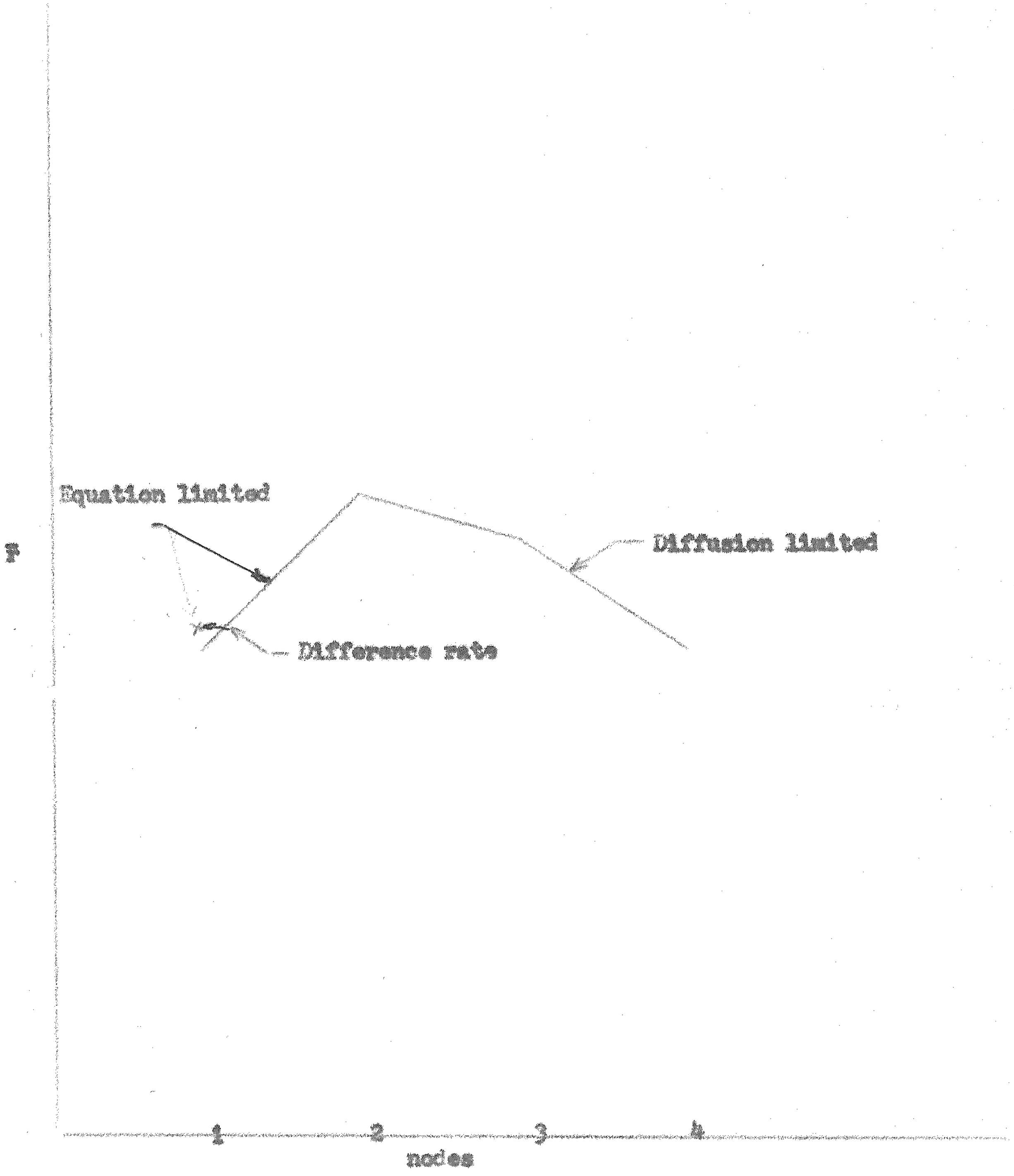


FIGURE 2

RATE VS NODE
(ZD * last node estimate)

Up to this point, we considered single pellet analyses. The least square approximation rate curve is defined from many pellets. As indicated earlier, the least square equation defined from all pellets is modified until node one equation rates r(1) for all pellets are incrementally smaller than the difference determined node one rates. This means that one pellet sets the low value of rates and of ZD. The other pellet node one rates determined via the difference approach will tend to be high compared to their final value. If the difference between the least square approximation calculated rates (R1CALC) and the difference determined node one rates is small, the equation is accepted. When the difference as indicated by the coefficient of variation between node one rates calculated from the least squares approximation and difference determined node one rates deviates so as to reject the equation, the last difference determined node one rates are used for the next least square approximation. Thus, the shape of the curve is altered to reflect the high or low node one rates resulting from the previous pellet calculations. Each iteration should bring the least square approximated curve closer to the node one difference estimates as indicated in Figure 3.

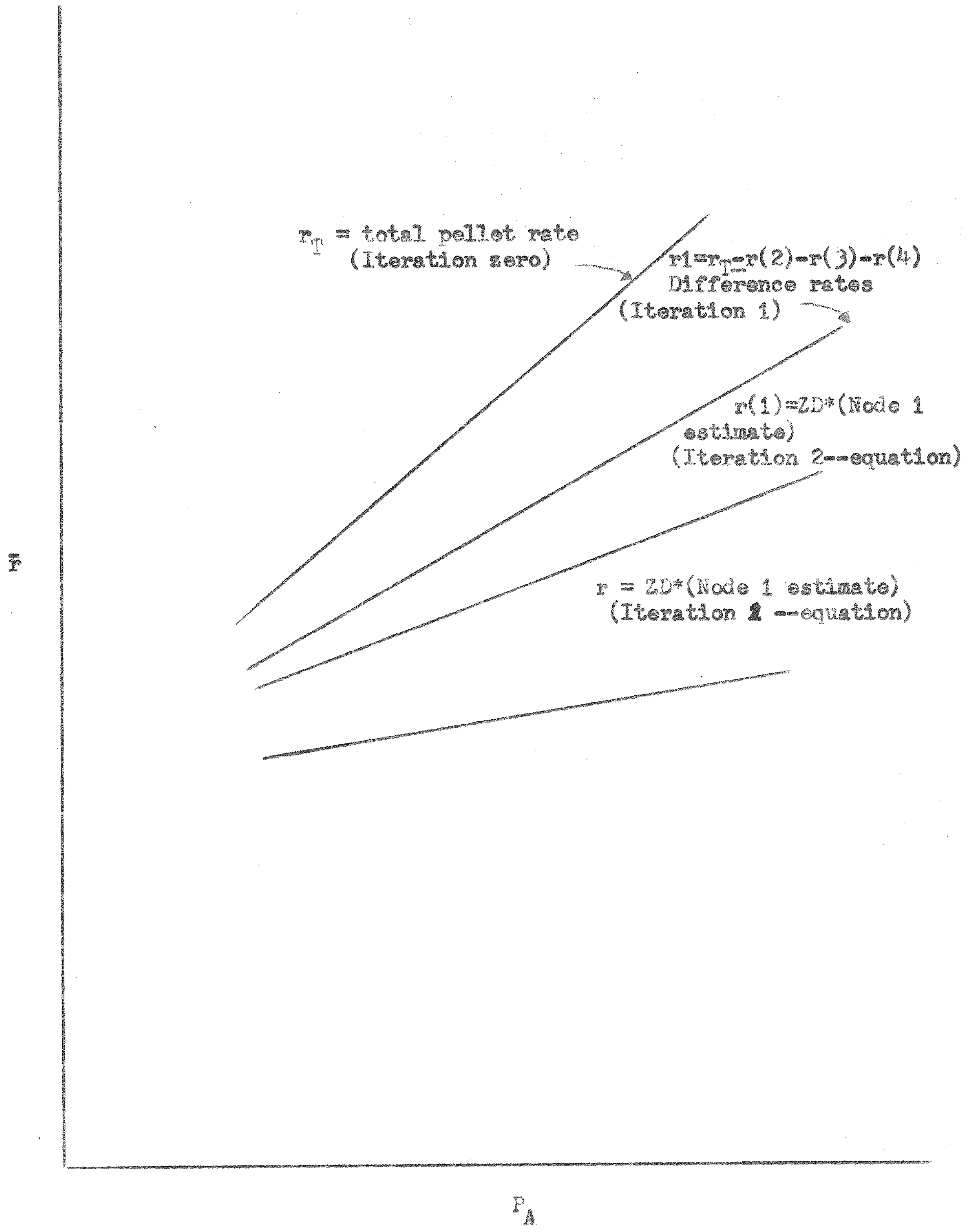


FIGURE 3

SUCCESSIVE NODE 1
VERSUS PARTIAL PRESSURE A ITERATIONS

E. Node Program Description

It was concluded from the analysis that a Node method for determining Hinshelwood equations from catalyst data was feasible. In view of the extensive number of calculations needed to converge to a representative Hinshelwood equation for the surface rates, a computer program appeared to be the only reasonable means of attaining the solution. A computer program was thus assembled which was composed of three major sections or loops designed to perform the following computation:

1. Least square node one approximation.
2. Diffusion, temperature and node one rate determination.
3. Comparison of difference determined node one rates with the least square approximation node one rates.

These loops are shown in the computer control diagram presented in Figure 4. The diagram indicates the controls statements but only calls out the analysis to be performed in each part. The three major loops are initiated from an if statement indicated by a diamond on page 25A. The diamonds (IN:2) are in the diagram lines containing indicators I = 1 and I = 2.

The indicators (I) are used to reference the storage matrices B and C. Storage matrices are defined as matrices in which experimental data has been placed. Prior to the three loop split the matrix values of B or C are transferred to working matrix A. Then, after performing computations in the first loop, the indicator I designates which matrix (B or C) the computed values are to be stored. We will consider operations in each loop in the following discussion. Input and output is discussed in the APPENDIX. A program printout is also shown in the APPENDIX.

FIGURE 4

COMPUTER CONTROL DIAGRAM (ONLY)
(Part A)

