CHEMICALLY REACTING FLOWS IN POROUS MEDIA

A THESIS
Presented to
The Faculty of the
Division of Graduate Studies
by
Allen Charles Merritt

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemical Engineering

Georgia Institute of Technology
May, 1976
CHEMICALLY REACTING FLOWS IN POROUS MEDIA

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Date Approved by Chairman: June 4, 1976
ACKNOWLEDGMENTS

The author wishes to thank his thesis advisor, Dr. C. W. Gorton, for his guidance and suggestions which were invaluable to the completion of this work.

In addition, Dr. W. Z. Black and Dr. H. C. Ward served on the thesis reading committee. Their constructive comments have certainly improved the quality of this work.

Thanks are also due to Continental Oil Company for a fellowship received during the early part of this study. The Georgia Institute of Technology Engineering Experiment Station also provided laboratory space for preliminary experiments.

Numerous people contributed to the conduct of this investigation and the author is grateful to them. The staff of the Rich Electronic Computer Center provided frequent assistance. Mr. Tomas F. Camacho provided many helpful suggestions. The clerical staff of the Gold Kist Engineering Department, especially Ms. Patty Woodall, Ms. Eva Rodum, and Ms. Elizabeth Farrow, typed the many drafts of this text.
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SUMMARY

In order to study the domains of Chemical Vapor Deposition in the industrial process of pack cementation, a comprehensive analytical model describing simultaneous transport phenomena in porous media is developed. Distinction is made between consolidated and unconsolidated media. Particular attention was paid to the models in the literature which described specific aspects of transport phenomena in porous media. In this work a novel approach to the equation of continuity is developed by using a single representation for effects in the solid and gas phases. Since no work previously discussed multicomponent diffusion in porous media, a model extending the "dusty gas theory" of Evans et al. is derived.

The specific problem in pack cementation chosen for study is the hydrogen reduction of $\text{HSiCl}_3$ to produce a silicon coating on an inert substrate. In this study, the substrate is also the wall of the pack cementation container. One of the objectives of this study is to show that coatings can be deposited on inert substrates due to the inherent advantages of the transient heat transfer, which exists early in the pack process. The generalized porous media transport equations are tailored to meet the constraints of the specific pack process chosen. These equations are then solved as an initial value problem through standard numerical techniques on a CDC digital computer. Due to depletion and deposition of a solid phase by chemical reaction at the walls and throughout the porous media, special boundary conditions and transport properties in the vicinity of the wall are developed.
Results are presented which show the effects of Knudsen diffusion on the amount of coating deposited and composition profiles. The effects of multicomponent diffusion are compared with those for equal binary diffusivities. Since actual experimental results are not available, accuracy of the numerical results is difficult to project. However, stability and convergence tests are used. In addition, results of the numerical mole flux calculations are compared to those from the Stephan-Maxwell equation. Early time results are compared to an analytical solution derived by Arnold.

The most important conclusion reached from the results of this thesis is that the model chosen for multicomponent diffusion will provide a successful solution for initial value problems in multicomponent mass transfer. The second important conclusion is that the assumption of equal binary diffusivities will provide a reasonable solution, thus greatly simplifying calculations. And finally, Knudsen diffusion can be a significant contribution to mass transfer in porous medium.

Several areas of further work and development in this area are evident from the results of this thesis. A nested iterative scheme to better calculate the molar concentrations in the porous media when deposition occurs should be developed. Laboratory experiments should be conducted to provide actual data for comparison with the model. And finally, experimental work to better relate porous media properties to transport properties should be conducted.
NOMENCLATURE

\( \alpha_i \) fraction of gas molecules diffusely reflected from capillary walls (dimensionless)

\( c \) molar density (lb-mole/ft^3)

\( \phi \) number of molecules per unit volume (molecules/ft^3)

\( \phi_i \) number of molecules of gas species \( i \) per unit volume (molecules/ft^3)

\( \phi_p \) number of molecules of solid species \( p \) per unit volume (molecules/ft^3)

\( \hat{c}_p \) molar heat capacity of the gas species (BTU/lb-mole °F)

\( \hat{c}_p \) heat capacity (BTU/lb-°F)

\( \hat{c}_{pp} \) of solid substrate \( p \)

\( \hat{c}_{pc} \) of coating \( c \)

\( \hat{c}_{pi} \) of gas species \( i \)

\( D_{ij} \) binary diffusivity for species pair \( ij \) (ft^2/hr)

\( D_{ij} \) effective binary diffusivity for dusty gas theory (ft^2/hr)

\( D_{ij} \) binary diffusion coefficient for dusty gas theory (ft^2/hr)

\( D_{im} \) effective multicomponent diffusion coefficient in porous media for gas species \( i \) (ft^2/hr)

\( D_{im} \) overall diffusivity for the core interface (ft^2/hr)

\( DI \) deposition index defined by equation 3-5 (dimensionless)

\( D_{ci} \) Knudsen diffusivity for gas species \( i \) (ft^2/hr)

\( D_p \) average particle diameter (\( \mu \))

\( g \) acceleration due to body force on fluid (ft/sec^2)

\( H \) constant defined by equation 2-20 (b)
\( \hat{\mathcal{H}} \) enthalpy (BTU/lb)
\( \hat{\mathcal{H}}_i \) of the gas species \( i \)
\( \hat{\mathcal{H}}_p \) of the solid substrate \( p \)
\( \hat{\mathcal{H}}_c \) of the coating \( c \)

\( \dot{\mathcal{J}}_i^* \) molar flux with respect to molar average velocity (lb-mole/hr-ft²)
\( \dot{\mathcal{J}}_i^{*e} \) effective molar flux with respect to molar average velocity (lb-mole/hr-ft²)
\( \dot{\mathcal{J}}_i^\circ \) effective mass flux with respect to mass average velocity (lb-mole/hr-ft²)

\( k_p \) equilibrium constant (dimensionless)
\( k_o \) porous media shape factor (dimensionless)
\( \bar{k} \) tortuosity factor (dimensionless)

\( k \) Boltzmann Constant

\( k_e \) static effective thermal conductivity of the porous media (BTU/hr-ft-°F)
\( \bar{k}_e \) overall thermal conductivity for the core interface (BTU/hr-ft-°F)
\( k_r \) apparent thermal conductivity of the porous media due to radiation (BTU/hr-ft-°F)
\( k_r^o \) radiation contribution to \( k_r \) defined by equation 2-21b

\( k_p \) thermal conductivity of the solid substrate material (BTU/hr-ft-°F)
\( k_i \) of the gas species \( i \)
\( k_f \) of the fluid
\( k_o \) of the shell or core material in a pack concentration model

\( L \) actual length of a pore channel along a tortuous path (ft)
\( c \) integer signifying the node point nearest the core-porous medium interface

\( L_e \) linear depth of a porous substrate (ft)
$L_0$  
length of the cylinder containing the pack (ft)

$M_w$  
molecular weight of a gas mixture (lb-mole)

$M_i$  
of gas species $i$

$\mu_i$  
of element $i$

$m_i$  
molecular mass of species $i$ (lb/molecule)

$m$  
reduced molecular mass (dimensionless)

$m_p$  
mass of the solid substrate and coating at time $t$ (lb)

$m_{p_0}$  
of the solid substrate at initial time

$m_c$  
of coating $c$

$\bar{N}_i$  
molar flux of species $i$ in a capillary (lb-mole/hr-ft$^2$)

$\bar{N}_i^e$  
effective molar flux of gas species $i$ (lb-mole/hr-ft$^2$)

$\bar{N}_p^e$  
effective molar flux of solid species $p$ (lb-mole/hr-ft$^2$)

$\bar{e}_i$  
effective mass flux of species $i$ (lb/hr-ft$^2$)

$\bar{e}_t$  
total mass flux in the porous medium for dusty gas theory (lb/hr-ft$^2$)

$\bar{e}^e$  
total effective mass flux (lb/hr-ft$^2$)

$n_i$  
number of molecules of the gas species $i$ per unit
volume (molecule/cu ft)

$n_p$  
number of molecules of the solid species $i$ per unit
volume (molecule/cu ft)

$n$  
sum of gas species molecules

$n'_i$  
sum of gas and solid molecules

$p$  
pressure (psf)

$p^o$  
reference pressure (psf)

$\bar{p}$  
average pressure in a porous medium (psf)

$p$  
represents solid species $p$

$q$  
total energy flux (BTU/hr-ft$^2$)
\( r_i \): generation term of species \( i \) (lb/hr-ft\(^3\))

\( R_c \): radius of the core material (ft)

\( R_p \): radius of the porous material (ft)

\( \bar{R}_p \): average radius of a particle (µ)

\( \bar{R} \): average radius of the pore (Å)

\( R \): universal gas constant (cal/gm-mole-°K)

\( r \): distance variable (ft)

\( S_o \): specific surface of the particles of porous media (ft\(^2\))

\( T \): temperature (°R)

\( T_{ci} \): critical temperature of species \( i \) (°K)

\( t \): time variable (hr)

\( V_{ci} \): critical volume of species \( i \) (cm\(^3\)/gm-mole)

\( V_p \): volume of solid substrate (ft\(^3\))

\( V_e \): total unit volume of porous medium (ft\(^3\))

\( \bar{V}_e \): superficial velocity through porous media (ft/hr)

\( \bar{v} \): actual velocity within a pore (ft/hr)

\( X \): total amount of elemental hydrogen (lb)

\( \bar{x}_i \): mole fraction of species \( i \) (dimensionless)

\( \Delta r_p \): incremental distance between the core and porous medium interface (ft)

\( \Delta p_r \): incremental distance between the shell and porous medium interface (ft)

\( \Delta r \): incremental radius (ft)

\( \Delta t \): incremental time (hr)

\( \alpha \): thermal diffusivity (ft\(^2\)/hr)

\( \varepsilon \): porosity or void volume of the porous medium (dimensionless)
\( \varepsilon_p \) volume fraction of solid substrate and coating in a porous medium (dimensionless)

\( \varepsilon_{p0} \) of solid substrate only

\( \varepsilon \) emissivity (dimensionless)

\( \phi \) term defined by equation 4-5b

\( \kappa \) permeability of porous media (ft\(^2\))

\( \beta \) permeability coefficient of porous media (ft\(^4\)/lb\(_f\)-sec)