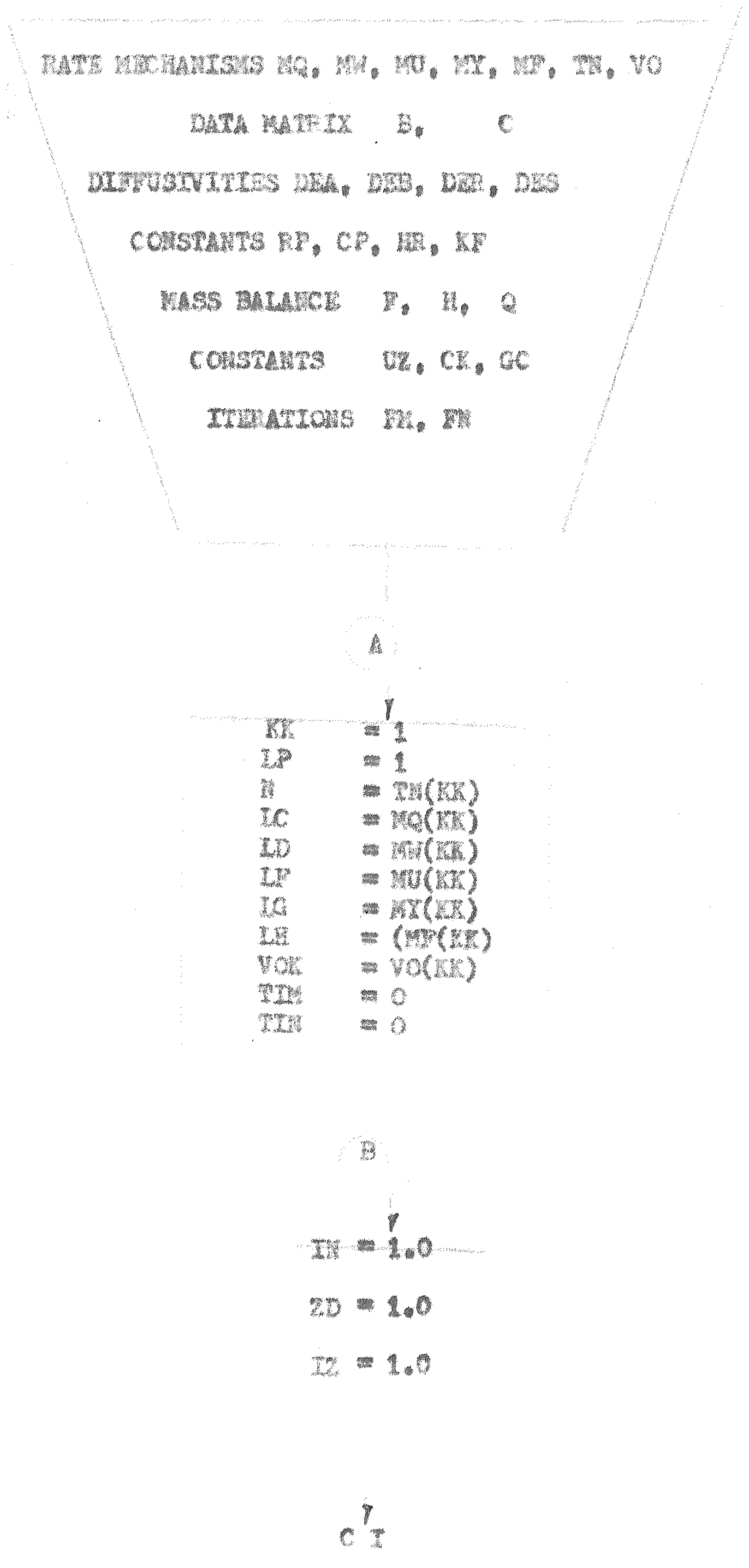
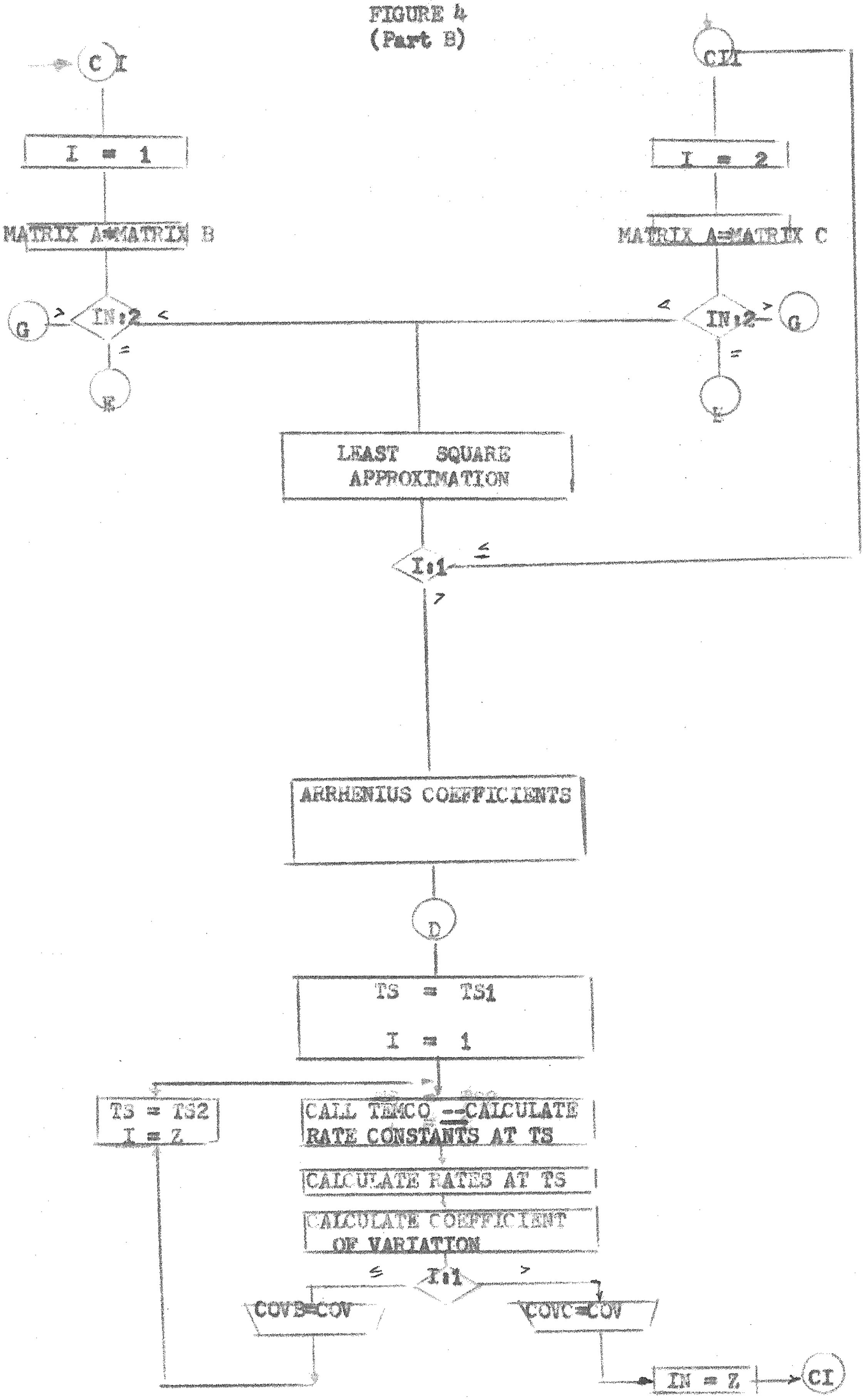


FIGURE 4
(Part B)



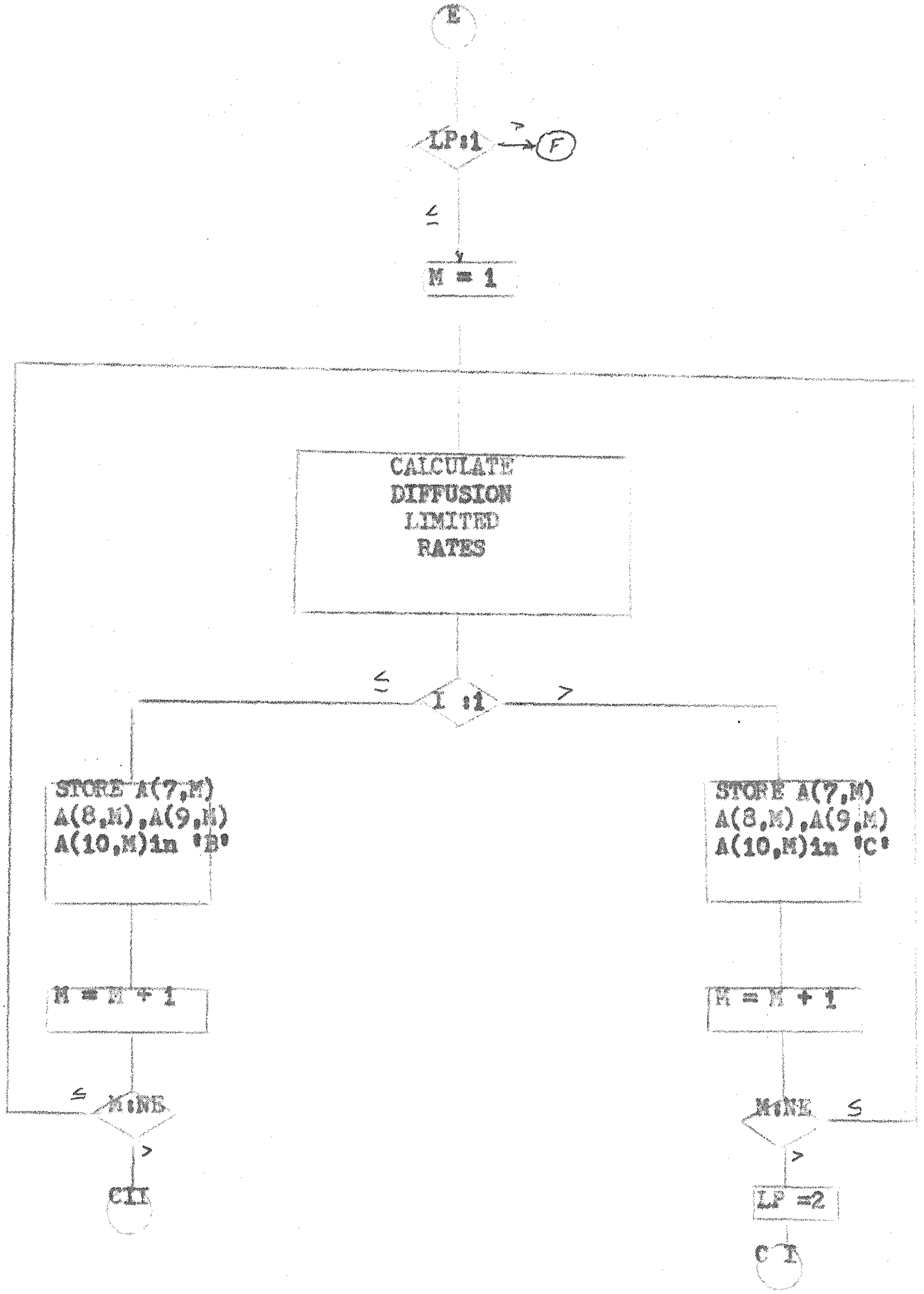


FIGURE 3
(Part C)

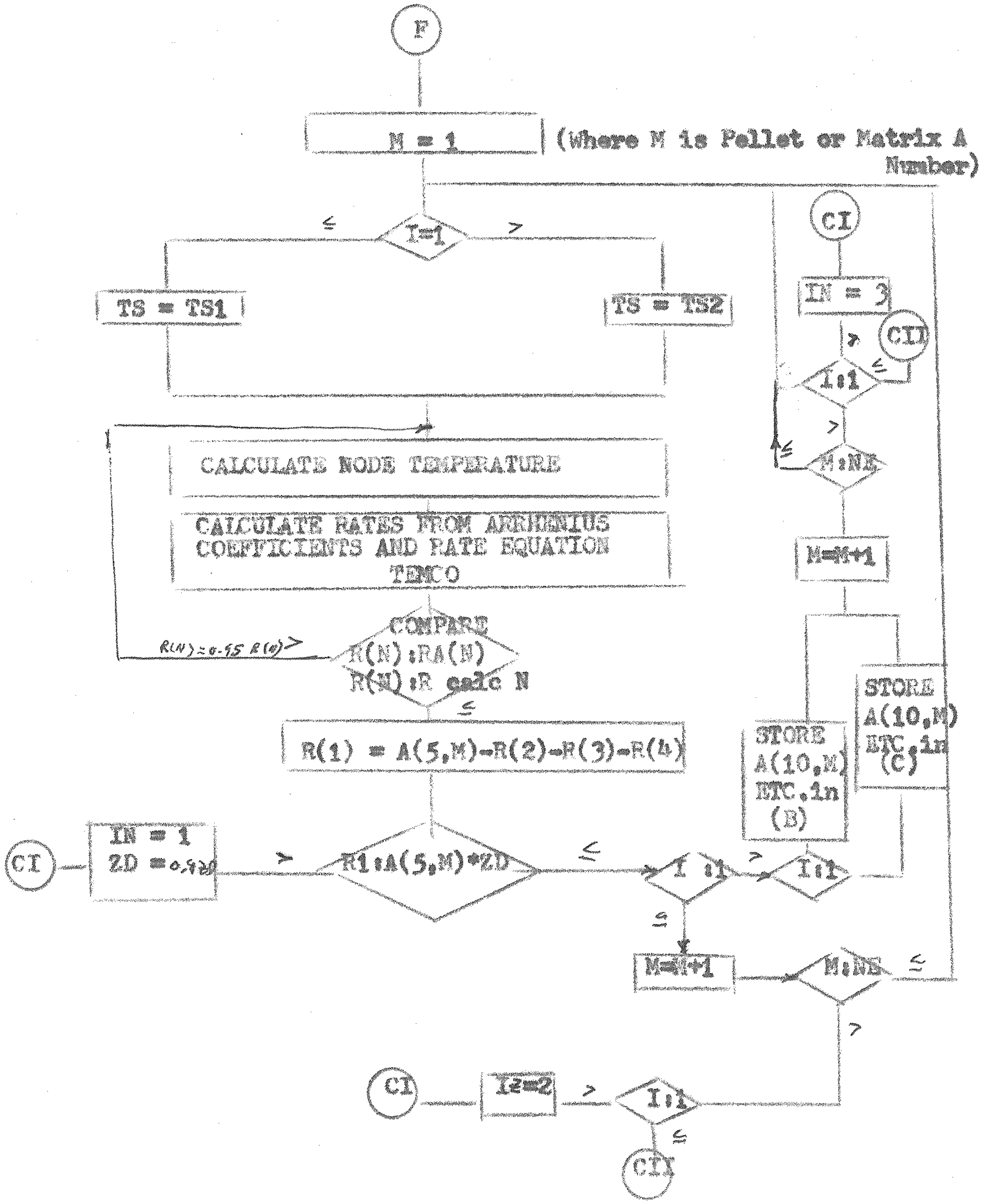


FIGURE 3
(Part D)

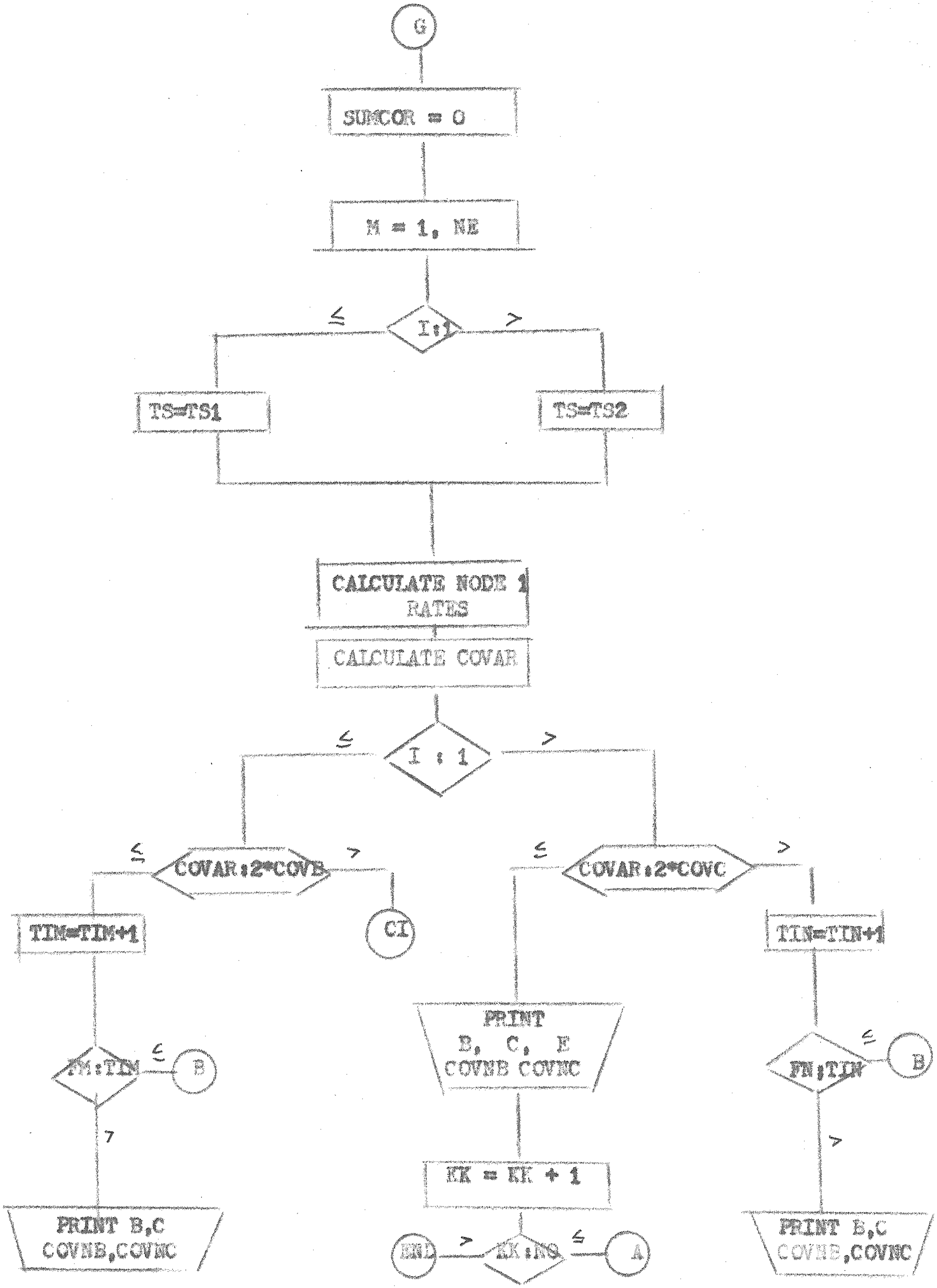


FIGURE 3
(Part E)

1. Least square approximation loop (IN = 1). In loop 1 and node 1, rates and concentrations are used for defining the Hinshelwood rate equation. Node one rate estimates are initially specified in the input data. The Hinshelwood rate form is preselected by the programmer and called out in the input to the computer. Using the preselected rate forms, the computer performs a linear least square analysis of the surface rates evaluating the equation for the rate equation constants. These constants are used to calculate the Arrhenius constants. The last operation in the loop determine the closeness of fit of the equation derived rates to the previously determined node one rates. Closeness of fit of the difference determined node one rates and the Hinshelwood equation calculated rates is indicated by a coefficient of variation.

a. Hinshelwood rate equation. The calculations performed in loop one are as follows: The rate equation is assembled by calling for terms from several function subroutines. Rate forms are designated from addresses included in the program input. Refer to the Appendix for a more detailed description. The generalized rate form is defined by the equation:

$$r = \frac{\text{Kinetic term} * \text{potential term}}{(\text{adsorption Term})^{N}}$$

Table I through IV provides a list of terms in Kinetic, potential and individual adsorption terms encompassing those included in the subroutines. The equation is rewritten in terms of reactant and product concentrations as follows:

$$K_1 + K_2 * P_A + K_3 * P_B + K_4 * P_R + K_5 * P_S = \left(\frac{POT}{r}\right)^{1/N} \qquad (40)$$

Table I Reaction Rate Mechanisms
(Tables are from Ref. 9)

Part A

DRIVING POTENTIAL TERMS

Reaction	$A \rightleftarrows R$	$A \rightleftarrows R+S$	$A+B \rightleftarrows R$	$A+B \rightleftarrows R+S$
Adsorption of A controlling	$a_A - \frac{a_R}{K}$	$a_A - \frac{a_R a_S}{K}$	$a_A - \frac{a_R}{K a_B}$	$a_A - \frac{a_R a_S}{K a_B}$
Adsorption of B controlling	0	0	$a_B - \frac{a_R}{K a_A}$	$a_B - \frac{a_R a_S}{K a_A}$
Desorption of R controlling	$a_A - \frac{a_R}{K}$	$\frac{a_A}{a_S} - \frac{a_R}{K}$	$a_A a_B - \frac{a_R}{K}$	$\frac{a_A a_B}{a_S} - \frac{a_R}{K}$
Surface reaction controlling	$a_A - \frac{a_R}{K}$	$a_A - \frac{a_R a_S}{K}$	$a_A a_B - \frac{a_R}{K}$	$a_A a_B - \frac{a_R a_S}{K}$
Impact of A controlling (A not adsorbed)	0	0	$a_A a_B - \frac{a_R}{K}$	$a_A a_B - \frac{a_R a_S}{K}$
Homogeneous reaction controlling	$a_A - \frac{a_R}{K}$	$a_A - \frac{a_R a_S}{K}$	$a_A a_B - \frac{a_R}{K}$	$a_A a_B - \frac{a_R a_S}{K}$

Part B

REPLACEMENTS IN THE GENERAL ADSORPTION TERMS.

$$\left[1 + K_A a_A + K_B a_B + K_R a_R + K_S a_S + K_I a_I\right]^n$$

Reaction	$A \rightleftarrows R$	$A \rightleftarrows R+S$	$A+B \rightleftarrows R$	$A+B \rightleftarrows R+S$
Where adsorption of A is rate controlling replace $K_A a_A$ by	$\frac{K_A a_R}{K}$	$\frac{K_A a_R a_S}{K}$	$\frac{K_A a_R}{K a_B}$	$\frac{K_A a_R a_S}{K a_B}$
Where ~~de~~adsorption of B is rate controlling replace $K_B a_B$ by	0	0	$\frac{K_B a_R}{K a_A}$	$\frac{K_B a_R a_S}{K a_A}$
Where desorption of R is rate controlling replace $K_R a_R$ by	$KK_R a_A$	$KK_A \frac{a_A}{a_S}$	$KK_R a_A a_B$	$KK_R \frac{a_R a_B}{a_A}$
Where adsorption of A is rate controlling with dissociation of A replace $K_A a_A$ by	$\sqrt{\frac{K_A a_R}{K}}$	$\sqrt{\frac{K_A a_R a_S}{K}}$	$\sqrt{\frac{K_A a_R}{K a_B}}$	$\sqrt{\frac{K_A a_R a_S}{K a_B}}$
Where equilibrium adsorption of A takes place with dissociation of A replace $K_A a_A$ by	$\sqrt{K_A a_A}$	$\sqrt{K_A a_A}$	$\sqrt{K_A a_A}$	$\sqrt{K_A a_A}$
and similarly for other components adsorbed with dissociation.				
Where A is not adsorbed replace $K_A a_A$ by	0	0	0	0
and similarly for other components which are not adsorbed.				

Table I Reaction Rate Mechanisms
(Continued)
(Tables are from Ref. 9)

Part C

KINETIC TERMS.

Multiply each of the terms below by EL except for the homogeneous reaction.

Adsorption of A controlling	k_A
Adsorption of B controlling	k_B
Desorption of R controlling	$k_R K$
Adsorption of A controlling with dissociation	$\frac{s}{2} k_A$
Impact of A controlling	$k_A K_B$
Homogeneous reaction controlling	k

Surface Reaction Controlling

	$A \rightleftarrows R$	$A \rightleftarrows R+S$	$A+B \rightleftarrows R$	$A+B \rightleftarrows R+S$
Without dissociation	$k_s K_A$	$k_s\ s\ K_A$	$k_s s\ K_A K_B$	$k_s\ s\ K_A K_B$
With dissociation of A	$k_s s\ K_A$	$k_s\ s\ K_A$	$k_s s(s-1K_A K_B$	$k_s s(s-1)K_A K_B$
B not adsorbed	$k_s\ K_A$	$k_s\ s\ K_A$	$k_s\ K_A$	$k_s\ s\ K_A$
B not adsorbed, A dissociated	$k_s\ s\ K_A$	$k_s\ s\ K_A$	$k_s\ s\ K_A$	$k_s \cdot s\ K_A$

Part D

EXPONENTS OF ADSORPTION TERMS

Adsorption of A controlling without dissociation	$n = 1$
Desorption of R controlling	$n = 1$
Adsorption of A controlling with dissociation	$n = 2$
Impact of A without dissociation $A + B \rightleftarrows R$	$n = 1$
Impact of A without dissociation $A+B \rightleftarrows R+S$	$n = 2$
Homogeneous reaction	$n = 0$

Surface Reaction Controlling

	$A \rightleftarrows R$	$A \rightleftarrows R+S$	$A+B \rightleftarrows R$	$A+B \rightleftarrows R+S$
No dissociation of A	1	2	2	2
Dissociation of A	2	2	3	3
Dissociation of A (B not adsorbed)	2	2	2	2
No dissociation of A (B not adsorbed)	1	2	1	2

This equation form is used for linear fitting of the node one rate data. The linear least square analysis is performed as described by Hougen and Watson (8). Values for the terms K_1, K_2, K_3, and K_4 and K_5 are stored in a matrix E in preparation for the next step that of computation of the Arrhenius constants.

b. Arrhenius constant determination. After the rate constants in loop one are calculated for the matrix B and matrix C data at two surface temperatures, the temperature dependence of the constants is represented by the Arrhenius exponential function:

$$K = K_o \exp(-A/RT) \tag{41}$$

Where K_o and A are constants to be determined, R is the universal gas constant and T is the temperature of the reaction. The Arrhenius constants are determined by taking the log form of the above equation. Substituting into two simultaneous equations the K1B and K1C constants from matrix E, A and K are then defined by the equations below.

$$A = R\ (TS1 - TS2/TS1 * TS2)\ \log\ (K_1B/K_1C)$$

$$K_o = K_1B\ EXP\ (A/R * TS1)$$

The Arrhenius constants in the computer program are defined as AK for K_o and DB for A.

c. Coefficient of variation. The coefficient of variation indicates how far apart the node one rates are from the equation determined rates. A coefficient of variation is determined for each matrix (B and C) in the following manner. We set the termperature (T) for the Arrhenius constant equal to the surface temperature and compute values for the Hinshelwood constants using the Arrhenius equation. Rates are calculated for each pellet based upon these constants and the surface concentrations of the species.

$$RC = \frac{K \quad * \quad POT}{(K_1 + K_2 * P_A + K_3 * P_B)^N} \tag{43}$$

These calculated rates are then compared with the rates R(1) determined from either the initial estimate supplied by the programmer in the input or from the difference determined node one rates which are calculated in loop two and stored in terms B(10,M) or C(10,M).

R (1) = (total rate) * (multiplier defined in the program)

The multiplier is the product of the node one rate fraction from matrix terms B(10,M) or C(10,M) and the value of ZD which is set equal to 1 for the first iteration but is decreased in loop two during subsequent iterations. The term M corresponds to the pellet assigned number in the matrix.

The coefficient of variation is determined from the rates by solving the following equation:

$$\text{COV (B or C)} = \sqrt{\frac{\Sigma((RC) - R(1))^2}{N - 1}} \tag{44}$$

When coefficients of variation have been computed for data in matrix B and C, the computer sets IN equal to 2 sending the program to loop two indicated as Location E in the diagram.

2. <u>Diffusion, temperature, and node one rate determination (IN = 2)</u>. The second loop location E, performs several key operations. The calculations performed in this loop determine diffusion rate limits, node

temperature, node concentrations, and node rates. The first calculation for diffusion limits is performed when indicator LP in loop two equals 1. The calculations employ average effective diffusivities at temperatures observed for the nodes. Temperature dependent diffusivities may be introduced into the program but average values were selected here to simplify calculation. After determining the diffusion limits for all data points, LP is set equal to 2 and further analyses bypass this section.

The second section of loop two calculates temperatures at each node. An initial rate estimate for the nodes is that the pellet reacting mass is diffused into the pellet as far as possible. In some cases this results in all of the reaction occurring in node four (all reacting mass diffusing into center node). The method of analysis used starts with high estimates of interior node rates and decreases the rates in each of the innermost nodes two, three and four by decreasing the linear least square approximation rates. The outermost node (node one) rate referred to as the difference determined rate is the rate determined from the total pellet rate less the rates from nodes two, three and four. When the difference determined node one rates become incrementally larger than the estimated surface rate we know the sum of the node rates must be slightly less than the total observed pellet reaction rate. This condition exists because the difference determined rate is larger than the surface rate estimate which was used to define the rate equation and calculate node two, three and four rates. These node one rates are forwarded to loop three for a final comparison of the rates determined from the equation versus those from the difference methods.

a. Diffusion limited rates. The calculations performed in loop two are as follows: In section one of loop two calculations of the mass flux between the nodes is determined. Several assumptions are made. The maximum flow of reactant into the pellet is assumed not to exceed the total reaction taking place in the pellet. Diffusion of each reactant and product is assumed related by the chemical reaction mass balance to one another. Thus, the reaction concentration diminishes proportionately to increases in product concentration. For a given pressure and temperature, the total number of moles/unit volume for a gas is known. The sum of the molar concentrations of the reactants and products in the node, moles per unit volume, must be equal to the total molar concentration moles/unit volume. Concentrations are subsequently calculated for each node with the exception that node one is assumed to have the same concentration as that of the main stream.