\( R_0 \) shape factor representative of a specific porous medium (dimensionless)

\( \lambda_0 \) mean free path at reference pressure \( P_0 \) (ft)

\( \lambda_i \) mean free path of a gas species \( i \) (ft)

\( \mu \) viscosity of the fluid (lb/ft-hr)

\( \mu_i \) of the gas species \( i \) (lb/ft-hr)

\( p \) density of the fluid (lb/ft\(^3\))

\( p_c \) of the coating \( c \)

\( p_i \) of the gas species \( i \)

\( p_p \) of the solid substrate \( p \)

\( p_{p0} \) of the solid substrate at initial time

\( p_\sigma \) of the core or shell material

\( \sigma_i \) collision diameter for the species \( i \) (ft)

\( \sigma_{ij} \) collision diameter for the pair \( ij \) (ft)

\( \tau \) tortuosity of the porous medium (dimensionless)

\( \delta_i \) term defined by equation 2-9c

\( \Omega_{ij} \) diffusion collision integral for the pair \( ij \) (dimensionless)

\( \Omega_{\mu i} \) collision integral for viscosity of the gas species \( i \) (dimensionless)
\( \omega_i \) mass fraction of gas species \( i \) (dimensionless)

\( \omega_{ci} \) of coating species \( i \)

\( n \) number of gas phase species (dimensionless)
CHAPTER I

INTRODUCTION

In the early stages of the multi-year program, "A Study of Interfacial Phenomena," sponsored at the Georgia Institute of Technology by the United States Air Force as part of the Project Themis, a search of the technical literature and a survey of the defense and space-oriented industry was conducted in the specific area of high temperature, oxidation resistant surface and diffusion coatings. This study was undertaken to identify technology gaps and to determine research needs in this special coatings field. One of the recommendations resulting from this study was to investigate the domains of chemical vapor deposition as a coating mechanism. Chemical vapor deposition (CVD) is a basic coating process which may include both homogeneous gas phase and heterogeneous chemical reactions to produce a coating on a heated substrate material. In response to this particular recommendation, an experimental and analytical investigation of the CVD process was undertaken. The chemical system chosen for this research was the hydrogen reduction of silicon tetrachloride to elemental silicon and hydrogen chloride. At the time of this study, silicide coatings were of considerable interest to the aerospace industry for protection of refractory metals in severe thermal environments under oxidizing conditions. One technique used for the deposition of these coatings is CVD. Coincidentally, considerable effort had also been spent during this period by the semi-conductor industry in the production of single crystals and epitaxial thin-films of pure silicon on suitable
substrates by CVD for use in electronic components manufacturing. In both of these coatings-oriented industries, analysis and improvement of the CVD coating process were approached with experiment techniques. Many associated technical papers dealt with metallurgical implications. In most of the thin-film and single crystal work, theoretical considerations were limited to thermodynamic predictions. Only a few papers concerned with coating or thin-film characterizations and performance analysis considered the aspects of transport phenomena in the production of the coating. This omission was also particularly evident in the analysis of the production of diffusion coatings by CVD. While the solid-solid diffusion of the coating material into the substrate to produce an alloy is an essential part of the overall deposition process, in many cases this phenomena may not be the controlling mechanism.

Specifically, the research program mentioned above was a parametric study of the deposition rate of silicon on a tungsten wire. The important parameters, besides deposition rate, were wire temperature, gas phase flow rate, gas phase composition, and wire diameter. This first CVD study was conducted in a simple glassware system composed of a drying tube, two condensers, a bubbler flask, and a deposition tube. The substrate was electrically heated. Enough data were obtained from this preliminary experimental work to design and build a more substantial CVD apparatus. The construction of this system allowed for operation under partial vacuum or in positive pressures. This equipment was also constructed so that either a gas-liquid, a gas-gas, a gas-solid, or a solid-solid feed system could be utilized. The solid-solid feed system required that one of the components decompose into gaseous products which would react with the other solids to
give the desired reaction gases. In this apparatus, CVD coatings could be deposited on inert oxide substrates. Several experiments were conducted with this experiment. Coatings were obtained on tungsten wires and on inert alumina substrates.

Because of production related problems, the pure CVD process was found to be used in limited, often laboratory, situations. In more common industrial coating operations, other techniques incorporating CVD concepts were prevalent. One such technique in wide use is termed "pack cementation." This name described a process that has changed considerably in basic concept since its inception. Originally, "pack cementation" implied that coatings were produced by diffusion from metal powders in physical contact with the substrate surface at elevated temperatures.

Examples of this process are the early cementation coatings of aluminum, zinc, or chromium on iron in the steel industry. In the chromizing process, pieces of iron or steel were packed in a retort surrounded by chromium powders. The pack was heated in a furnace at a temperature of 1300° C for four hours. To avoid excessive sintering of the coating material, inert refractory powders were mixed with the finely divided chromium. In 1927, Marshall modified the pack design in the chromizing process to include carrier gases which combined with chromium in the solid phase to form a gas phase species. This gas then reacted with the iron surface to produce a coating. The reaction of a carrier gas with the substrate is almost universal in modern pack cementation processes, thus chemical vapor deposition has become the basic coating mechanism in this operation. Several descriptions of the pack process for uses other than chromium coatings on iron may be found in references...
18 through 22. In addition, workers have more recently used pack cementation successfully to produce complex coatings containing several elements which are deposited simultaneously.\textsuperscript{23,24}

The pack cementation process has been generally limited to diffusion coatings produced by solid-solid reactions or substitution reactions between the coating element and substrate, where the entire bulk of the material within the retort is maintained at constant temperature. Although very desirable, no results have been found in the literature which indicate pack cementation coatings can be produced on inert substrates. In pure CVD processes, however, inert substrates may be coated by surface reaction if the substrate temperature is sufficiently high. This phenomena may occur in a pack process during the transient period when the mass is heated from ambient to furnace temperatures.

In this thesis, the possibility of the production of a coating on an inert substrate is analyzed. In the past, only a few researchers have considered aspects of depletion, heat transfer, or flow within the pack.\textsuperscript{24,25} Any attempt to analyze this process will require an understanding of transport phenomena in porous media. A search of the literature did not reveal any considerations of pack cementation or other porous media related processes that incorporated flow, heat transfer, and mass transfer simultaneously. Several researchers have discussed separate aspects of transport phenomena in porous media, particularly the development of diffusivity and thermal conductivity. These discussions have been included in a general set of equations describing transport phenomena for porous media. These equations are presented in detail in the next chapter. The nature of this development is not limited just to the analysis of pack
cementation. Application can be found for these theories in several seemingly diverse fields including grain drying or aeration, shale oil recovery, and catalyst performance prediction.

In Chapter III, the general transport equations for porous media presented in Chapter II are applied to the specific problem in pack cementation mentioned above. Results of a digital computer solution to this problem based on finite difference equations are discussed in Chapter IV. Recommendations and conclusions follow in Chapter V.
CHAPTER II

TRANSPORT PHENOMENA IN POROUS MEDIA

Analytical analysis of simultaneous heat, mass, and momentum transport in porous media is relatively undeveloped. As was mentioned in the Introduction, certain aspects of the individual conservation equations have been studied by researchers of different disciplines. For example, hydrologists have investigated flow through sand beds and have proposed empirical relations for the steady state equation of motion. Chemical engineers have experimented with diffusion in catalyst pellets and have proposed semi-empirical relations for the diffusion coefficient. Because most of the reported work is experimental in nature, the resulting relationships are practically oriented and not readily suited to theoretical application. A good example of this deficiency concerns studies of heat transfer with flow through a porous medium in which the convective effect and the Knudsen effect are treated as conduction and included in the apparent thermal conductivity.

Comparison of the various relations describing transport phenomena in porous media is further complicated because substantially different models were chosen to characterize the media. In many flow and heat transfer studies, media structures have been classified as either "consolidated" or "unconsolidated." Unconsolidated media are formed from randomly oriented particles. Consolidated media are those media which may have closed ended or completed closed pores. These media could have originated from
an unconsolidated structure which could have sintered or undergone some other process to close the pores. Much of the literature involved with flow and heat transfer studies concerns the porous media characterizations with different models for the pore size distribution within a given structure. In diffusion studies, especially where catalyst pellets have been formed from porous particles, the structure has not been classified. However, different models are used to describe the pore size.

In the discussions of this chapter, a comprehensive analytical model describing simultaneous transport phenomena in porous media will be developed. Because results of the present study might be applied to either of the two general classifications of porous structure, the following discussions will include consolidated and unconsolidated media. Effects of the various pore size models will also be discussed where appropriate. The development of each transport equation will be separately shown. The particular transport properties associated with porous media will also be discussed in each appropriate section. Equations for calculation of the properties not influenced by porous media effects, such as gas density and gas heat capacity, will be presented later.

Equation of Motion

The equation of motion for flow through porous media is an expression of the experimental results of several workers. Notable among them is Darcy. His work has been formulated into an equation which bears his name and is given below as equation 2-1. This relation and its historical development are well documented.26,27,28
\[ \bar{v}_e = -\frac{K}{\mu} (\nabla P - \rho \bar{g}) \]  

(2-1)

where  
\( \bar{v}_e \) is the superficial velocity of the fluid flowing in the porous medium  

\( K \) is the permeability  

\( \mu \) is the fluid viscosity  

\( \nabla P \) is the pressure gradient  

\( \rho \) is the fluid density  

\( \bar{g} \) is the body force on the fluid.

Darcy's Law differs considerably from the classical equation of motion (as it appears in Bird et al.\textsuperscript{29} for example); however, this relation applies to macroscopic rather than microscopic observations of a fluid passing through fine channels in porous media. Although no transient terms appear in Darcy's Law, this equation is used in the solution of time dependent problems.\textsuperscript{29} To better describe certain specific problems such as in flow through a porous mass and an adjoining empty space, Brinkmann has proposed a modification to equation 2-1 which reduces to Darcy's Law for low values of the permeability.\textsuperscript{30} This relation was more rigorously derived by Slattery.\textsuperscript{31}

Since Darcy's Law was determined experimentally for flow through unconsolidated porous media with a uniform pore size, a correction must be made for application to consolidated porous media. The accounting for the different types of porous media is incorporated in the value used for the permeability. Carman has discussed methods for the determination of this property and other problems encountered in the characterization of porous media for flow in detail. Results of his efforts and others
are presented briefly below for both consolidated and unconsolidated media.