Starting with total rate of reaction of A in the pellet to be that diffusing to node two, the concentrations at node two is determined from the following equations. Terms AR and DR are the mean transfer area and distance between nodes respectively and RA is the diffusion rate of specie A. Terms C_{AS} to C_{SS} are surface concentrations.

$$\begin{aligned}
C_A &= - RA * DR(2)/(DEA * AR(2)) + C_{AS} \\
C_B &= - F * RA * DR(2)/(DEB * AR\ (2)) + C_{BS} \\
C_R &= + H * RA * DR(2)/(DER * AR\ (2)) + C_{RS} \\
C_S &= + Q * RA * DR(2)/(DES * AR\ (2)) + C_{SS}
\end{aligned} \tag{45}$$

This process is repeated for node three assuming the values of C_A

through C_S determined for node two are the new values of C_{AS} to C_{SS}. After calculating each set of concentrations, the concentrations are summed and compared with the total number of moles which a node (1/4 pellet volume) will hold. The total node quantity is bracketed by limits FD and FR placed in the program input.

$$(C_A + C_B + C_R = C_S) : FD$$
$$(C_A + C_B + C_R + C_S) : FR \tag{46}$$

If the sum falls outside these limits, the value of RA is decreased.

$$RA = 0.95 * RA \tag{47}$$

It is known that for RA equal to zero the concentration must be that of the surface concentrations C_{AS} + C_{AB} etc. Thus it is expected as RA goes to zero that some value of RA will provide a total concentration that falls within the defined limits FD and FR.

b. <u>Temperature determination in nodes</u>. Returning to section two of loop two, the temperatures are determined on the basis that heat generated by the reaction must flow out of the pellet for thermal equilibrium . The $\triangle T$ can be determined if an effective conductivity is used in the following equation:

$$Q = R(N) * HR = (CK * AR(N) * \triangle T)/DR(N) \tag{48}$$

The temperature rise from node to node is determined and added to the surface temperature to determine the node temperature. For each iteration node temperatures are recomputed.

$$T = TS + \Sigma \triangle T \tag{49}$$

c. <u>Difference determination of node 1 rates.</u> R(N) In the determination of representative node one rates a reduced rate term R(N) is compared with diffusion limit rate RA(N) and the calculated rate R1 CALC. R1 CALC is determined from the least square approximation using node temperatures and concentrations estimated. If R(N) is larger than either of these rates, an increment of rate is removed from the node reducing R(N). The increment of reaction is then placed in the next outermost node.

Since initial node rates are determined from difference of diffusion into and out of the nodes, all of the reacting mass RA (N) is allowed to diffuse to the innermost nodes, therefore if anything is changed, it is the removing of some of the reaction from the inner nodes. The rates in each node one to four are compared with diffusion limited rate and with the calculated rates from the Hinshelwood equation employing Arrhenius constants. If there is more reaction in the node than allowed by these limits, R(N) is decreased.

$$R(N) = 0.95 * R(N) \tag{50}$$

When R(N) falls within these limits (Least square approximation and diffusion limits) the rate is considered representative of that node rate. Then, using a node one difference rate (total rate less inner node rates) a comparison is made between the node one rate and one defined by the product of ZD and the initial node 1 rate estimate. To obtain the initial node one estimate, the product A(10,M) * A(5,M) is determined where A(10,M) is the node rate fraction inputted or calculated and A(5,M) is the total rate. If from the comparison we find the difference rate is the lesser, the value of ZD is decreased.

$$ZD = 0.8 * ZD \tag{51}$$

The new value of ZD is sent back to loop one and multiplies all node one rates stored in matrix B and C. The ZD modified rates are used to obtain another least square approximation; a new Arrhenius constant, a new coefficient of variation and the program returns to loop two where the same rate adjustment process is continued. This process is repeated until the difference determined rates for the pellets are greater than the respective values of the product ZD and the initial node one rate estimate. When the node one rates are defined, they are stored in matrix B and C as B(10,M) and C(10,M) and are forwarded to loop three.

3. Loop three acceptance or rejection of least square linear approximation. The last loop (G) determines a second coefficient of variation. This time it provides a measure of deviation between the difference determined node one rates and the least square equation node one rates. The new coefficient of variation COVAR is then compared with the previous coefficient of variation COV. In the program as it presently stands, if COVAR is less than twice COV, the equation is accepted and constants printed out.

The calculations performed in this section repeat those performed in section one, part C, with the exception that the initial and final coefficients of variation (COV and COVAR) are compared.

F. Hydrogen Oxygen Catalysis - Sample Problem

A sample case, Hydrogen - Oxygen over platinum catalyst was used to determine the types of problems which might be encountered in the proposed computer analysis. Data was reviewed from two papers. The papers described experimental studies in which the first paper investigated catalyst particles and pellets subjected to mixed streams of Hydrogen and Oxygen gas simulating a stirred tank reactor, and the second paper studied catalysis of Hydrogen/Oxygen in a small tubular flow integral reactor. In the former paper by Maymo and Smith (6) the low oxygen concentration range (0-4 mole %) was examined and it was concluded that rates were nearly first order with respect to oxygen partial pressure:

$$R = 0.655 \exp\left(\frac{-5230}{RT}\right) P_{O2}{}^{0.804} \qquad (52)$$

Leder and Butt (7) studied the low hydrogen end of the gas mixture range and concluded that a Hinshelwood equation represented the data. They concluded that surface adsorbed oxygen reacting with hydrogen in the gas phase controlled rates thus providing correlation with the following rate equation:

$$R = \frac{K\, P_{O2}\, P_{H2}{}^{2}}{1 + K_O\, P_{O2} + K_w P_w} \qquad (53)$$

Maymo and Smith also noted that reactions at high oxygen/low hydrogen mixture ratios were second order with respect to hydrogen concentration. The problem posed is: does the mechanism implied by the Hinshelwood equation submitted by Leder and Butt provide an acceptable rate form for the data at the opposite ends of the hydrogen/oxygen mixture range obtained by Maymo and Smith?

1. Test data. Data from (5) is summarized in Table II, part A. Rates were reported by Maymo and Smith in moles per gram - second but in this application, rates for entire pellets (average weight 2.0 grams) are listed because the total pellet rate was used in the analysis. The rates at oxygen partial pressure varying from 0.009 to 0.111 atmospheres ranged from 19.2 X 10^{-6} $\frac{\text{moles}}{\text{pellet sec.}}$ to 267 X 10^{-6} $\frac{\text{moles}}{\text{pellet sec.}}$ The observed surface temperatures were between 89°C and 180°C. Other parameters reported and used in the computer analysis were the effective diffusion rate for oxygen of 0.166 cm^2/sec, the effective conductivity of the pellet 6.4 X 10^{-4} cal/cm(sec) (°C) and the heat of reaction of 115,000 cal/gm mole. All other values used were selected or calculated. Diffusivities of hydrogen (4.37 $\frac{\text{cm}^2}{\text{sec}}$) and water vapor (0.6 cm^2/sec) were estimated from the effective diffusivity equations employing bulk and Knudsen diffusion. Specific heat and equilibrium constant were obtained from the Handbook of Physics and Chemistry. The results of several computer runs performed with input data (Table II, Part B) are discussed in the following sections.

2. Computer results. Several computer runs were made to determine if the Hinshelwood equation proposed by Leder and Butt would fit the experimental rate data of Maymo and Smith. The forms used were as follows:

$$\begin{aligned} &(a)\ r = P_{O2}/(K_1 + K_2 * P_{O2}) \\ &(b)\ r = P_{O2} * P_{H2}/(K_1 + K_2 * P_{O2}) \end{aligned} \qquad (54)$$

In determining the equation constants the program employs the partial pressures of Hydrogen and Oxygen in the following equations:

$$K_1 + K_2 * P_{o2} + K_3 * P_{H2} = \frac{(P_{o2}\, P_{H2} - P_{H2O}/KE)}{r} \qquad (55)$$

TABLE II

PART A

RATE DATA (6)

Pellet Number	Surface Temperature °C	Oxygen Concentration ~~mole/cm^3~~ atm	Hydrogen Concentration ~~mole/cm^3~~ atm	Pellet Rate mole/pellet sec (r X 10^6)
11-1	101	0.029	0.971	57.8
11-2	101	0.054	0.946	101.0
11-3	100	0.0094	0.991	19.2
12-3	102	0.060	0.940	106.0
24-1	206	0.046	0.954	267.0
24-3	130	0.046	0.954	110.0
24-1	117	0.111	0.889	248
21	127	0.027	0.923	81
21	181	0.027	0.973	118

TABLE II

PART B

IN-PUT DATA (7)

	In-Put Description	Computer Term	Example Value
1.	Number of rate mechanisms	NO	2
2.	Rate mechanism (addresses)	MQ, MU, MV, MY, MZ, TN, VO	2, 11, 1, 2, 2, 1, 3
3.	Number of Data Points	MF, NF	4, 2
4.	Matrix B Data	B(1, 1) B(14, MF)	.027, 0.973, 0, 0, 0.1E-04, 1, 1, 1, 1, .025, 1.0, 1.0, 1.0, 1.0
5.	Matrix C Data	C(1, 1) B(14, MF)	Same
6.	Diffusion Constants	DEA, DEB, DER, DES	0.166, 0.60, 1.0, 0
7.	Constants: Pellet radius, Specific Heat of Gas, Heat of Reaction, Equilibrium Constant	RP, CP, HR, KE	0.93, 7.0, 115,000, 2,000
8.	Constant: From Mass Balance $A + F*B \rightarrow H*R + Q*S$ $O_2 + 2H_2 \rightarrow 2H_2O$	F, H, Q	2, 2, 0
9.	Surface Temperatures	TS1, TS2	$373^\circ K$, $403^\circ K$
10.	Constants: Number of Constants to be solved for, effective Thermal Conductivity of Pellet, Universal Gas Constant	U2, CK, GC	2, 6.5×10^{-4}, 1.98
11.	Number of Iterations	FM, FN	3, 3

Solution involves determination of K_1, K_2, and K_3 for each mechanism investigated. The constant for water is indeterminable because of pellet surface water vapor pressure being negligible. To determine if the constant K_3 is zero for the case of adsorbed oxygen reacting with hydrogen in the gas phase, it is necessary to solve for the three constants but if one of the constants is zero, the subroutine SOLV now in use (see Appendix) writes out the word EXTOL. The computer bypasses further calculation of that case. Thus the method of evaluating the constant is to run three rate forms. The first form with all constants K_1, K_2, and K_3. The second rate form with K_1 and K_2 only setting K_3 equal to zero, and the third rate form containing only K_1 and K_3 setting K_2 equal to zero. It is noted that the simultaneous equation solution performed by subroutines MAT and SOLV when replaced by the existing computer library subroutines will print out zeros for these constants which are zero and accomplish this analysis in one run.

3. Discussion of Computer analysis performed. During this investigation, computer runs were performed on oxygen/hydrogen rate data. The analyses considered calculation of constants K_1 and K_2 assuming K_3 zero. Equations examined were as follows:

$$(1) \quad r = \frac{P_{O2}}{K_1 + K_2 * P_{O2}}$$

and (56)

$$(2) \quad r = \frac{P_{O2} * PH_2^2}{K_1 + K_2 * P_{O2}}$$

Four data points were placed in matrix B all having surface temperatures of 373° K and two pellet data points placed in matrix C with surface temperatures of 403° K. An iteration limit of three was imposed to limit machine time. Initial runs indicated that convergence was occurring extremely slowly and results of node one rate comparison indicated wide deviation existed at the end of three iterations and so the number of pellet points were reduced to three in matrix B. The next run appeared to converge more rapidly than the previous one, but did not reach convergence within the three iterations allowed. Therefore, the number of points in matrix B was decreased to two and the iteration limit increased to five. Convergence to a fixed value appeared to have been achieved in this run. The coefficients of variation for the two mechanisms were close with the coefficient for mechanism two appearing slightly better as indicated in Table III. The rate equation defined for the second mechanism can be written as follows placing the values of K_1 and K_2 in Arrhenius constant form in the denominator:

$$r = \frac{P_{O2}\,P_{H2}^{\;2}}{0.0128 \exp\left(\frac{10800}{RT}\right) + (639T - 2{,}600{,}000)\,P_{O2}} \tag{57}$$

The linear form of the equation for the temperature dependant constant is used if one or more constants determined from least square analysis are negative. The Hinshelwood constants printed out in program are tabulated in Table IV.

The rate data comparison between calculated node one and difference determined node one rate are summarized in Table V.

TABLE III

COEFFICIENTS OF VARIATION

Mechanism	COVN B	COVN C
$r = P_{O2}/(K_1 + K_2 * P_{O2})$	0.166 E-04	0.224 E-04
$r = P_{O2}\ P_{H2}^2/(K_1 + K_2 * P_{O2})$	0.164 E-04	0.140 E-04

TABLE IV

RATE CONSTANTS (H_2/O_2)

		Hinshelwood	Coefficients
	Temperature	K_1	K_2
Matrix B	373° K	2230	- 22000
Matrix C	403° K	765	- 2840

TABLE V

COMPARISON OF RATE DATA
(Iteration Mechanism)

	P_{O2}	P_{H2}	Node 1 Calc.	Node 1 Difference	Total Pellet Rate
Matrix	.0283	0.972	16.6×10^{-6}	20.9×10^{-6}	57.8×10^{-6}
B	.0580	0.942	54.0×10^{-6}	68.0×10^{-6}	106×10^{-6}
Matrix	.027	0.973	37.1×10^{-6}	49.5×10^{-6}	81×10^{-6}
C	0.044	0.956	62.9×10^{-6}	78.6×10^{-6}	110×10^{-6}

The calculated rate varies from the difference determined rates in each case by a factor of 0.8 which is equal to the size of an iteration step used. Iteration steps were made large to reduce computer run time but for greater accuracy the iteration step needs to be decreased such that the product of ZD and the rate multiplier varies only a few percent instead of the 20% used in this case. A second conclusion drawn from the table is that a large portion of the total rate is estimated to be occurring in node one. Looking at the matrix print out we get a reading of the reacted fractions for each node in Table VI. From the node rate fractions shown in the table the amount of the reaction taking place in node one increases with pellet rate. In the ensuing discussion it is seen that this condition is a result of the temperature sensitivity of the Hinshelwood rate constants which may or may not result from a recognizable physical phenomenon.

4. Discussion of analysis. From the analysis we are interested in whether the Hinshelwood rate form fits the data and whether the node one rates are of similar magnitude to the intrinsic rates obtained for particles. The first question is undoubtedly debatable because very little data was used, and there is some question of how representative the data was. However, in reviewing the runs performed, there appeared to be a consistent pattern in the way the Hinshelwood constants (K_1 and K_2) in the equation:

$$K_1 + K_2 * P_{02} = \frac{POT}{r} \tag{58}$$

behaved with temperature. In all cases K_1 decreased slightly (see Table IV) with temperature increase while K_2 underwent a major increase.

TABLE VI

NODE RATE FRACTIONS

	MATRIX B		MATRIX C	
Point	1	2	1	2
Node 1	0.36	0.642	0.609	0.714
Node 2	0.352	0.207	0.199	0.146
Node 3	0.201	0.107	0.123	0.0963
Node 4	0.0859	0.044	0.0687	0.044

The rise in K_2 was so pronounced that rates dropped off with distance into the interior of the pellets. Physically it does not appear reasonable that such a change in adsorption equilibrium constant would take place, and for this reason the mechanism proposed by Leder and Butt at low hydrogen high oxygen concentration does not seem applicable to the Maymo and Smith data.

In regard to calculated rates equations several results are noted. The first iteration in the case number 2 provided an equation indicated as follows:

$$r = \frac{P_{02} \; P_{H2}^{2}}{0.411 \exp\left(\frac{6180}{RT}\right) + 1.66 \text{ X } 10^{11} \exp\left(\frac{-13100}{RT}\right. \; P_{02}} \qquad (59)$$

If we assume negligible value for P_{02} we can rewrite the equation as follows:

$$r = 2.5 \exp\left(\frac{-6180}{RT}\right) \; P_{02} \; P_{H2}^{2} \qquad (60)$$

This activation energy (6180) does not differ greatly from that reported by Maymo and Smith.

$$r = 0.655 \exp^{\frac{(-5230)}{RT}} * P_{02} \qquad (61)$$

However, after five iterations, the equation was altered to the following form:

$$r = \frac{P_{02} \; P_{H2}^{2}}{.0128 \exp^{\frac{(10800)}{RT}} + (639T - 2{,}600{,}000) \; P_{02}} \qquad (62)$$

or in this case, assuming negligible P_{02} the equation becomes the following:

$$r = 80 \exp^{\frac{(-10800)}{RT}} \; P_{02} \; P_{H2}^{2} \qquad (63)$$

The activation energy of 10.8 kilo calories is quite close to that of Leder and Butt who reported 10 ± 2 kilo calories as the activation energy for the Hinshelwood equation they defined in their data. These equations are illustrated in Figure 5 showing each of the above equations plotted as rate versus the partial pressure of oxygen. The rates are for node one of the pellet and thus, results in rates of reaction per 1/4 pellet or per 1/2 gram. In all cases the program calculated curves have steeper slopes than the rate curve defined by Maymo and Smith paper. At low partial pressures the rates are about the same for each equation but rates differ significantly at high partial pressures. Deviation is caused by the combined effects of the rate form being examined and the temperature variation of the data.

This problem also showed that the selection of specific rate forms have a major influence upon the percentage of reaction occurring in each node as a function of pellet radius. This was evidenced in the Maymo and Smith data as represented by the Hinshelwood equation proposed by Leder and Butt. The equilibrium constant (adsorption of oxygen) in the denominator of the rate equation increases rapidly with temperature, which would not happen if this specific constant was assumed zero and another one studied. This results in rate decreasing with temperature.

Since the temperature rises with distance into the pellet, the resultant decrease observed in rate might be explained by decreases in adsorbed oxygen. In view of this conclusion, a look at how the oxygen adsorption for platinum varies with temperature should be made.

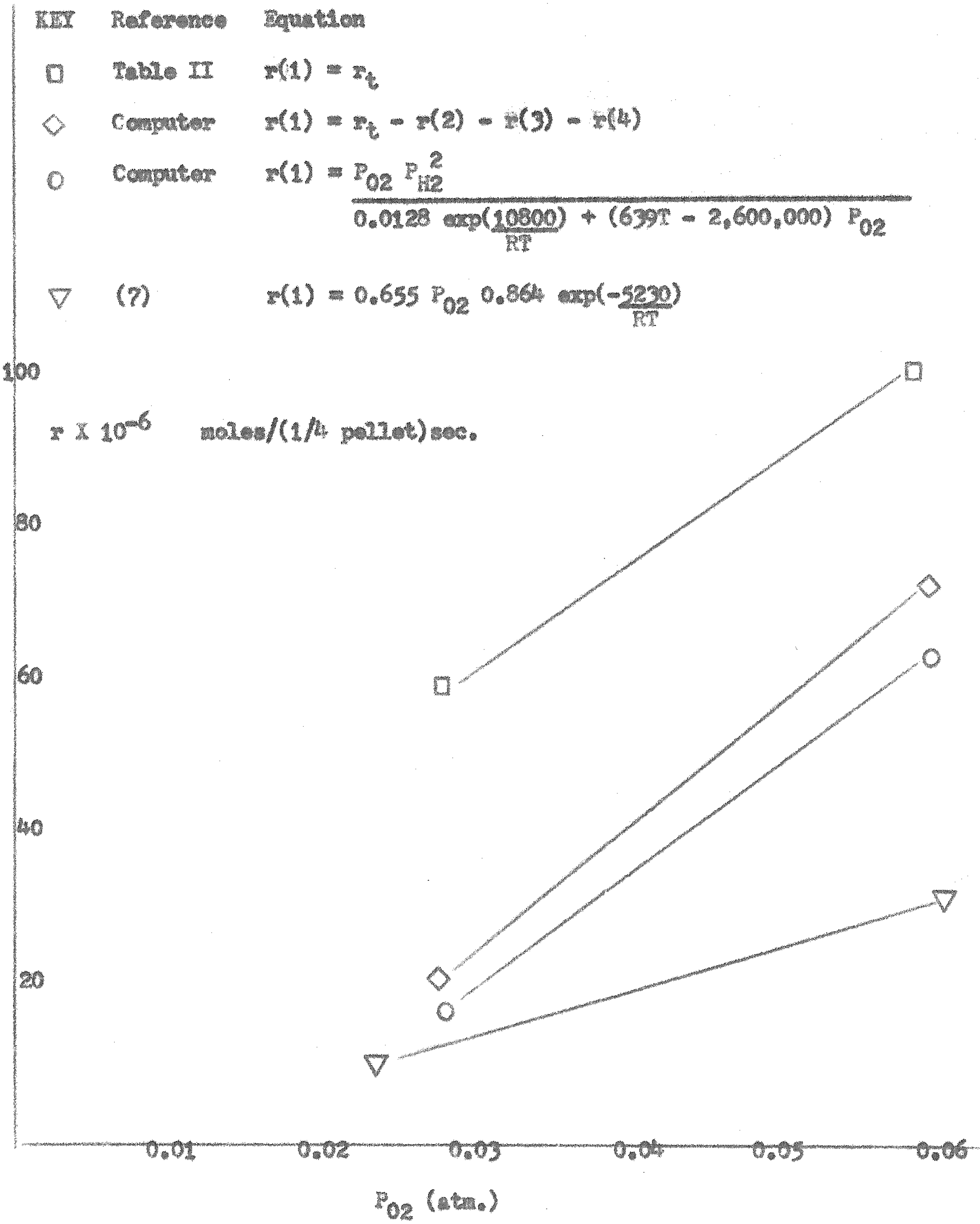


FIGURE 5

RATE VERSUS PARTIAL PRESSURE OF A
HYDROGEN OXYGEN CATALYSIS
OVER PLATINUM

It was found that adsorption rate decreases with temperature (2) according to the following equation:

$$\frac{\partial N}{\partial t} = \frac{P(1 - \theta)}{(2\pi MKT)^{1/2}} - \beta \theta \tag{64}$$

Since this indicates the forward rate of oxygen adsorption is decreasing with temperature for equilibrium, the desorption rate must also decrease indicating a lower rate of product formation. From equation 64 a 30% to 40% decrease may occur for a 2 to 1 change in temperature but no change as great as that observed in the computer analysis. It is, therefore, believed that the large variation in this coefficient is unlikely.

SECTION III

CONCLUSIONS

A computer program has been constructed that takes data from heterogenious reactions, gas phase reaction with solid pellet catalyst, and for given mainstream compositions, pellet surface temperatures, catalyst properties, and reaction rates estimates the representative Hinshelwood rate equation. In the sample problem (hydrogen and oxygen catalized by platinum) the calculated equations for the first iteration exhibited a similar activation energy to that determined by authors of (7).

Equation: (7)

$$r = 0.655 \exp\left(- \frac{5230}{RT} \right) \quad (P_{O2}) \tag{65}$$

Computer Calculated Hinshelwood Equation:

$$r = \frac{P_{O2} \cdot P_{H2}^{2}}{0.411 \exp\left(\frac{+6180}{RT}\right) + 1.66 \times 10^{11} \exp\left(\frac{-13100}{RT}\right) (P_{O2})} \tag{66}$$

which at low values of P_{O2} provides the following equation:

$$r = 2.4 \exp\left(\frac{-6180}{RT}\right) \quad (P_{O2}) \quad (P_{H2})^{2} \tag{67}$$

The activation energy 6180 cal/mole is of similar magnitude to 5230 cal/mole in spite of the fact that rate forms assumed (first order versus Hinshelwood) were different. This rate form, however, did not fully explain the temperature characteristics of the system and the final equation had an activation energy of approximately 10.8 kilo calories more nearly agreeing with the 10 ± 2K calories observed for hydrogen oxygen over platinum study of (8).

A negative low temperature oxygen adsorption constant was obtained rejecting this equation.

The findings of the computer program are by no means conclusive but several observations are significant in determining the type of information which may be obtained.

First rate fractions (of total pellet rate) are defined for each node in each pellet. Applying the equations defining temperature drop and concentration variation as a function of node rates from Section 2 of Part E, temperature and concentration through the pellet may be calculated. From temperature and concentration versus radius plots, it is possible to determine how the rate equations affect the shape of these plots. This may be instrumental in selection of the representative rate mechanisms.

Such a result was inadvertantly encountered when the temperature sensitivity of the Hinshelwood constants in the sample problem Part F produced decreases in rate as the temperature rose with distance into the pellet. While such decreases can occur as a result of changes in adsorption constants the abruptness of the change placed this rate form in doubt.

It is conjectured that when Hinshelwood rate equations represent the data, Kinetic phenomena controls rates at the pellet surface but as the reactant diffuses into the center, diffusion can control. Furthermore with variation in chemical reactant or product concentrations it is possible that further inside the pellet chemical rates may again control rate. Such variations are not likely to be picked up by first order rate approximations but would be recognized in the node analyses.

This form of analysis, because of its sensitivity to these parameter variations can be more useful in selecting rate equations than other methods now in use.

The accuracy of the analyses performed is dependent upon the presence of accurate values for effective diffusivities and effective thermal conductivity. The node analysis can be made as accurate as required by increasing the number of nodes, obtaining data describing catalyst properties and by accurate measurement of chemical concentrations and reaction rates.

IV

RECOMMENDATIONS

The computer program in this study has been designed to give maximum freedom to the programmer for alteration as may be required for any heterogenious reaction. It is recommended that the computer program be made more accurate by decreasing size of iteration steps and by calling for the library sub-routine for simultaneous linear solutions of the rate equations for the Hinshelwood constants.