Carman based his work on the earlier studies of Blake\textsuperscript{32} and Kozeny.\textsuperscript{33} These independent efforts were among the first to apply the concept of a hydraulic radius to the viscous flow of fluids through unconsolidated porous media with uniform pore size. Carman chose to describe flow through the porous medium in terms of the superficial velocity \( \bar{v} \) and the bed depth \( L_e \) instead of the actual quantities, \( \bar{V} \) and \( L \), for the individual capillaries of the medium. In doing so, he defined a new variable, \( \tau \), called the tortuosity, to represent the ratio \( \frac{L}{L_e} \). Then he modified the results of Dupuit\textsuperscript{34}, which relate actual velocity, \( \bar{V} \), to the apparent velocity, \( \bar{v} \), to include the tortuosity. These modifications have been included in the definition of the permeability which is given below:

\[
K = \frac{\varepsilon^3}{\kappa \mathcal{S}_e (1 - \varepsilon)^2} \tag{2-2}
\]

where

- \( \varepsilon \) is the porosity or the void fraction
- \( \mathcal{S}_e \) is the specific surface of the particles
- \( \kappa \) is the tortuosity factor which is a function of \( \varepsilon^2 \) and a shape factor \( \mathcal{K}_o \).

All of the quantities in equation 2-2 may be determined experimentally with relative ease with the exception of the tortuosity factor, \( \kappa \).

Carman has reported results of many experiments to evaluate this quantity. Carman has also stated that for most unconsolidated media, the value of \( \kappa \) is approximately 5.0 inches\textsuperscript{2}.

Evaluation of the quantities in equation 2-2 for consolidated
porous media is more difficult. Usual experimental procedures to determine the value of $S_0$ (e.g., nitrogen absorption) are not applicable since these procedures include closed ended pores where flow does not occur. Wyllie and Rose have proposed a relation to calculate the tortuosity factor of consolidated media.\textsuperscript{35} The result of their work as reported by Carman is given below:

$$\bar{\zeta} = 2.5 \zeta^{-2} \quad (2-3)$$

Experimental values reported in Carman indicate that this relation is adequate for the porosities expected for consolidated media. As with the definition for the permeability for unconsolidated media, experiments are required to arrive at a value for $\zeta$. Carman also mentions the problem of a nonuniform pore size and provides, as a solution, an integral technique for the range of particle sizes under consideration.

Recent results of diffusion studies in catalyst pellets imply that the tortuosity can be simply related to porosity for specific types of porous media. These results will be discussed in detail in a following section of this chapter.

**Equation of Continuity**

In general, the equation of continuity for flow through porous media has been written in two parts, one for the gas phase and one for the solid phase.\textsuperscript{36} In the present study, the porosity will be allowed to change, so, for convenience, a single continuity equation for both phases will be derived.

A volume element composed of solid particles and gas is shown in Figure 1. The solid particles are assumed to be composed of a substrate
Figure 1. Schematic Representation of a Volume Element of Coated Porous Media.
with constant density $\rho_a$ and a film of coating with constant density $\rho_c$. After suitable mathematical manipulation (see Appendix I for details), the density of the solid particle composed of the original substrate plus the coating may be determined as follows:

$$\rho_p = \rho_c + (\rho_a - \rho_c) \frac{\varepsilon_{\rho_b}}{\varepsilon_p}$$  \hspace{1cm} (2-4)

where $\varepsilon_p$ is the volume fraction of solid per unit volume of solid and gas for any time.

$\varepsilon_{\rho_b}$ is the initial volume fraction of solid per unit volume of solid and gas.

The equation of continuity for a volume composed of both solid particles and gases where the mass velocity of the solid is zero is also derived in Appendix I. The result of this development is given below:

$$\frac{\partial}{\partial t} (\varepsilon_p \rho) + \nabla \cdot (\varepsilon_p \rho \vec{v}) + \nabla \cdot \rho \vec{v} = 0$$  \hspace{1cm} (2-5)

where $t$ is time.

Substitution of equation 2-4, the expression for the density of the solid particles, into equation 2-5 yields:

$$\frac{\partial}{\partial t} (\varepsilon_p \rho) + \nabla \cdot (\rho (\varepsilon_p - \varepsilon_{\rho_b})) + \nabla \cdot \rho \vec{v} = 0$$  \hspace{1cm} (2-6)

Noting that the change in the initial porosity with time is zero, equation 2-6 may be reduced to the continuity equation used in this work which is presented below:
Equation of Continuity Species $i$

The equation of continuity for species $i$ is derived in a manner similar to that for the overall continuity equation and is given below:

\[ \frac{\partial}{\partial x} (\varepsilon \rho) + \rho_c \frac{\partial \varepsilon}{\partial t} + \nabla \cdot \rho \nabla \varepsilon = 0 \]  \hspace{1cm} (2-7)

\[ \frac{\partial}{\partial x} (\varepsilon \rho \omega_i) + \rho_c \frac{\partial (\varepsilon \rho \omega_i)}{\partial t} + \nabla \cdot \vec{n}_i^e = r_i \]  \hspace{1cm} (2-8)

where \( \omega_i \) is the mass fraction of the species $i$ in the gas phase

\( r_i \) is the generation term for species $i$

\( \vec{n}_i^e \) is the effective mass flux of species $i$ based on a unit area of both solid and gas

\( \omega_c \) is the mass fraction of the species $i$ in the coating.

Over the last several years, many papers have been published on methods used to determine values for the diffusion coefficient for use in the mass or mole flux relationship. Much of this work was generated by the increased interest in catalyst pellets formed by pressing together small porous particles. At low pressures, the usual pore size distribution was such that both normal diffusion and Knudsen diffusion occurred. As previously mentioned, all of the publications reviewed involved only binary diffusion. However, Evan, Watson and Mason proposed a diffusion model for constant pressure and temperature based on a "dusty gas" theory that offered promise for adaptation to a multi-component system. In this model, the Stefan-Maxwell equations were written to include the solid as a giant molecule with zero mass velocity. This approach resulted in an equation which conformed to the accepted relations describing the
transition region between normal diffusion and free molecular flow. This equation also reduced to the proper form for conditions at either limiting case. The results of the work by Evans et al. are given below as equation 2-9a. A brief summary of the derivation of these equations is presented in Appendix II.

\[ \tilde{N}_i^e = -D_i^e \frac{\partial n_i}{\partial x} + \frac{n_i}{n} \tilde{N}_i \]  

(2-9a)

where

\[ D_i^e = \frac{n_i}{n} \delta_i \frac{D_i^e}{D_i^P} \]  

(2-9b)

\[ \delta_i = \left( 1 + \frac{n_i}{n} \frac{D_i^e}{D_i^P} \right)^{-1} \]  

(2-9c)

and

- \( \tilde{N}_i^e \) is the molecular flux of species i based on a cross-sectional area of both solid and gas
- \( n_i \) is the number of molecules of the gas phase species i per unit total volume
- \( n \) is the total number of gas phase molecules per unit total volume
- \( n_P \) is the number of molecules of the solid per unit total volume
- \( n_1 \) is the sum of \( n \) and \( n_P \)
- \( D_{ij}^e \) is the effective diffusion coefficient for a porous medium
- \( D_{ij}^e \) is the effective Knudsen diffusivity for a porous medium.

The effective diffusion coefficients are related to the normal diffusivities by the generally accepted relationship given in equation 2-10. Through the definition of \( \sigma \), specific contributions to the diffusion by consolidated or unconsolidated media can be made.
\[
D_{ij}' = \frac{\varepsilon}{\varepsilon} D_{ij} 
\]

where \( \varepsilon \) is the porosity
\( \tau \) is the tortuousity
\( D_{ij}' \) is the binary diffusivity for the dusty gas theory.

The binary diffusivity for the gas phase species can be obtained from the following equation:

\[
\begin{align*}
D_{ij}' &= \left( \frac{16}{3} n' \left( \frac{m_i m_j}{2 \pi k T} \right)^{\frac{1}{2}} \left( \frac{\pi \sigma_{ij}^2 \Omega_{ij}}{2} \right) \right)^{-1} \\
&= \left( \frac{16}{3} n' \left( \frac{m_i m_j}{2 \pi k T} \right)^{\frac{1}{2}} \left( \frac{\pi \sigma_{ij}^2 \Omega_{ij}}{2} \right) \right)^{-1} \\
&= \left( \frac{16}{3} n' \left( \frac{m_i m_j}{2 \pi k T} \right)^{\frac{1}{2}} \left( \frac{\pi \sigma_{ij}^2 \Omega_{ij}}{2} \right) \right)^{-1}
\end{align*}
\]  

(2-11a)

where

\[
\bar{m} = \frac{m_i m_j}{m_i + m_j}
\]

(2-11b)

and

\( m_i \) is the molecular mass of species \( i \)
\( k \) is the Boltzmann constant
\( T \) is the absolute temperature
\( \sigma_{ij} \) is the collision diameter
\( \Omega_{ij} \) is the collision integral.

The diffusivity, \( D_{ij}' \), representing the interaction between the solid and gas species is equivalent to a Knudsen diffusivity. Based on assumptions provided by Evans et al., this diffusivity is calculated by assuming the reduced mass, \( \bar{m} \), becomes \( m_i \), and the collision diameter, \( \sigma_{ij} \), becomes \( R_p \), the radius of the solid particles. According to Epstein, as reported by Evans et al., the collision integral, \( \Omega_{ij} \), reduces to \( \left( 1 + \frac{\alpha m_i}{\sigma_{ij}} \right)^{-1} \). The equation for \( D_{ij}' \) thus becomes:

\[
D_{ij}' = \frac{\varepsilon}{\varepsilon} \left( \frac{16}{3} n' \left( \frac{m_i m_j}{2 \pi k T} \right)^{\frac{1}{2}} \left( \pi R_p^2 \right) \left( 1 + \frac{\alpha m_i}{\sigma_{ij}} \right) \right)^{-1}
\]

(2-12)
where $\bar{R}_p$ is the radius of the solid particles and $\alpha_i$ is the fraction of species $i$ diffusely scattered by the wall.