It is recommended that the computer program be used to study industrial reactor data and that the Hinshelwood rate equations from the pellet data be compared with previous correlations derived from particles or pellets. Results are expected to define areas where further experimental study may be profitable.

In general, it is felt that this computer program can act effectively in augmenting experimental investigations.

APPENDIX

COMPUTER PROGRAM INPUT AND OUTPUT CONSIDERATIONS

This discussion is designed to be a guide to utilizing the "Hinshelwood rate from catalyst data" computer program. In brief, this discussion considers the input data package and then some areas where hang-ups may occur. A nomenclature list summarizes the principal variables on pages

1. Input Considerations

First, it is noted that there are eleven dimension statements and one common statement. Matrices B and C are storage matrices. B and C contain the input data with fourteen bits of information used per data point. The term GC is the universal gas constant and is input in whatever dimensions the programmer wishes to use. The program is thus able to work in any set of dimensions but the programmer must make certain that the input data is in consistent dimensions.

The input data begins with the statement read 5, NO and continues for twelve statements to read 13, FM, FN.

Summary input parameters. The following outlines the data as input to the computer based upon an equilibrium equation of the reaction of the type A + B $\rightarrow$ R + S.

1. NO - The number of cases (KK) or mechanisms to be run and specifies number of cards in the next sequence.

2. MW, MQ, MU, MY, TN, VO - The values MW through MZ define addresses in function routines used for rate mechanisms. MW is the address in the potential function of POTF: MQ the address of the A adsorption term in function routine KSORPA: MU is the address of the B adsorption term in KSORPB and likewise, MQ, MZ are addresses in the function subroutines for defining adsorption terms R and S in KSORPR and KSORPS. The term TN indicates the power which the adsorption terms are raised. The term VO defines the terms that are to be used in the SOLV subroutine. This accomplished by directing the computer to place terms generated from the least squares computation in matrix G or in matrix GV in the correct form for simultaneous linear equation solution. The equations are solved in subroutine SOLV. VO also is then used to define the value of the Hinshelwood constants that are returned from SOLV back to the main program. As may be noted from this sequence described above, potential program hang-up may have greatest chance of occurring in selection of the correct value of VO.

3. The terms MF and NF define the number of points to be placed in matrix B and matrix C. The two matrices are selected for use with two pellet surface temperatures observed. The values MF and NF also determine the number of input cards to follow. Since half the data per point is allotted to a card, the number of cards will be double that of MF and NF.

4 - 5. Matrix B(J,L1) and (J2, L2) input data. These matrices are doubly subscripted. The first number (J) representing a unit of data point and (L) representing the data point number. The first four values

of J are partial pressures or concentrations of component A, B, R and S. The fifth value is the total pellet rate. Terms J6 through 9 are the diffusion limits at nodes one, two, three, four defined by some fraction of the total rate for which diffusion may occur. That is RA(M)/A(5,M) RA representing diffusion rate which could reach node N from the next outermost node. The value (A(5,M) is the total reaction rate which was input to matrix B or C. The last terms J10 to 13 are rate limits based upon combined rate equation and diffusion limits depending upon which is controlling the rate in each node two to four. The last column J14 is now stores surface temperature but may be used to store additional data if desired, since surface temperature is introduced in another input location.

6. The diffusion constant DE ( ) are values of diffusivities of species A, B, R and S representing best average value for the four nodes investigated. For greater accuracy it may be desirable to introduce an equation to correct diffusivities for varying node conditions.

7. Next, several constant RP -- pellet radius, CP gas-specific heat, HR heat of reaction and KE equilibrium constant are introduced.

8. Then temperatures applying to surface temperature of pellets matrix B is TS1 and for matrix C is TS2.

9. Another set of constants included are F, H and Q which are the node relation of species B, R and S to specie A.

$(F = \frac{\text{moles B}}{\text{moles A}}$ for mass balance)

10. Additional information introduced includes the number of unknown constants to be solved for in the least squares solution (U2), the effective thermal conductivity of the pellet/gas combination (CK) and the universal gas constant (GC).

11. Values of FR and FD terms 2 to 4 indicate the allowable deviation of the sum of the concentrations in nodes two to four defined for the diffusion program.

12. Last, the values for the number of iterations per mechanism to be allowed in the calculations. It is estimated that convergence from initial estimate of total pellet reaction taking place in node one requires at least three iterations. Then, review of data and better initial estimates of node one rates should provide convergence more rapidly.

II. Problem Areas Computer May Encounter

First, in providing the matrix GV which is subsequently sent to the subroutine SOLV. It is necessary to place the pertinent matrix terms in form such that unknowns appear in the first (U2) columns with the residual or known term column in (U2 + 1) column. Thus the subroutine mat has been used to move the pertinent variable to the correct matrix locations for solution. At present, mat does not have all the possible combinations and it may be necessary to add additional ones for GU sets to be evaluated. Similar considerations of output for the correct Hinshelwood coefficient from subroutine SOLV may be required.

It is possible that subroutine SOLV may bomb out if any of the coefficients being solved for go to zero at which point the subroutine prints out the word "EXTOL" indicating a zero coefficient and the program will go to the next case NO(KK). Other than these locations, the program will probably run to completion unless a term exceeds the storage capacity of the computer.

The program has taken into consideration that Hinshelwood coefficients may be zero and to by-pass difficulties in being stopped at an early iteration because of difficulties in computing temperature correlation based upon Arrhenius equation. The subroutine temco computes either an Arrhenius or a linear relation and uses that for the next iteration. Thus the print-out of the Hinshelwood constants at the end of a run should be made to see if constants are negative. This is done by checking values printed out of the matrix E(2, 5) where values of AK and DB are listed. AK is the constant and DB is the exponential term (or slope in linear result) exp(DB/RT).

Output data. The program is designed to print out the final values of the terms in matrix A and B thus giving fractional rates in terms of diffusion limits and diffusion/rate limits combines. Also printed out is the coefficient of variation for the difference between node one rates and the equation derived rates. This is printed out of matrix COVNB(KK) and COVNC(KK). Further data is printed out of the AK and DB matrices which provide Arrhenius relation coefficients as indicated in the following equation:

$$K = (AK) \exp\left(\frac{DB}{RT}\right)$$

As a check on the validity of AK and DB is matrix E which provides the Hinshelwood coefficients for each matrix from which the Arrhenius coefficients have been calculated. From these data most pertinent results can be determined both in terms of individual nodes and node one versus rate equation comparisons. It may be of interest to store calculated rates and node one rates at the end of the last iteration for each matrix. This will undoubtedly require additional storage matrices.

NOMENCLATURE

(Computer)

COMPUTER PROGRAM

MW	Address in subroutine POTF
MQ	Address in subroutine KSORPA
MV	Address in subroutine KSORPB
MY	Address in subroutine KSORPR
MZ	Address in subroutine KSORPS
TW	Exponent of the adsorption term
VO	Designates addresses in subroutine MAT and SOLV
A	Matrix values used in working program
B	Matrix used to store data before use in matrix A
C	Matrix used to store data before use in matrix A
E	Matrix used to store Hinshelwood coefficients (K1B...K5B) (K1C...K5C)
EM	Matrix used in subroutine TEMCO to store $K_1(\ \ )$... $K_5(\ \ )$
AK	Arrhenius coefficient
DB	Arrhenius coefficient in exponential term
G and GV	Matrices in which summation used in least squares routine are held prior to simultaneous linear equation solution
K(1)——K(6)	Constants returned by subroutine SOLV
RA(n)	Diffusion limited rate
R(N)	Node rates limited by both rate equation and diffusion
R1 calc (N)	Rates calculated from rate equation
TA(n)	Node temperatures

WK and YK	Temperature dependent constants calculated from Arrhenius equation
DR(N)	Distance between nodes (diffusion path)
AR(N)	Near area between node locations for heat and mass flow
CA(N) or PA	Concentration of species A for node N
CB(N) or PB	Concentration of species B for node N
CR(N) or PR	Concentration of species R for node N
CS(N) or PS	Concentration of species S for node N
	NOTE: With "S" added to end — stands for stream condition
FD(N)	Concentration sum node limit
FR(N)	Concentration sum node limit
KSORPA	Function subroutine A adsorption value
KSORPB	Function subroutine B adsorption value
KSORPR	Function subroutine R adsorption value
KSORPS	Function subroutine S adsorption value
MF	Number of data points in matrix B
NF	Number of data points in matrix C
RP	Pellet radius
CP	Specific heat of gas composition
HR	Heat of reaction
KE	Reaction equilibrium coefficient
K	Matrix storing values from solutions in SOLV subroutines
DEA) DEB) DER) DES)	Diffusion coefficients of species A, B, R and S

TS1 and TS2	Surface temperatures of pellets whose data is supplied in matrix B and C respectively
F, H, and Q	Moles of B, R, or S involved in reaction per mole of A reacted
UZ	Number of unknown in least square solution
CK	Effective thermal conductivity of pellet
GC	Universal gas constant
FD and FR	Limit of concentration of species summed at each node
LP	Indicator defining whether diffusion branch of program is to be run or not
TIM	Iteration counter in program matrix B
TIN	Iteration counter in program matrix C
I	Matrix B or C indicator
IN	Loop indicator
M	Data point indicator for working matrix
ZD	Multiplier for adjustment of rate equation in iteration process
IZ	Indicator which prevents storage of rate values until ZD achieves satisfactory value
COV( )	Coefficient of variation (different endings with Location in program)
DEN	The denominator of the rate equation containing the KSCRP terms
SIGF	Subroutine which checks sign of sums of concentrations

```
         DIMENSION MW(9),MQ(9),MU(9),MY(9),MZ(9),TN(9),VO(9)
          DIMENSION A(14,10),B(14,10),C(14,10)
           DIMENSION E(2,5)
          DIMENSION EM(5)
         DIMENSION DB(5),AK(5)
          DIMENSION G(5,6),GV(5,6),K(6)
          DIMENSION R(4),RA(4),RCALC(4),TA(4), WK(4),YK(4),DR(4),AR(4)
         DIMENSION CA(4),CB(4),CR(4),CS(4)
         DIMENSION FD(4),FR(4)
          DIMENSION COVNB(9),COVNC(9)
         DIMENSION D(4)
          REAL MW,MQ,MU,MY,MZ
          REAL KE
           REAL K1B,K2B,K3B,K4B,K5B,K1C,K2C,K3C,K4C,K5C
          REAL KSORPA,KSORPB,KSORPR,KSORPS
          REAL K
          READ 5,NO
          READ 4,(MW(KK),MQ(KK),MU(KK),MY(KK),MZ(KK),TN(KK),VO(KK),KK=1,NO
          READ 15,MF,NF
         DO 6  L1=1,MF
    6    READ( 1,106) (B(J,L1),J=1,14)
          DO 10   L2=1,NF
     10   READ( 1,106) (C(J2,L2),J2=1,14)
     7      READ 12, DEA,DEB,DER,DES
     8      READ 12,RP,CP,HR,KE
     9      READ 13,TS1,TS2
          READ 14,F,H,Q
          READ 14,U2,CK,GC
          READ 13,(FD(LD),FR(LD),LD=2,4)
          READ 13,FM,FN
      4  FORMAT(7F4.0)
    5     FORMAT(I12)
     11   FORMAT (6F4.0)
     12   FORMAT(4E10.3)
     13  FORMAT(2F10.2)
    14    FORMAT( 3E10.3)
     15  FORMAT(2I4)
    75    FORMAT(1X,27H HINSHELWOOD RATE MECHANISM// ,7F10.3)
     76   FORMAT(1X,9H MATRIX B,(7E12.3))
    77   FORMAT(14H DIFFUSIVITIES//,4E10.3)
    78   FORMAT(1X,2H F,E10.3,5X,2H H,E10.3,5X,2H Q,E10.3)
     79   FORMAT(1X,3H RP,E10.3,3X,3H CP,E10.3,3X,3H HR,E10.3,3H KE,E10.3)
    80    FORMAT(//1X,3H U2,E10.3,10X,3H CK,E10.3,10X,3H GC,E10.3)
    81    FORMAT(//1X,10H ITERATION,2F10.2)
     82   FORMAT(1X//1X,6H COVNB,2E15.3)
     83   FORMAT(1X//1X,9H MATRIX E,5E10.3,//1X,3H AK,5E10.3,3H DB,5E10.3)
    84    FORMAT(1X,9H MATRIX C//,(7E12.3))
    106  FORMAT(7E10.3)
          DO 40   KK=1,NO
```

```
      40    PRINT 75,MW(KK),MQ(KK),MU(KK),MY(KK),MZ(KK),TN(KK),VO(KK)
            DO 41  L1=1,MF
       41   PRINT 76,(B(J,L1),J=1,14)
            DO 42   L2=1,NF
       42   PRINT 84,(C(J2,L2),J2=1,14)
            PRINT 77,DEA,DEB,DER,DES
            PRINT 79,RP,CP,HR,KE
            PRINT 78,F,H,Q
            PRINT 80,L2,CK,GC
            PRINT 81,FM,FN
      98     KK=1
            LP=1
      99    N=TN(KK)
            LC=MQ(KK)
            LD=MW(KK)
            LF=MU(KK)
            LG=MY(KK)
            LH=MZ(KK)
            TIM=0.0
            TIN=0.0
       100        IN = 1
            ZD=1.0
            IZ=1
      101          I  =  1
           VOK=VO(KK)
            NE=MF
           EN=MF
      107         J  =  1
                 L1  =  1
      109   KJ=J
      110  M=L1
            A(KJ,M) =B(J,L1)
           J=J+1
       111   IF(J-14) 109,109,112
      112        J  =  1
             L1  =  L1  +  1
            IF(L1-MF) 109,109,114
      114   IF(IN-2) 200,299,599
       115        I  =  2
            VOK=VO(KK)
            NE=NF
           EN=NF
      119         J2  =  1
                   L2  =  1
      120   KJ=J2
              M  =  L2
      121   A(KJ,M)=C(J2,L2)
             J2  =  J2  +  1
      122   IF(J2-14) 120,120,123
```

```
 123      J2 =1
         L2 = L2 + 1
        IF(L2-NF)120,120,125
 125    IF(IN-2) 200,299,599
 200      SUMV=0
         SUMVA1=0
         SUMVA2   =0
         SUMVA3=0
         SUMVA4=0
         SUMA1=0
         SUMA2=0
         SUMA3=0
         SUMA4=0
          SUMA1X=0
         SUMA12=0
         SUMA13=0
         SUMA14=0
          SUMA2X=0
         SUMA23=0
         SUMA24=0
         SUMA3X=0
         SUMA34=0
         SUMA4X=0
 201    DO 221  M=1,NE
          PA  =  A(1,M)
          PB  =  A(2,M)
          PR  =  A(3,M)
          PS  =  A(4,M)
        A1=KSORPA(LE,PA,PB,PR,PS,KE)
        A2=KSORPB(LF,PA,PB,PR,PS,KE)
        A3=KSORPR(LG,PA,PB,PR,PS,KE)
        A4=KSORPS(LH,PA,PB,PR,PS,KE)
        PT=POT(LD,PA,PB,PR,PS,KE)
        V=(PT/(A(5,M)*A(10,M)*ZD))**(1.0/N)
          SUMV=SUMV+V
 203          VA1  =  V*A1
         SUMVA1=SUMVA1+VA1
 204          VA2  =  V*A2
         SUMVA2=SUMVA2+VA2
 205          VA3  =  V*A3
         SUMVA3=SUMVA3+VA3
 206          VA4  =  V*A4
         SUMVA4=SUMVA4+VA4
 207      SUMA1=SUMA1+A1
 208      SUMA2=SUMA2+A2
 209      SUMA3=SUMA3+A3
 210      SUMA4=SUMA4+A4
 211        A1X  =  A1  **2
         SUMA1X=SUMA1X+A1X
```

```
0148          212         A12 = A1 *A2
0149                   SUMA12=SUMA12+A12
0150          213         A13 = A1*A3
0151                   SUMA13=SUMA13+A13
0152          214         A14 = A1*A4
0153                   SUMA14=SUMA14+A14
0154          215         A2X = A2**2
0155                   SUMA2X=SUMA2X+A2X
0156          216         A23 = A2*A3
0157                   SUMA23=SUMA23+A23
0158          217         A24 = A2*A4
0159                   SUMA24=SUMA24+A24
0160          218         A3X = A3**2
0161                   SUMA3X=SUMA3X+A3X
0162          219         A34 = A3*A4
0163                   SUMA34=SUMA34+A34
0164          220         A4X = A4**2
0165          221       SUMA4X=SUMA4X+A4X
0166                  G(1,1)=EN
0167                   G(2,1)=SUMA1
0168                   G(3,1)=SUMA2
0169                   G(4,1)=SUMA3
0170                   G(5,1)=SUMA4
0171                   G(1,2)=SUMA1
0172                   G(2,2)=SUMA1X
0173                   G(3,2)=SUMA12
0174                   G(4,2)=SUMA13
0175                   G(5,2)=SUMA14
0176                   G(1,3)=SUMA2
0177                   G(2,3)=SUMA12
0178                   G(3,3)=SUMA2X
0179                   G(4,3)=SUMA23
0180                   G(5,3)=SUMA24
0181                   G(1,4)=SUMA3
0182                   G(2,4)=SUMA13
0183                   G(3,4)=SUMA23
0184                   G(4,4)=SUMA3X
0185                   G(5,4)=SUMA34
0186                   G(1,5)=SUMA4
0187                   G(2,5)=SUMA14
0188                   G(3,5)=SUMA24
0189                   G(4,5)=SUMA34
0190                   G(5,5)=SUMA4X
0191                   G(1,6)=SUMV
0192                   G(2,6)=SUMVA1
0193                   G(3,6)=SUMVA2
0194                   G(4,6)=SUMVA3
0195                   G(5,6)=SUMVA4
0196                   IF(VOK-1) 222,224,224
```

```
222    CALL SOLV(G,VOK,C2,TCLR,K)
       IF(K(6)-1) 223,223,617
223    IF(I-1) 226,226,227
224     CALL MAT(G,VOK,GV)
       CALL SOLV(GV,VOK,C2,TCLR,K)
       IF(K(6)-1) 225,225,617
225     IF(I-1) 226,226,227
226     K1B=K(1)
      K2B=K(2)
      K3B=K(3)
      K4B=K(4)
      K5B=K(5)
       I=2
       GO TO 115
227     K1C=K(1)
      K2C=K(2)
      K3C=K(3)
      K4C=K(4)
      K5C=K(5)
         E(1,1)=K1B
        E(2,1)=K1C
        E(1,2) =K2B
        E(2,2)=K2C
        E(1,3)=K3B
        E(2,3)=K3C
        E(1,4)=K4B
        E(2,4)=K4C
        E(1,5)=K5B
        E(2,5)=K5C
       DO 233  NL=1,5
229    IF(E(2,NL))231,231,230
230    IF(E(1,NL))231,231,232
231    AK(NL)=(E(2,NL)-E(1,NL))/(TS2-TS1)
       DB(NL)=E(1,NL)-AK(NL)*TS1
       GO TO 233
232    DB(NL)=   GC*(TS1*TS2)/(TS1-TS2)*ALOG(E(1,NL)/E(2,NL))
       AK(NL)=E(1,NL)*EXP(DB(NL)/(GC*TS1))
233    CONTINUE
246    TS=TS1
       I=1
       GO TO 248
247    TS=TS2
248    CALL TEMCO(E,TS,AK,DB,EM)
       K(1)=EM(1)
       K(2)=EM(2)
       K(3)=EM(3)
       K(4)=EM(4)
       K(5)=EM(5)
      DO 280  NL=1,5
```

```
       280  PRINT 281,AK(NE),DB(NE)
       281    FORMAT(4H AK,E10.3,4H DB,E10.3)
       249    SUMCO=0
       250   DO 255 M=1,NE
              PA  = A(1,M)
                 PB  = A(2,M)
                 PR  = A(3,M)
                 PS  = A(4,M)
             A1=KSORPA(LC,PA,PB,PR,PS,KE)
             A2=KSORPB(LF,PA,PB,PR,PS,KE)
             A3=KSORPR(LG,PA,PB,PR,PS,KE)
             A4=KSORPS(LH,PA,PB,PR,PS,KE)
             PT=PCT(LD,PA,PB,PR,PS,KE)
            DEN=(K(1)+K(2)*A1+K(3)*A2+K(4)*A3+K(5)*A4)**N
             V=(PT/(A(5,M)*A(10,M)*ZD))**(1.0/N)
             RC=A(5,M)*A(10,M)*ZD
             IF(DEN-0.1*V)251,252,252
       251   IF(DEN+0.1*V) 252,252,253
       252  RCAL=PT/DEN
             GO TO 254
       253   RCAL =PT/(0.1*V)
       254   CO=(RCAL-RC)**2
       255   SUMCO =SUMCO + CO
             COV=(SUMCO/EN)**0.5
       256      IF(I - 1 ) 257,257,259
       257     COVB = COV
             PRINT 258,COVB
       258    FORMAT(5H COVB,E10.3)
             I=2
             GO TO 247
       259  COVC=COV
             PRINT 260,COVC
        260   FORMAT(5H COVC,E10.3)
       282  IN=2
              GO TO 101
       299   IF(LP-1) 300,300,399
       300   M=1
             DR(2)=0.1037*RP
             DR(3)=0.141*RP
             DR(4)=0.315*RP
             AR(2)=12.53*0.953*0.848*RP**2
             AR(3)=12.53*0.848*0.7076*RP**2
             AR(4)=12.53*0.7076*0.315*RP**2
       301   CAS=A(1,M)
            CBS=A(2,M)
            CRS=A(3,M)
            CSS=A(4,M)
             DO 309 MR=2,4
            RA(MR)=A(5,M)
```

```
 302   CA(MR)=-RA(MR)*DR(MR)/(DEA*AR(MR))+CAS
       CB(MR)=-F*RA(MR)*DR(MR)/(DEB*AR(MR))+CBS
       CR(MR)=H*RA(MR)*DR(MR)/(DER*AR(MR))+CRS
       CS(MR)=Q*RA(MR)*DR(MR)/(DES*AR(MR))+CSS
      CALL SIGF( CA,CB,CR,CS,IK)
      IF( IK-1) 303,303,304
 303  RA(MR)=0.95*RA(MR)
      GO TO 302
 304  SUMC =CA(MR)+CB(MR)+CR(MR)+CS(MR)
       PRINT 311,SUMC
      IF(FD(MR)-SUMC) 305,306,306
 305  RA(MR)=0.95*RA(MR)
      GO TO  302
 306    IF(FR(MR)-SUMC) 308,308,307
 307  RA(MR)=0.95*RA(MR)
      GO TO 302
 308    CAS=CA(MR)
      CBS=CB(MR)
      CRS=CR(MR)
      CSS=CS(MR)
  309  CONTINUE
       A(7,M)=RA(2)/A(5,M)
       A(8,M)=RA(3)/A(5,M)
       A(9,M)= RA(4)/A(5,M)
       PRINT 311,A(7,M)
 311   FORMAT(3H A7,E10.3)
       M=M+1
       IF(M-NE) 301,301,310
 310  IF(I-1)325,325,328
 325   DO 326  M=1,NE
       B(7,M)=A(7,M)
       B(8,M)=A(8,M)
       B(9,M)=A(9,M)
 326   CONTINUE
       GO TO 115
 328   DO 329  M=1,NE
       C(7,M)=A(7,M)
       C(8,M)=A(8,M)
       C(9,M)=A(9,M)
 329   CONTINUE
 330   LP=2
       GO TO 101
 399   M=1
 400   IF( I-1) 401,401,402
 401   TSA=TS1
        GO TO 403
 402   TSA=TS2
 403  RD1=A(5,M)
      RD2=A(5,M)*A(7,M)
```

```
              RD3=A(5,M)*A(8,M)