According to Schmitt, again as reported in Evans et al., $\alpha_i$ is usually equal to unity. Independently, Rothfield derived a similar expression for equation 2-9a based on momentum balances. In this model, a special definition for the Knudsen diffusivity was used which contained a bulk flow term. Scott and Dullien, in their analysis of mixed mode diffusion in porous media, first derived a diffusion equation for a single circular capillary where both normal and Knudsen diffusion applied. To extend their model to porous media, they also used a value determined by the ratio $F$ to express the effects of porous media on the binary diffusivity. Integrated forms of the equation of Evans et al., Scott and Dullien, and Rothfield have all been shown to be equal. These equations are discussed further in Appendix III.

From first appearances, the definition for the effective Knudsen diffusivity derived by Evans et al., as shown in equation 2-12, will allow for direct calculation from basic porous media property data. With the more common definition (see for example Pollard and Present), diffusion studies are required to evaluate a constant in the Knudsen diffusivity equation, $K_\infty$, which accounts for the porous media effects. In comparing their equation to these earlier works, Evans et al. state that the collection of terms $\frac{F}{E} n' \bar{R}_p \bar{R}_p (1 + \alpha_i) \pi$ must be evaluated from diffusion experiments rather than calculated directly. In effect, Evans et al. have simply expanded the definition for the experimental constant $K_\infty$.

Most of the later papers on diffusion in porous media have been concerned with modifications of the early work to better account for the
effect of actual porous structures on the diffusivities. These models have utilized either experimental diffusion data or porous media characterization data to predict results for new diffusion conditions. For example, several papers published by J. M. Smith and his co-workers were based on diffusion in catalyst pellets assumed to have a bi-disperse, randomly oriented, non-continuous pore structure.\textsuperscript{45,46,47} Johnson and Stewart developed a different model to show the effect of pore geometry on the effective diffusivity.\textsuperscript{48} This modification also assumed randomly oriented circular pores but considered the distribution to be continuous rather than bi-disperse and non-continuous. The results of Johnson and Stewart and Smith and co-workers are consistent. Brown et al. compared the two techniques with experimental data and reached a similar conclusion.\textsuperscript{49} The results of Smith and co-workers are particularly important to the present study. According to these workers, if the porous media has a single mode pore size distribution with a single radius, $\frac{\varepsilon}{\varepsilon^2}$ would be equal to $\varepsilon^2$ in the local diffusion equation. Thus the need for experimental determination of $\varepsilon$ is eliminated. For a bimodal distribution, the definition of the ratio $\frac{\varepsilon}{\varepsilon^2}$ would be more complex. Considerable data are presented in Carman which can be used to show that $\frac{\varepsilon}{\varepsilon^2}$ is approximated by $\varepsilon^2$.\textsuperscript{26} In addition, Smith and coworkers show that pore size distribution data can be used to calculate the Knudsen diffusivity without results from prior diffusion studies.\textsuperscript{45}

Smith and co-workers have also extended their work on pure diffusion processes in porous media to include the effects of chemical reaction and of absorption on the diffusion phenomena.\textsuperscript{50-54} Wakao and Smith proposed a modification for the effective diffusion coefficient in which reaction
or absorption is occurring. Scott has proposed a similar model to account for the effect of reaction during diffusion in porous media. As was previously mentioned, no work has yet been presented for multi-component diffusion in porous media. The approach used in this work to analyze such a problem is based on an extension of the method given by Evans et al. In addition, the benefit of the later work by Smith and co-workers and Johnson and Stewart which provides better definitions for the term $\frac{E}{\Gamma}$ and the Knudsen diffusivity will be utilized. The results of the derivation of the multi-component mass flux term $\vec{m}^e$ is presented below.

By rearranging the basic diffusion equation proposed by Evans et al. in terms of concentrations based on a unit volume of both solid and gas molecules, the following equation results:

$$\nabla \chi = \frac{1}{\rho} \left( \left( \chi \vec{N}_i^e \cdot \chi \vec{N}_i^e - \chi \vec{N}_s^e \right) \right) + \left( \chi \vec{N}_i^e \cdot \chi \vec{N}_s^e - \chi \right) \vec{N}_s^e \tag{2-13}$$

where
- $c'$ is the molar concentration of the gas and solid
- $\rho$ is the number of solid molecules per unit volume
- $\chi$ is the mole fraction of the gas species $i$
- $\vec{N}_i^e$ is the molar flux of the gas species $i$
- $\vec{N}_s^e$ is the molar flux of the solid species.

The derivation of this equation is presented in Appendix IV. The molar flux of the solid,$\vec{N}_s^e$, is assumed to be identically equal to zero. Further, the quantity $c'\vec{D}_i^e$ may be rearranged to give:

$$c'\vec{D}_i^e = c \vec{D}_i^e \tag{2-14}$$
Insertion of these results into equation 2-13 gives:

\[ \nabla \nu_i = \sum_{k \neq j} \left( (c'_D)^e (\chi_{ik}\tilde{N}_k^e - \chi_i\tilde{N}_i^e) \right) - (c_D)^e \tilde{N}_i^e \]  
(2-15)

For the gas phase species, the term \( c'_D \) is equal to \( c_D \). If the molar flux of species \( i \) is defined as follows:

\[ \tilde{N}_i^e = \tilde{J}_i^e + \chi_i \tilde{N}_i^e \]  
(2-16a)

where

\[ \tilde{J}_i^e = -c_i\rho_m \nabla \chi_i \]  
(2-16b)

equation 2-15 and 2-16a may be combined to give:

\[ c_i\tilde{\rho}_m^e = \left( \frac{\frac{\nu}{\rho_m} (c_D)^e (\chi_{ik}\tilde{N}_k^e - \chi_i\tilde{N}_i^e) + (c_D)^e \tilde{N}_i^e)}{\tilde{N}_i^e - \chi_i \tilde{N}_i^e} \right)^{-1} \]  
(2-17)

The mass flux is obtained from the following relation:

\[ \tilde{m}_i^e = (-\rho \tilde{\rho}_m^e \nabla \chi_i + \chi_i \tilde{N}_i^e) M_i \]  
(2-18)

where \( M_m \) is the molecular weight of the mixture and \( M_i \) is the molecular weight of the gas species \( i \).

**Equation of Energy**

The derivation of the equation for energy conservation in porous media begins with a generalized form in which potential and kinetic terms are neglected. This relation must be modified to include the contributions
of both the solid and gas phases. Therefore the change in enthalpy within a unit volume composed of a solid and flowing gas is assumed to reflect both the change of the enthalpy of the gas and solid on an additive basis. The generalized equation is further modified by assuming that the velocity of the solid is zero and that the change in solid density with time is zero. The modified energy equation is given below as equation 2-19. This derivation is presented in detail in Appendix V.

\[
\begin{align*}
&\left(\varepsilon p c_p + \varepsilon_{p_b} \rho_b c_{pb} + (\varepsilon p - \varepsilon_{p_b}) \rho_c c_{pc} \right) \frac{\partial T}{\partial t} + \varphi \rho c_p T \frac{\partial^2 T}{\partial x^2}
+ \varepsilon p c_p \left( \frac{\partial \omega_i}{\partial x} \right) = -\rho c_p \varphi \frac{\partial^2 T}{\partial x^2} - \rho \varphi \frac{\partial E}{\partial x} - \rho \varphi \frac{\partial \omega_i}{\partial x}
- \nu \frac{\partial^2 \omega_i}{\partial x^2} + \xi \frac{\partial P}{\partial x} + \nu \cdot k_e \frac{\partial T}{\partial x}
\end{align*}
\]  

(2-19)

where

- \( \hat{H}_g \) is the mass enthalpy of the gas species i
- \( \hat{H}_c \) is the enthalpy of the coating
- \( k_e \) is the effective thermal conductivity.

In a manner analogous to the previous section, the effect of the porous media on heat conduction is expressed in the thermal conductivity.

Considerable literature has been published describing various models for the thermal conductivity in porous media. A number of studies have dealt with heat transfer in a porous solid filled with a static fluid. \(^{56-62}\) Studies have also been conducted for heat transfer in porous media with flowing fluids. \(^{63,64,65}\) In many of these publications, considerations have also been made for the difference between consolidated and unconsolidated materials. One paper included the effects of gas-solid
reactions on the thermal conductivity. Recently, Huang proposed that for porous rock, the static thermal conductivity be given by the following equations:

\[ k_e = \varepsilon p k_p \exp\left(\frac{-\eta}{\varepsilon p}\right) + \varepsilon (k_f + k_r) \exp\left(\frac{-\eta}{\varepsilon p}\right) + \frac{h^2}{\pi} (1 - \exp\left(\frac{-\eta}{\varepsilon p}\right))^{1/2} \]  

(2-20a)

where

\[ h = 1 - \varepsilon \exp\left(\frac{-\eta}{\varepsilon p}\right) - \varepsilon p \exp\left(\frac{-\eta}{\varepsilon p}\right) \]  

(2-20b)

and \( \varepsilon \) is the porosity, \( \eta \) is the pore geometric factor, \( k_p \) is the solid thermal conductivity, \( k_f \) is the fluid thermal conductivity, and \( k_r \) is the apparent radiation thermal conductivity.

Huang based his derivation on a probability argument for a model combining three mechanisms: heat transfer by conduction through the solid, heat transfer through the solid and fluid in series by conduction and radiation, and heat transfer through the fluid phase by conduction and radiation. This relation is applicable to both consolidated and unconsolidated porous media through the value chosen for \( \eta \).

Various relations have also been proposed to calculate \( k_r, k_p, \) and \( k_f \). Schotte has proposed the following relation for \( k_r \) in packed beds:

\[ k_r = \left(\frac{1 - \varepsilon}{k_p} + \frac{1}{k_r^0}\right) + \varepsilon k_r^0 \]  

(2-21a)

where

\[ k_r^0 = 0.692 \varepsilon p \left(\frac{T}{100}\right)^3 \]  

(2-21b)
and \( \varepsilon \) is the emissivity

\( D_p \) is the particle diameter.

Schotte compared his results with the experimental data of Yagi and Kunii\(^5^{7}\) with good success.

The term \( k_p \) is the thermal conductivity of the solid material and can be found in specific literature related to that material. The term \( k_f \), which is the fluid conductivity, must be corrected for pore size if the fluid is a gas with a low pressure. Huang has proposed the following relation:\(^6^{7}\)

\[
k_f^* = k_f \left( 1 + \frac{S}{5} \right)
\]

where

\[
S = \frac{2 \overline{R}_p}{\lambda_0 p^*}
\]

and

\( k_f \) is the conductivity of the gas mixture

\( P \) is the pressure

\( p^* \) is the reference pressure

\( \lambda_0 \) is the gas mean free path at the reference pressure

\( \overline{R}_p \) is the mean particle radius.

For a multi-component gas mixture, an averaging technique must be used to calculate the mean free path. The multi-component gas conductivity, \( k_f^* \), will be calculated as described in the next chapter.
CHAPTER III

ANALYSIS OF PACK CEMENTATION

As was mentioned in the Introduction, the specific problem chosen for analysis in this thesis is the deposition of solid silicon on an inert alumina shell by the pack cementation process. In order to postulate a problem whose solution can be obtained with a realistic amount of computer time while still preserving all of the essential features, a single chemical vapor deposition reaction based on the hydrogen reduction of trichlorosilic acid to form hydrogen chloride and solid silicon is specified. In the past, workers concerned with this chemical system chose silicon tetrachloride as the predominant gas phase silicon bearing species (see for example, reference 68). Recent studies by Harper and Lewis have shown that the particular species chosen for this thesis are predominant.\(^69\)

In the proposed process, a ceramic cylinder, filled with a porous pack material with a solid silicon core at the center, all at constant temperature, is placed in a hot furnace. The porous mass is assumed to contain a mixture of hydrogen, hydrogen chloride, and trichlorosilic acid. At the start, heat is added to the outside surface of the alumina shell. As the temperature of the system rises, hydrogen chloride reacts with the silicon at the core surface to form trichlorosilic acid and hydrogen. As the species diffuse outward toward the hot alumina shell and attain a higher temperature, the equilibrium shifts so that solid silicon is deposited as a coating.\(^69\)

For this problem, all transport phenomena effects are assumed to
be symmetrical about the cylindrical axis. The analysis of this process is based on a reduced set of the generalized transport equations for consolidated porous media as presented in Chapter II. The specific equations are given below. In addition, the remaining constraints necessary for analysis of the proposed problem are presented below. Unfortunately, analytical techniques for the simultaneous solution below of these relations are not available. As is typical of many such problems, numerical solution schemes using a digital computer have been combined to provide an algorithm which may be used to predict events in pack cementation. In this chapter, details of this algorithm are also presented. Boundary and initial conditions are discussed in terms of their numerical representations.

**Porous Media Description**

The hypothetical porous media selected for this study is assumed to be consolidated and made from pressed alumina powder with a single pore radius. These assumptions allow for the calculation of the tortuosity from the porosity without experimental determination and thus simplify the porous media effect on both the diffusivity and permeability as previously discussed. The actual material properties selected are those used in many previous diffusion and heat conduction studies as reported in Smith et al. Pertinent data are summarized as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>$\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter</td>
<td>90$\mu$</td>
</tr>
<tr>
<td>Macropore radius</td>
<td>To be determined</td>
</tr>
<tr>
<td>Particle density</td>
<td>2.45 gm/cc</td>
</tr>
</tbody>
</table>

The value for $n$ in equation 2-20 for this material as reported by Huang is approximately 1.0. 67
Transport Equations

The general transport equations for porous media presented in the previous chapter may be simplified for the analysis of this pack coating process. Because the coating is composed of a single component, silicon, and because this species does not exist in the gas phase, the conservation of silicon represented by equation 2-8 becomes:

\[- \rho_s \frac{\partial \epsilon}{\partial t} = r_{Si} \]  \hspace{1cm} (3-1)

Equation 2-8 for the continuity of the gas phase species also reduces as follows:

\[ \frac{\partial}{\partial t} (\rho \omega_i) + \nabla \cdot \vec{n}_i = r_i \]  \hspace{1cm} (3-2)

Application of the assumptions mentioned in the previous paragraph to equation 2-19 gives the equation for energy conservation,

\[ (\epsilon \rho \rho_e \epsilon_{\rho} \rho_{\epsilon} + (\epsilon_p - \epsilon) \rho_{\epsilon} \rho_{\epsilon} \rho_{\epsilon}) \frac{\partial T}{\partial t} \pm \dot{\epsilon} \frac{\partial \epsilon}{\partial t} \nabla \cdot \dot{\epsilon} \frac{\partial \epsilon}{\partial t} + \rho \epsilon \nabla \cdot \vec{v} = \vec{v} \cdot \nabla \epsilon \]  \hspace{1cm} (3-3)

For this problem, the equation of motion remains as equation 2-1. The overall equation of continuity, equation 2-7, also remains the same as previously derived.

The only transport equation needed to describe both the core material and the inert shell for the problem chosen for this work concerns
conservation of energy. Even though the shell is composed of a ceramic material, temperatures anticipated in this problem are not sufficient to cause changes in pressure with time or distance. The equation used to describe the conservation of energy for either the shell or the core is given below:

\[ \sum c_p \frac{\partial T}{\partial t} = \nabla \cdot \kappa \nabla T \]  

(3-4)

**Auxiliary Equations and Further Assumptions**

One of the more interesting aspects of the present problem lies in the deposition of a condensed phase by chemical reaction. Unfortunately, experimental data of sufficient accuracy are not available to obtain a reliable empirical relationship to predict condensation rates for the chemical system considered in the present study. In addition, theories for condensation kinetics are not well developed so theoretical results are also not available. Thus, the assumption is made that the gas phase is in equilibrium with the condensed phase, should one be present. The implication in this assumption is that the condensation kinetics are infinite or at least so rapid that species transport processes are rate controlling. The extent to which assumption is valid must rest on experimental data obtained under conditions in which the diffusional and equilibrium conditions have been precisely determined. In order to determine when condensation occurs, the following procedure is followed in the present study. For convenience a deposition index, DI, is defined as:

\[ DI = \frac{r\gamma e_3}{\chi e_3 e} \]  

(3-5)
The numerical value of DI is compared with the numerical value of the equilibrium constant, $K_p$, for the specific gas phase-condensed phase equilibrium. If DI is less than $K_p$, the thermodynamic implication is that a condensed phase is formed. The gas phase composition is calculated accordingly. Use of the appropriate continuity equation results in a prediction of the amount of the solid phase deposited.

In addition to this major point, several other relationships must be used to analyze the pack cementation process. These equations are discussed in the following paragraphs.

The ideal gas law needed to calculate the systems pressure is presented below in equation 3-6:

$$P = \frac{P_R T}{Mw}$$  \hspace{1cm} (3-6)

Another set of constraints which must be satisfied concerns the conservation of the elements. Equations are given below for the specific chemical system at hand.

$$2 \frac{M_N}{M_{H_2}} \gamma_{H_2} + \frac{M_H}{M_{HCl}} \gamma_{HCl} + \frac{M_N}{M_{H_3SiC_3}} \gamma_{H_3SiC_3} = 0$$  \hspace{1cm} (3-7)

$$3 \frac{M_{Cl}}{M_{H_3SiC_3}} \gamma_{H_3SiC_3} + \frac{M_{Cl}}{M_{HCl}} \gamma_{HCl} = 0$$  \hspace{1cm} (3-8)

$$\frac{M_{Si}}{M_{H_3SiC_3}} \gamma_{H_3SiC_3} + \gamma_{Si} = 0$$  \hspace{1cm} (3-9)
The final equation used in the mathematical description of this pack cementation problem satisfies the requirement that the sum of the mass fractions in the gas phase must equal unity. This relation is mathematically represented below:

$$\sum_{i=1}^{n} \omega_i = 1$$  \hspace{1cm} (3-10)

**Finite Difference Equations**

The initial step in the solution to the problem for this thesis concerns the representation of the partial differential equations and the accompanying boundary conditions as numerical relations. In the method selected, the derivative terms in the partial differential equations are replaced by finite difference ratios. Detailed discussions of this technique to solve differential equations are presented by Mickley et al.\textsuperscript{70}

The following is a brief summary of the approach used here.

Finite difference ratios are easily derived from a Taylor's series. As an example, the time derivative of temperature, \( \frac{\partial T}{\partial t} \), where temperature is both a function of space and time can be considered. A Taylor's series expansion of temperature at a fixed point with time as a variable is given below:

$$T(r, t + \Delta t) = T(r, t) + \Delta t \frac{\partial T}{\partial t} + \frac{\Delta t^2}{2} \frac{\partial^2 T}{\partial t^2} + \frac{\Delta t^3}{6} \frac{\partial^3 T}{\partial t^3} + \cdots \hspace{1cm} (3-11)$$

If time increments are sufficiently small, terms in \( \Delta t \) of second order of higher may be neglected. Thus the derivative of temperature with respect
to time may be approximated as:

$$T(r, t + \Delta t) = T(r, t) + \Delta t \frac{d^nT}{dr^n}$$  \hspace{1cm} (3-12)

This equation is described as "forward marching" in time. For partial derivatives of temperature with respect to the position variable \(r\), third order terms of \(\Delta r\) are neglected and two series approximations combined to give:

$$\frac{\partial T}{\partial r} = \frac{T(r+\Delta r, t) - T(r-\Delta r, t)}{2\Delta r}$$  \hspace{1cm} (3-13)

For second derivatives with respect to \(r\), suitable manipulation of the two series yields:

$$\frac{\partial^2 T}{\partial r^2} = \frac{T(r+\Delta r, t) - 2T(r, t) + T(r-\Delta r, t)}{\Delta r^2}$$  \hspace{1cm} (3-14)

Equations 3-13 and 3-14 are described as "centered" difference relations. In some cases, the space variable increments may not be equal. To obtain a finite difference relation, two series equations with different incremental distances are utilized to give:

$$\frac{\partial T}{\partial r} = \frac{\Delta T}{\Delta s} \left( T(r + \Delta s, t) - T(r, t) \right) + \frac{\Delta T}{\Delta \Delta s} \left( T(r, t) - T(r - \Delta \Delta s, t) \right)$$  \hspace{1cm} (3-15)

Similar manipulations of the Taylor's series expansions will yield a finite difference equation for the second derivative of temperature with respect
to the space variable where the incremental space variables are not identical.