              RD4=A(5,M)*A(9,M)
              R(1)=A(5,M)-RD2
              R(2)=RD2-RD3
              R(3)=RD3-RD4
              R(4)=RD4
      404     DT2=DR(2)*(R(2)+R(3)+R(4))*HR/(CK*AR(2))
              DT3=DR(3)*(R(3)+R(4))*HR/(CK*AR(3))
              DT4=DR(4)*(R(4))*HR/(CK*AR(4))
      405     TA(1)=TSA
              TA(2)=TSA+DT2
              TA(3)=TA(2)+DT3
              TA(4)=TA(3)+DT4
      496     CAS=A(1,M)
             CBS=A(2,M)
             CRS=A(3,M)
             CSS=A(4,M)
      497     DO 505  ML=2,4
             DO 501    LK=1,5
              IF(E(1,LK)) 499,499,498
      498     IF(E(2,LK)) 499,499,500
      499     WK(LK)=AK(LK)*TA(ML)+CE(LK)
              GO TO 501
      500     WK(LK)=AK(LK)*EXP(-DB(LK)/(GC*TA(ML)))
      501     CONTINUE
             D(2)=R(2)+R(3)+R(4)
             D(3)=R(3)+R(4)
             D(4)=R(4)
             PA=-D(ML)*DR(ML)/(DEA*AR(ML))+CAS
             PB=-F*D(ML)*DR(ML)/(DEB*AR(ML))+CBS
             PR= H*D(ML)*DR(ML)/(DER*AR(ML))+CRS
             PS= Q*D(ML)*DR(ML)/(DES*AR(ML))+CSS
              A1=KSORPA(LC,PA,PB,PR,PS,KE)
              A2=KSORPB(LF,PA,PB,PR,PS,KE)
              A3=KSORPR(LG,PA,PB,PR,PS,KE)
              A4=KSORPS(LH,PA,PB,PR,PS,KE)
              SRA=A1*WK(2)
              SRB=A2*WK(3)
              SRR=A3*WK(4)
              SRS=A4*WK(5)
              PT=POT(LD,PA,PB,PR,PS,KE)
             CAS=PA
             CBS=PB
             CRS=PR
             CSS=PS
             DEN=(WK(1)+SRA+SRB+SRR+SRS)
              V=(PT/(A(5,M)*A(10,M)*ZD))**(1.0/N)
              IF(DEN-0.1*V) 502,504,504
      502     IF(DEN+0.1*V)504,504,503
```

```
  503   RCALC(ML)=PT/(0.1*V)
        GO TO 505
  504  RCALC(ML)=PT/DEN
  505   CONTINUE
  506  IF(RCALC(2)-R(2)) 512,507,507
  507  IF(RCALC(3)-R(3)) 513,508,508
  508  IF(RCALC(4)-R(4)) 514,509,509
  509   IF(RD2-R(2)-R(3)-R(4)) 512,510,510
  510   IF(RD3-R(3)-R(4)) 513,511,511
  511  IF(RD4-R(4)) 514,515,515
  512   R(2)=0.8*R(2)
       GO TO 404
  513   R(3)=0.8*R(3)
        R(2)=R(2)+0.2*(R(3)/0.8)
       GO TO 404
  514   R(4)=R(4)*0.8
        R(3)=R(3)+0.2*(R(4)/0.8)
        GO TO 404
  515   R(1)=A(5,M)-R(2)-R(3)-R(4)
        PRINT 406,R(3)
  406   FORMAT(3H R3,E10.3)
        IF(A(5,M)*A(10,M)*ZD-R(1)) 517,517,516
  516   ZD=0.8*ZD
        IN=1
        GO TO 101
  517   IF(IZ-1) 518,518,521
  518   M=M+1
        IF(M-NE)400,400,519
  519   IF(I-1) 115,115,520
  520   IZ=2
        GO TO 101
  521   IF(I-1) 522,522,523
  522   B(10,M)=R(1)/A(5,M)
        B(11,M)=R(2)/A(5,M)
        B(12,M)=R(3)/A(5,M)
        B(13,M)=R(4)/A(5,M)
       B(14,M)=TA(2)
        GO TO 524
  523   C(10,M)=R(1)/A(5,M)
        C(11,M)=R(2)/A(5,M)
        C(12,M)=R(3)/A(5,M)
        C(13,M)=R(4)/A(5,M)
       C(14,M)=TA(2)
  524   M=M+1
        IF(M-NE) 400,400,526
  526   IF(I-1) 527,527,530
  527   GO TO 115
  530   IN=3
       GO TO 101
```

```
 599    SUMCOR=0
        DO 607  M=1,NE
        IF(I-1) 600,600,601
 600    TS=TS1
        GO TO 602
 601    TS=TS2
 602    PA=A(1,M)
       PB=A(2,M)
       PR=A(3,M)
       PS=A(4,M)
        CALL TEMCO(E,TS,AK,DB,EM)
        YK(1)=EM(1)
        YK(2)=EM(2)
        YK(3)=EM(3)
        YK(4)=EM(4)
        YK(5)=EM(5)
        A1=KSORPA(LC,PA,PB,PR,PS,KE)
        A2=KSORPB(LF,PA,PB,PR,PS,KE)
        A3=KSORPR(LG,PA,PB,PR,PS,KE)
        A4=KSORPS(LH,PA,PB,PR,PS,KE)
        PT=POT(LD,PA,PB,PR,PS,KE)
         SPA=A1*YK(2)
        SPB=A2*YK(3)
        SPR=A3*YK(4)
        SPS=A4*YK(5)
       DEN=(YK(1)+SPA+SPB+SPR+SPS)**N
        R1=A(5,M)*A(10,M)
        V=(PT/(A(5,M)*A(10,M)))**(1.0/N)
        IF(DEN -0.1*V) 603,605,605
 603    IF(DEN+0.1*V ) 605,605,604
 604    R1CALC =PT/(0.1*V)
        GO TO 606
 605    R1CALC=PT/DEN
        PRINT 629,R1CALC,R1
 606    COR=(R1CALC-R1)**2
 607   SUMCOR=SUMCOR+COR
        COVAR=SQRT(SUMCOR/EN)
        PRINT 616,COVAR
 616    FORMAT(6H COVAR,E10.3 )
 608   IF(I-1)609,609,612
 609    COVIB=2.0*COVB
        COVNB(KK)=COVAR
       IF(COVIB-COVAR) 610,610,611
610     IN=1
        TIM=TIM+1
        IF(TIM-FM) 100,617,617
 611     GO TO 115
 612    COVIC=2.0*COVC
        COVNC(KK)=COVAR
```

```
              IF(COVIC-COVAR)613,613,614
        613    IN=1
               TIN=TIN+1
               IF(TIN-FN) 100,617,617
        614     CONTINUE
        617    DO 618   L1=1,MF
               DO 618  J=1,14
        618  PRINT 76,B(J,L1)
        619    PRINT 83,E,AK,DB
               DO 620  M=1,MF
        620    B(10,M)=1.0
               DO 621   L2=1,NF
               DO 621  J2=1,14
         621    PRINT 84,C(J2,L2)
               DO 622  M=1,NF
        622    C(10,M)=1.0
        624    KK=KK+1
               IF(KK-NO) 99,99,625
         625    DO 626  KK=1,NO
        626    PRINT 82,COVNB(KK),COVNC(KK)
        629    FORMAT(7H RICALC,E10.3,5X,3H RI,E10.3)
              STOP
               END
```

```
ORTRAN IV     MODEL 44  PS          VERSION 3,  LEVEL 1   DATE  69119

              FUNCTION POT(LD,PA,PB,PR,PS,KE)
              REAL KE
              GO TO (151,152,153,154,156,157,158,159,160),LD
         151  POT=0
                GO TO 160
         152  POT=PA-PR/KE
                GO TO 160
         153  POT=PA-(PR*PS)/KE
                GO TO 160
         154  POT=(PA/PS)-(PR/KE)
                GO TO 160
         156  POT= PA*PR-PR/KE
                GO TO 160
          157 POT=PA*PB**2-PR/KE
                GO TO 160
         158  POT=PA*PB-PR/KE
                GO TO 160
         159  POT=PA*PB-PR*PS/KE
         160  RETURN
              END
```

```
FORTRAN IV     MODEL 44  PS          VERSION 3,  LEVEL 1   DATE  69119

                 REAL FUNCTION KSORPA(LC,PA,PB,PR,PS,KE)
                 REAL KE
                 GO TO(171,172,173,174,175,176,177,178,179,180,181,182),LC
          171   KSORPA=0
                 GO TO 182
          172   KSORPA=PR/KE
                 GO TO 182
          173   KSORPA=(PA)**(1/2)
                 GO TO 182
          174   KSORPA=(PR*PS)/KE
                 GO TO 182
          175    KSORPA=(PR/KE)**(1/2)
                 GO TO 182
          176   KSORPA=(PR*PS/KE)**(1/2)
                 GO TO 182
          177   KSORPA=PR/(KE*PB)
                 GO TO 182
          178   KSORPA=(PR/(KE*PB))**(1/2)
                 GO TO 182
          179   KSORPA= PR*PS/(KE*PB)
                 GO TO 182
          180   KSORPA=(PR*PS/(KE*PB))**(1/2)
                 GO TO 182
          181   KSORPA= PA
          182    RETURN
                 END
```

```
ORTRAN IV     MODEL 44  PS          VERSION 3,  LEVEL 1   DATE  69119

                 REAL FUNCTION KSORPB(LF,PA,PB,PR,PS,KE)
                 REAL KE
                 GO TO (184,185,186,187),LF
           184  KSORPB=0
                 GO TO 188
           185  KSORPB=PR/(KE*PA)
                 GO TO 188
           186  KSORPB=PR*PS/(KE*PS)
                 GO TO 188
           187  KSORPB=PB
           188  RETURN
                 END
```

```
                REAL FUNCTION KSORPR(LG,PA,PB,PR,PS,KE)
                REAL KE
                GO TO (189,190,191,192,193,194)  ,LG
          189  KSORPR=PR
               GO TO 195
          190  KSORPR=0
                GO TO 195
          191  KSORPR=KE*PA
                GO TO 195
         192    KSORPR=KE*PA/PS
                GO TO 195
          193  KSORPR=KE*PA*PB
                GO TO 195
          194  KSORPR=KE*PA*PB/PS
          195  RETURN
                END
```

```
FORTRAN IV    MODEL 44  PS        VERSION 3,  LEVEL 1   DATE  69119

                        REAL FUNCTION KSORPS(LH,PA,PE,PR,PS,KE)
                        REAL KE
                        GO TO (197,198),LH
               197         KSORPS=PS
                         GO TO 199
               198      KSORPS=0
               199      RETURN
                        END
```

```
FORTRAN IV     MODEL 44  PS         VERSION 3,  LEVEL 1   DATE  69119

0001                 SUBROUTINE SIGN(CA,CB,CR,CS,/IK/)
0002                IF(CA-0) 700,697,697
0003          697   IF(CB-0) 700,698,698
0004          698    IF(CR-0) 700,699,699
0005          699    IF(CS-0) 700,701,701
0006          700    IK=1
0007                 GO TO 702
0008          701    IK=2
0009          702     RETURN
0010                END
```

```
ORTRAN IV     MODEL 44  PS         VERSION 3,  LEVEL 1   DATE  69119

0001                 SUBROUTINE TEMCC(E,TS,AK,DB,/EM/)
0002                 GC=1.98
0003                 DIMENSION E(2,5),AK(5),DB(5),EM(5)
0004          1      DO 5  MV=1,5
0005                 IF(E(1,MV)) 3,3,2
0006          2      IF(E(2,MV)) 3,3,4
0007          3      EM(MV)=AK(MV)*TS+DB(MV)
0008                 GO TO 5
0009          4      EM(MV)=AK(MV)*EXP(-DB(MV)/(GC*TS))
0010          5      CONTINUE
0011          6      RETURN
0012                 END
```

```
       SUBROUTINE MAT(G,VCK,/GV/)
       DIMENSION G(5,6)
       DIMENSION GV(5,6)
       KP=VCK
       GO TO (1,2,3,4),KP
    1 GV(1,1)=G(1,1)
      GV(2,1)=G(2,1)
      GV(3,1)=G(3,1)
      GV(1,2)=G(1,2)
      GV(2,2)=G(2,2)
      GV(3,2)=G(3,2)
      GV(1,3)=G(1,3)
      GV(2,3)=G(2,3)
      GV(3,3)=G(3,3)
      GV(2,4)= (2,6)
      GV(3,4)= (3,6)
    2 GV(1,1)=G(1,1)
      GV(2,1)=G(2,1)
      GV(3,1)=G(3,1)
      GV(4,1)=G(4,1)
      GV(1,2)=G(1,2)
      GV(2,2)=G(2,2)
      GV(3,2)=G(3,2)
      GV(4,2)=G(4,2)
      GV(5,2)=G(5,2)
      GV(1,3)=G(1,3)
      GV(2,3)=G(2,3)
      GV(3,3)=G(3,3)
      GV(4,3)=G(4,3)
      GV(1,4)=G(1,4)
      GV(2,4)=G(2,4)
      GV(3,4)=G(3,4)
      GV(4,4)=G(4,4)
       GO TO 5
    3 GV(1,1)=G(1,1)
       GV(2,1)=G(2,1)
       GV(1,2)=G(1,2)
       GV(2,2)=G(2,2)
       GV(1,3)=G(1,6)
       GV(2,3)=G(2,6)
       GO TO 5
    4 GV(1,1)=G(1,1)
       GV(2,1)=G(3,1)
       GV(1,2)=G(1,3)
       GV(2,2)=G(3,3)
      GV(1,3)=G(1,6)
       GV(2,3)=G(3,6)
    5 RETURN
      END
```

```
FORTRAN IV     MODEL 44  PS          VERSION 3,  LEVEL 1    DATE  69119

      SUBROUTINE SOLV(A,VOK,U2,TOLR,/K/)
      DIMENSION A(5,6),K(6)
      REAL K
      N2=U2
      N1=N2+1
      DO 14  I=1,N2
      DIAG=A(I,I)
      IF(DIAG) 5,25,5
    5 DO 6 J=1,N1
    6 A(I,J)=A(I,J)/DIAG
      KJ=1
    9 IF(KJ-I) 11,13,11
   11 FCTR=A(KJ,I)
      DO 12 J=1,N1
   12 A(KJ,J)=A(KJ,J)-FCTR*A(I,J)
   13 KJ=KJ+1
      IF(KJ-N2) 9,9,14
   14 CONTINUE
      IF(VOK-1) 20,20,21
   20 K(1)=A(1,6)
      K(2)=A(2,6)
      K(3)=A(3,6)
      K(4)=0
      K(5)=0
      K(6)=1
   21 IF(VOK-3) 22,23,24
   22 K(1)=A(1,5)
      K(2)=A(2,5)
      K(3)=A(3,5)
      K(4)=A(4,5)
      K(5)=0
      K(6)=1
      GO TO 27
   23 K(1)=A(1,3)
      K(2)=A(2,3)
      K(3)=0
      K(5)=0
      K(6)=1
      GO TO 27
   24 K(1)=A(1,3)
      K(2)=0
      K(3)=A(2,3)
      K(4)=0
      K(5)=0
      K(6)=1
      GO TO 27
   19 FORMAT(E13.2)
   25 PRINT 26,A(I,I)
      K(6)=2
```

```
ORTRAN IV     MODEL 44  PS          VERSION 3,  LEVEL 1   DATE  69119

0050              26     FORMAT (6H EXTOL,E10.3)
0051             27      RETURN
0052                   END
```

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