The choice of a "forward marching" difference equation for the time derivative and a "centered" difference equation for the space derivatives is typical for the solution of initial value problems. In this case, values for all variables are known at the initial time. Values at the next time may be calculated by the algebraic solution of the suitable finite temperature at time \( t + \Delta t \), as for example the equation for transient heat conduction with constant properties:

\[
T(r, t + \Delta t) = T(r, t) + \frac{\Delta t}{\rho \varepsilon p} \left( \frac{T(r, \Omega t) - 2T(r, t) + T(r, 2 \Omega t)}{\Delta r^2} \right) \tag{3-16}
\]

Other, more accurate difference equations may be derived from alternate forms of the Taylor's series expansion. For example, the time derivative may be based on \( \Delta t^2 \), or higher terms may be included. However, these equations require an iterative scheme for solution. As a result, these alternatives will use greater amounts of computer time for solution for the same increment size. In any finite difference representation of a differential equation, the accuracy of the solution will be determined by the size of the increments of the numerical solution if both stable and convergent. These two basic criteria are discussed further below.

**Stability and Convergence**

If there is an exact solution for a given partial differential equation, there is an exact solution for any given finite difference equation used to represent this partial differential equation. Any difference
between these two solutions is known as the truncation error. If the exact solution to the finite difference equation approaches the solution to the partial differential equation in the limit as the incremental variable approaches to zero, the finite difference equation is said to be convergent.\textsuperscript{71}

In a practical solution of a given problem utilizing finite difference equations, only a finite number of significant figures can be carried in the computations. The difference between the exact solution of the finite difference equations and this practical solution is known as the numerical error. Generally, these errors are predominantly errors of round-off. A practical solution to a difference equation in which the numerical error does not increase as the solution progresses is said to be stable.\textsuperscript{71} Unless a proposed numerical solution is both stable and convergent, or unless the instability is predictable, the accuracy of the results is unknown. Several tests have been published which may be used to determine the stability and convergence of the special class of numerical schemes which represent linear partial differential equations with constant coefficients.\textsuperscript{71} For the transient heat conduction equation with constant properties, stability is insured if a modulus, defined as $\alpha \frac{\Delta t}{\Delta x^2}$, is less than 0.5. If stability is assured, the solution will also be convergent and the accuracy will only be a function of the increment sizes chosen.\textsuperscript{71}

In such cases where variable properties or nonlinear equations are involved, the modulus $\alpha \frac{\Delta t}{\Delta x^2}$ cannot be used to predict stability and convergence. However, this concept may serve as a guide to test a proposed solution. If a solution exhibits oscillation or unreasonable physical results, the modulus can be changed and the new results studied. Results
Boundary and Initial Conditions

For the solution to the problem of pack cementation, conditions at three interfaces must be specified. In the following paragraphs, boundary conditions for the shell-furnace interface and the center of the core are presented first. These discussions are followed with derivations for the relations which apply at the core-porous medium interfaces. Relationships for the second porous medium interface will be similar and will not be given here.

At the interface between the surface of the shell and furnace environment, only heat is transferred across the boundary, so only energy related conditions are required. For this boundary, the shell surface temperature is assumed to be known as a function of time. Determination of these values is readily done experimentally. A Hermite interpolation polynomial is used to generate additional values between postulated experimental data points. To improve the accuracy of the numerical solution in the vicinity of the surface, a special calculation for the temperature at the station just inside the shell surface is used. This technique ensures that the heat flux predicted by the finite difference solution at this interior station is consistent with the implied heat flux resulting from an experimental surface temperature. The development of this equation is given in Appendix VI. This procedure has been used in other work.

Assuming symmetry, the heat flux at the center of the silicon core must be zero. The value for the temperature at this location is assumed to be equal to the temperature at the station nearest the center. As with the surface of the shell and the furnace, only energy related boundary
conditions apply at this interface.

At the interface between the porous medium and the core material, or between the porous medium and the shell, unusual boundary conditions are required. In this numerical solution, an interface is treated as an increment rather than a surface of zero thickness. As a result, volume element terms must be included in the derivation of the equations which describe the boundary conditions. For the mass boundary condition between the porous medium and the core, a storage term and a generation term are required. The equation representing these considerations is presented below. A similar equation is needed for the other interface.

\[
\frac{\partial}{\partial t} \left( \pi R(l_{\text{cw}1}) \rho_0 \left( \frac{\Delta r}{r_0} \right) c_i \right) + \frac{\partial}{\partial r} \left( \pi R(l_{\text{cw}1}) \rho_0 \left( \frac{\Delta r}{r_0} \right) \frac{c_i}{r} \right) = \pi R(l_{\text{cw}1}) \rho_0 \left( \frac{\Delta r}{r_0} \right) \frac{\partial c_i}{\partial r} + \pi R(l_{\text{cw}1}) \rho_0 \left( \frac{\Delta r}{r_0} \right) \frac{\partial c_i}{\partial r}
\]

(3-17)

where

\[\bar{\pi}_i(l_{\text{cw}1})\]

is the mass flux of species \( i \) as evaluated at the station in the porous medium nearest the interface

\[\rho_0\]

is the cylinder length

\[\Delta r\]

is the incremental distance between the core material interface and the first node point in the porous material

\[\Delta r_0\]

is the initial value of \( \Delta r \).

Because chemical reactions at the interfaces may either deplete or deposit solid silicon, the incremental distance between the core interface and the first node point in the porous medium will vary with time. An equation has been developed to calculate the change in thickness and equation of continuity for this increment. Details of these derivations are given in Appendix VII. Results are given below for the thickness of the increment between the porous medium and the core. A similar equation is used
for the increment between the porous medium and the shell.

\[ \Delta r_m(t+\Delta t) = \Delta r_m(t) - \frac{\Delta t}{\rho} \left( \Delta r_m(t) \frac{\partial \rho}{\partial t} + \rho \frac{\partial \Delta r_m(t)}{\partial t} \right) \]  

\[ \Delta r_c(t+\Delta t) = \Delta r_c(t) - \frac{\Delta t}{\rho_c} \left( \Delta r_c(t) \frac{\partial \rho_c}{\partial t} + \rho_c \frac{\partial \Delta r_c(t)}{\partial t} \right) \]  

where \( \Delta r_m \) is the initial value for \( \Delta r_m \)  
\( \Delta r_c \) is the initial value for \( \Delta r_c \)  

Because the boundary condition is most conveniently used in terms of concentration rather than as a derivative, equation 3-17 is used in the definition of a finite difference time derivative to calculate the value. 

This resulting relation is presented below in equation 3-19. As mentioned above, large differences in the derivatives between any two successive times are not expected to occur. However, at early times when reaction does occur, substantial inaccuracies in derivative calculations can be created because of the nature of the numerical solution. To minimize the effect, time derivatives of the species calculations are averaged.
As before, a similar equation is used for the other interface and is presented in Appendix VIII.

In addition to equation 3-17, two other constraints must be satisfied simultaneously at the boundaries between the solid layers. Equilibrium is assumed to exist at all times and the sum of the mass fractions must equal unity.

When reaction does not occur, the velocity at the wall is equal to zero. When reaction does occur, the velocity is calculated as follows:

$$v_e = \frac{\dot{\gamma} \bar{\tilde{n}}^e}{\rho} \quad (3-20)$$

The calculation for the energy related boundary conditions at the two solid interfaces are performed in a manner similar to the method described above for mass considerations. This equation is presented below:

$$T(Lcw, t + \Delta t) = \left( T(Lcw, t) + \Delta t \left( \frac{\partial T(Lcw)}{\partial Lcw} \right) \left( -\frac{\dot{\gamma} \bar{\tilde{n}}^e}{\rho} \right) \right)$$

$$\left( Lcwpi, t + \Delta t \right) + k(Lcwpi, t + \Delta t) T(Lcwpi, t + \Delta t)$$

$$\frac{\partial T}{\partial \rho} + \frac{\partial T}{\partial \rho} k(Lcwmi, t + \Delta t) T(Lcwmi, t + \Delta t) / \Delta \rho = \text{ARGETA}$$

$$\frac{\partial \tilde{T}}{\partial \tilde{T}} = \text{ARGHBO} \frac{\partial \tilde{T}}{\partial \tilde{T}} + \text{ARGDRT} \frac{\partial \tilde{T}}{\partial \tilde{T}} / \text{ERC}$$

As before, a similar equation is used for the other interface and is presented in Appendix VIII.
The equations for the other interface and the arguments are shown in Appendix IX.

Because the depletion of solid silicon at the interface between the core and the porous medium will create a gap, the thermal conductivity and the diffusivity for the increment between the interface and the first node point in the porous medium must be modified to include the contribution due to the gap. The approach used in this thesis is to calculate an overall diffusivity and an overall thermal conductivity in a similar manner as an overall heat transfer coefficient is calculated for heat conduction through composite materials. The development of these equations is given in Appendix X. Results are given below in equations 3-22 and 3-23.

\[
\bar{D}_\text{im} = \bar{D}_\text{im}^c \left( \frac{\ln \left( \frac{R_e \cdot \bar{D}_\text{im}^c}{R_e \cdot \bar{D}_\text{im} \left( \text{ccw} \right)} \right)}{\bar{D}_\text{im} \left( \text{ccw} \right)} + \ln \left( \frac{R_e \cdot \bar{D}_\text{im} \left( \text{ccw} \right)}{R_e} \right) \right)^{-1} 
\]

\[
\bar{k}_e = \frac{\bar{k}_e \left( \text{ccwp} \right)}{\bar{k}_e \left( \text{ccw} \right)} \left( \frac{\ln \left( \frac{R_e \cdot \bar{k}_e \left( \text{ccwp} \right)}{R_e \cdot \bar{k}_e \left( \text{ccw} \right)} \right)}{\bar{k}_e \left( \text{ccw} \right)} + \ln \left( \frac{R_e \cdot \bar{k}_e \left( \text{ccw} \right)}{R_e} \right) \right)^{-1} 
\]

where \( \bar{D}_\text{im} \) is the overall diffusivity for the composite.

where \( \bar{k}_e \) is the overall thermal conductivity for the composite.
Computer Program

The computer program for the numerical solution of the equations describing the pack cementation problem is divided into several elements. Element 1 reads input data and establishes initial conditions such as temperature and concentration profiles. The remaining elements of the program constitute a primary loop with time as the incremental stepping variable. Element 2 calculates the temperature profile in the core material. Element 3 calculates the temperature, concentration, and velocity profiles for the porous media. Element 4 calculates the boundary conditions for the interface between the core material and the porous media. Element 5 calculates the temperature profile in the shell material, and Element 6 calculates the boundary conditions for the interface between the porous media and the shell material. The remaining portion of the program calculates the pressure in the porous medium, the amount of core depleted, and the amount of coating deposited. Also calculated are normalized values of concentration and distance for comparison with the Arnold Solution as discussed later. Finally, old values of certain variables are established and output data generated.

With knowledge of all variables at the initial time, the program calculates values for all variables at the next time by starting at the center of the core and progressing outward to the surface. At the surface, the program requires the temperature to be input from experimental data or from a proposed profile. In actual practice, the pack cementation device would be placed in a furnace and the surface temperature measured as discrete points in time. The program receives these discrete points as input data and interpolates additional values as may be required. After values
for all variables have been calculated, the computer returns to Element 2 and begins computation again for a new time. A copy of the software is included as Appendix XI. For convenience, values for the diffusivity are calculated in a sub-routine to the main program. Software for this procedure is also included in Appendix XI.

In order to increase the usefulness of the results of the present study, the computer program has been written in a general way to accommodate practical dimensions and other actual physical data for a system composed of three gas phase species and a single coating species. For example, thermodynamic properties of chemical components may be easily changed as long as these data fit the polynomial equations used in the computer program. In addition, the program will process problems with radii greater than exact multiples of the selected stepping increment.
CHAPTER IV

IMPLEMENTATION OF THE NUMERICAL SOLUTION AND RESULTS

In Chapter III, the specific transport equations describing the deposition of solid silicon on an alumina substrate during pack cementation were presented. Also proposed was a digital computer program to obtain the numerical solution to the transport equations. In this chapter, the results of the numerical solution are presented. This discussion is preceded by a description of the relations for the various component and mixture physical and transport properties. Even though considerable time was spent reviewing recent developments in this area, relationships for the gas mixture properties and the individual species properties were selected to some extent on a basis of convenience in the numerical solution as increased accuracy in this area will not significantly improve the results of the primary goal of analysis of the pack cementation problem. Also presented is a discussion of the transport and thermodynamic properties of the solid materials. Other input data are shown later.

Thermodynamic and Transport Properties of the Gas Species

The equations used to calculate the heat capacity and enthalpy of the gas mixture are given below:

\[ \hat{C}_p = \frac{\sum_i \hat{C}_p^i}{M_w} \]  \hspace{1cm} (4-1)
The generalized equation for the heat capacity of the individual gas phase species is given below in units of Kcal/mole °K. This equation represents a regression analysis of experimental data as a function of temperature in degrees Kelvin over the range 273 to 1500° K.

\[ \bar{C}_p = A + B T + C T^2 + D T^3 + \frac{E}{T^2} \]  

Values for the constants in equation 4-3 are reported in Appendix XII for each of the species. Also included are values for the standard heat of formation at 298.16° K, in units of Kcal/mole, and the reference to the values for the heat capacity constants. The standard heats of formation used are those reported in reference 73.

The thermodynamic value for the equilibrium constant for the reaction proposed above is obtained from data presented in reference 73. These data have been fitted to an equation as a function of temperature as shown below.

\[ \log K_p = A + \frac{B}{T} \]  

Values for the constants in equation 4-4 are presented in Appendix XII.

The equation used to calculate the viscosity of the gas mixture is based on an extension of the Chapman-Enskog theory by Curtis and Hirschfelder and further modified by Wilke. This equation is given below:
\[
\mu = \sum_{i=1}^{n} \left( \sum_{j=1}^{n} \phi_{ij} \right) \quad (4-5a)
\]

where
\[
\phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{m_i}{m_j} \right)^{3/2} \left( 1 + \frac{\mu_i}{\mu_j} \right)^{3/2} \left( \frac{m_j}{m_i} \right)^{1/4} \quad (4-5b)
\]

and \(\mu_i\) is the species viscosity.

The equation used to calculate the viscosity of the individual gas species is given below in equation 4-6. This relation has been previously reported in Bird et al.\textsuperscript{29} for both monatomic and polyatomic gases.

\[
\mu_i = 2.6933 \times 10^{-5} \frac{\sqrt{M_i T}}{\sigma_i \Omega_{\mu_i}} \quad (4-6)
\]

where \(\sigma_i\) is the collision diameter and \(\Omega_{\mu_i}\) is the collision integral for viscosity.

The collision integral has been tabulated as a function of reduced temperature by Hirschfelder et al.\textsuperscript{76} Values for this integral in the reduced temperature range 1.4 to 30 have been fit to the following equation:\textsuperscript{77}

\[
\Omega_{\mu_i} = \left( 0.697 \left( 1.0 + 0.323 \ln \left( \frac{M_i T}{\sigma_i^2} \right) \right) \right)^{-1} \quad (4-7a)
\]

where
\[
T_r = \left( \frac{E}{k_i} \right)^{-1} \quad (4-7b)
\]

and \(\left( \frac{E}{k_i} \right)^{-1}\) is a constant unique for each species.

Several techniques have been proposed to calculate \(\sigma_i\) and \(\left( \frac{E}{k_i} \right)^{-1}\) and are
reviewed in reference 29 and 78. The method used in this work is given below:

\[
\left( \frac{\sigma}{k} \right)_i = 0.77 T_{ci} \tag{4-8a}
\]

and

\[
\sigma_i = 0.841 \, \tilde{V}_{ci} \tag{4-8b}
\]

where \( T_{ci} \) is the critical temperature for species \( i \)

\( \tilde{V}_{ci} \) is the critical molar volume for species \( i \).

Values for \( T_{ci} \) and \( \tilde{V}_{ci} \) are given in Appendix XII.

The equation for the gas mixture thermal conductivity is based on

a modification by Bird et al.,\textsuperscript{29} of an equation first proposed by Mason and Saxena.\textsuperscript{78} This equation is given below:

\[
k_f = \sum_{i=1}^{Z} \left( \frac{k_i}{\bar{V}_i} \right) \tag{4-9}
\]

where \( k_i \) is the species thermal conductivity.

Equations to calculate the thermal conductivity of monatomic gases

have been proposed which are similar to those used for the viscosity.\textsuperscript{29,76} Extension of these equations for use with polyatomic gases has not been as successful.\textsuperscript{29} A model used in this work was proposed by Mason and Monchick and is presented below.\textsuperscript{79}

\[
k_i = (\tilde{c}_{p_{ci}} \times 1.25 R) \mu_i \tag{4-10}
\]
A considerable number of papers have been published on ways to calculate the binary diffusion coefficients of gas species combinations. Values for this property are needed for calculation of the effective diffusion coefficient discussed in the previous chapter. The method used in this work is that reported by Hirschfelder, Curtis, and Bird and is given below in equation 4-11a. Even though this method is one of the earlier works, most of the newer methods do not give significantly better accuracy for a majority of combinations. In addition, this method is consistent with those used to calculate $\mu$ and $k_i$. A comparison of the several methods is given in reference 88 along with experimental data.

$$D_{ij} = 1.8583 \left(10^{-3}\right) \frac{\sqrt{M_i T_j^3}}{P_{ij} D_{ij}}$$  (4-11a)

where

$$\bar{M} = \left(\frac{1}{M_i} + \frac{1}{M_j}\right)$$  (4-11b)

and $\sigma_{ij}$ is the collision diameter for the pair $ij$ and $\Omega_{ij}$ is the collision integral for the pair $ij$.

The collision integral for diffusion is calculated by a similar method to that for viscosity based on specific table values for diffusion reported by Hirschfelder et al. The equation for the diffusion collision integral is given below for the reduced temperature in the range 1.4 to 30.

$$\Omega_{ij} = \left(0.7549 \left(1.0 + 0.3476 \ln T_r\right)\right)^{-1/3}$$  (4-12)

For these calculations, $\frac{\Omega_{ij}^*}{\Omega_{ij}}$ and $\sigma_{ij}$ are calculated as suggested in reference
29 as follows:

\[
\left( \frac{E}{k} \right)_{ij} = \left( \left( \frac{E}{k} \right)_{i} \right)^{\frac{1}{2}}
\]  \hspace{1cm} (4-13)

\[
\sigma_{ij} = \frac{1}{2} \sigma_i \sigma_j
\]  \hspace{1cm} (4-14)

The value for the Knudsen diffusivity for the gas phase species is calculated from an equation reported by Youngquist.\(^{43}\) This relation may be modified to include the results of Smith and coworkers to calculate a value for the pore radius.\(^{45}\)

\[
D_{i\mathcal{P}} = \frac{2}{3} \bar{R} \left( \frac{8kT}{\pi M_i} \right)^{\frac{1}{2}} \left( \frac{2 - a_i}{\bar{a}_i} \right)
\]  \hspace{1cm} (4-15)

where \( \bar{R} \) is the average pore radius.

As mentioned in Chapter II, \( a_i \) is probably equal to unity so the last term in equation 4-15 is also equal to unity.

**Thermodynamic and Transport Properties of the Solid**

The equation for the heat capacity of solid silicon is given below in equation 4-16. This relation is reported to represent experimental values in units of cal/mole °K for the temperature range 273.16° to 1173°K.\(^{89}\)

\[
\tilde{C}_p = 5.74 + 0.614 (10^{-3}) T - 1.01 (10^{-5}) / T^2
\]  \hspace{1cm} (4-16)

The equation for the heat capacity of alumina, which comprises both the porous media substrate and the outer shell, is given in equation 4-17.
This relation is reported to represent experimental values in units of BTU/lb°-F for temperature in degrees Fahrenheit over the range 325° F to 2930° F. Similar values were reported in three other independent observations and compiled in reference 91.

\[ \dot{C}_p = 0.239 + 0.0402 \left( \theta - \theta_0 \right) \]  

(4-17)

Jakob has shown that the thermal conductivity of non-metallic crystalline materials is inversely proportional to the temperature and would fit an equation of the following form: \[ k_s = A \left( \frac{B}{T} \right) \]  

(4-18)

Values of the constants for the solid materials used in this work are presented in Appendix XIII.

**Further Modification of the Momentum Equation**

Early runs with the computer program resulted in unstable solutions. Even though the stability moduli for the heat and mass transfer equations were maintained at very low values, the instability persisted. Finally, the problem was identified in the use of the momentum equation. Even though the momentum equation, given as equation 2-1, does not contain a second derivative or a time derivative term, values for the pressure are calculated from values of the mixture density which is calculated from the continuity equation. Thus, a third stability modulus must be considered. The time increment to produce a stable solution from the momentum equation based on the third stability modulus was estimated to be less than 10^{-4} seconds. In comparison, the value for the increment which will satisfy the other moduli
is only less than $10^{-2}$ seconds. As a result, the pressure can be assumed to be independent of position. If this assumption is used, the momentum equation is not needed. In addition, this assumption implies that a change in pressure at any point, as a result of other transport or reaction phenomena, very quickly changes the pressure throughout the porous media. This assumption changes the initial algorithm. The velocity at any point is now calculated as follows:

$$\vec{v}_e = \frac{\sum_{\alpha} n^e \vec{a}}{\rho} \quad (4-19)$$

The density is calculated from the ideal gas law. The pressure is allowed to vary with time, but its value is the same at all node points at any instant. Values for the instantaneous pressure are calculated from the equation below. This equation is based on the assumption that the total amount of elemental hydrogen throughout the entire porous media does not change.

$$\bar{P} = \frac{X}{L_0} \frac{R_0}{\varepsilon} \left( \int_{R_0}^{R_0^P} \frac{F_{MW} \left( \frac{\omega_{\text{HI}}}{{\text{MW}1}} + \frac{\omega_{\text{H2}}}{{\text{MW}2}} + \frac{\omega_{\text{H3}}}{\text{MW3}} \right)}{\varepsilon} dR \right) \quad (4-20)$$

where \( \frac{X}{L_0} \) is a constant.

The derivation of equation 4-20 is given in Appendix XIV. In order to estimate the reliability of the assumption that the gradient of pressure is small, the gradient is calculated in the computer solution from the
momentum equation. Results of the calculation, as well as other results of the numerical solution are discussed in a following section.

**Input Data**

Because many iterations are required to reach a solution to the problem at hand, considerable computer time is used for each run. In order to conserve computer time, the decision was made after observing results from early runs to set the initial temperature of the system at 300° F, rather than ambient, as would occur in actual practice. In addition, the surface temperature of the shell was input at 1000° F for all time. Input values which determine the properties of the shell were set so that the properties were also held constant. Constants which determine the thermal conductivity of the porous substrate were arbitrarily multiplied by ten. These constraints allowed the temperature of the porous medium to rise faster than would normally occur, thus causing interface reaction at an earlier time. Since the performance of the shell heat transfer relations were shown to be successful in another work,\(^7\) these constraints were not thought to compromise the study of important phenomena of diffusion and reaction in the porous medium.

One other constraint has been placed on the solutions presented herein. In actual practice for pack cementation, only hydrogen chloride would probably be injected into the pack at time zero. This case cannot be studied in this work due to limitations of the computer program. Values for all species must be greater than zero or indefinite numbers occur. In addition, early runs using small values of \(H_2\) and \(HSiCl_3\) resulted in dramatic changes in mixture molecular weight at the core interface producing an instability similar to that encountered with the continuity equation as discussed in
the previous section. To overcome this problem, excess hydrogen is used for all runs. Initial composition and other input data are summarized in Table 1.

Table 1. Input Data

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature</td>
<td>300° F.</td>
</tr>
<tr>
<td>Base temperature</td>
<td>70° F.</td>
</tr>
<tr>
<td>Surface temperature</td>
<td>1000° F.</td>
</tr>
<tr>
<td>Total pack radius</td>
<td>12.60 in.</td>
</tr>
<tr>
<td>Core radius</td>
<td>4.75 in.</td>
</tr>
<tr>
<td>Porous medium radius</td>
<td>10.70 in.</td>
</tr>
<tr>
<td>Pore radius</td>
<td>Variable</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>90.00μ</td>
</tr>
<tr>
<td>Space increment</td>
<td>0.50 in.</td>
</tr>
<tr>
<td>Emissivity</td>
<td>0.50</td>
</tr>
<tr>
<td>Initial porosity</td>
<td>0.51</td>
</tr>
<tr>
<td>Time increment</td>
<td>Variable</td>
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Results

The primary objective of this work is to show that the relations proposed in previous chapters do indeed provide a solution to the problem of pack cementation. Since no experiments were performed with an actual system, no true conclusion as to the results of the solution can be presented. Considerable experimental results have already been presented for the heat transfer and binary diffusion aspects of the porous material selected. In this light, the important considerations of this thesis thus become the performance of the relations regarding multicomponent diffusion and Knudsen diffusion. In the following paragraphs, results are presented which show that a solution to the multicomponent diffusion problem does exist. These results are then compared to the special case of equal binary diffusivity. And finally, results are presented which show the effects of Knudsen diffusion on pack cementation.

In the following Tables 2 through 5, results of the solution for the multicomponent case are presented after 100 seconds, 1,000 seconds, 1,900 seconds, and 2,000 seconds in the furnace. The pore radius specified is 90,000 Å and is not sufficient to produce a significant contribution due to Knudsen diffusion. While the program ran for 3,600 seconds, which was designated as the end of the run, data after 1,900 seconds are not valid. At approximately 1,920 seconds, temperatures and concentrations in the porous medium were sufficient to cause deposition of silicon in the pores. Apparently this phenomena could not be adequately accounted for in the algorithm proposed for the step size used, and the solution became unstable. Attempts to promote a more stable solution by reduction of the diffusion modulus were unsuccessful. More will be said about this problem in the next section.
Table 2. Results of the Solution for the Multicomponent Case After 100 Seconds

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### Table 3. Results of the Solution for the Multicomponent Case After 1000 Seconds

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In order to show that the multicomponent solution is successful, concentration profiles are presented in Figure 2 for the species HCl at several times. The results are considered stable because the profiles do not oscillate. Profiles for the other species are not plotted because they do not exhibit significant change. As was previously mentioned, concentrations for these species were set in excess initially.

In many engineering applications, the use of a single binary diffusivity in a multicomponent diffusion problem is expedient, provided errors are small. For this reason, a solution was obtained for the hypothetical case where the binary diffusivities for each specie pair were set equal to the value for $D_{1,2}$ and any effects due to Knudsen diffusion were not allowed through an option in the software. Results of this solution are presented in Tables 6 through 9 at 100 seconds, 1,000 seconds, 1,900 seconds and 2,000 seconds. Concentration profiles of the species HCl were nearly identical to those for the multicomponent case and thus are not plotted. Comparison of the effective diffusivities for the multicomponent and the equal binary diffusion cases is presented in Figure 3 at 100 seconds and in Figure 4 at 1,900 seconds. As can be easily seen, there is significant difference between the values for the multicomponent case and those for the special case. As another comparison, the amount of coating deposited is plotted for each case as a function of time in Figure 5. There is some difference in the coating deposition rates.

In order to determine the effect of Knudsen diffusion on the algorithm several runs were made with different pore radii for the multicomponent case and the case where all binary diffusivities are equal to $D_{1,2}$. As in discussions above, results are presented below in terms of
Figure 2. Mole Fraction of HCl versus Station at Times Shown for the Multicomponent Case.
Table 6. Results of the Solution for the Case Where All Binary Diffusivities are Equal with No Knudsen Diffusion After 100 Seconds

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Table 6 (Continued). Results of the Solution for the Case Where All Binary Diffusivities are Equal with No Knudsen Diffusion After 100 Seconds

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Table 8 (Continued). Results of the Solution for the Case Where All Binary Diffusivities are Equal with No Knudsen Diffusion After 1900 Seconds

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Table 9. Results of the Solution for the Case Where All Binary Diffusivities are Equal with No Knudsen Diffusion After 2000 Seconds
Table 9 (Continued) Results of the Solution for the Case Where All Binary Diffusivities are Equal with No Knudsen Diffusion After 2000 Seconds

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Figure 3. Comparison of Diffusivity for the Multicomponent Case and the Case of Equal Binary Diffusivities After 300 Seconds.
Figure 4. Diffusivity versus Station After 1,900 Seconds.
Figure 5. Comparison of Coating Deposited versus Time for Diffusion Cases with No Knudsen Diffusion.
concentration profiles, diffusivity, and coating deposition. The mole fraction of HCl is plotted in Figure 6 versus station for several times and for several pore radii for the multicomponent case. Results after 100 seconds could not be distinguished for any pore radii studied. After 300 seconds, runs with pore radii less than 50,000 Å produced oscillations in the HCl profiles indicating instability. Diffusion moduli were also consistently greater than 0.5 further indicating instability. More will be said about this indicator in the next section. After 1,900 seconds results are only available for pore radii equal to 90,000 Å and 50,000 Å. Other runs with smaller pore radii were so unstable that indefinite numbers had already been produced in the calculations, thus stopping the run through an error exit on the computer. Figure 7 is a plot of similar results for the special case for equal binary diffusivities. As with results for the multicomponent case, the HCl profile is very similar after 100 seconds for all pore radii studied. After 300 seconds, results for a pore radius of 30.7 Å are not valid. Much smaller pore radii can be studied for the special case of equal binary diffusivity because the multicomponent effect does not magnify the problem.

In order to show the Knudsen diffusion effect on diffusivity, effective diffusivities are plotted in Figure 8 for the different pore radii at 1,900 seconds for the special case of equal binary diffusivity. Because all binary diffusivities are equal to $D_{1,2}$, the difference in the effective diffusivity values is a result of the Knudsen component.

The effect of pore radius on the amount of coating deposited versus time is shown for each case and for each different pore radius in Figures 9 and 10. Broken line curves represent results from unstable
Figure 6. Mole Fraction of HCl versus Station for Times and Pore Radii Shown for the Multicomponent Case.
Figure 7. Mole Fraction of HCl versus Station for Times and Pore Radii Shown for the Equal Binary Diffusivities Case.
Figure 8. Diffusivity versus Station for Pore Radii

Shown at 1,900 Seconds.
Figure 9. Coating Thickness versus Time for Pore Radii Shown for the Multicomponent Case.
Figure 10. Coating Thickness versus Time for Pore Radii Shown for the Equal Binary Diffusivities Case.
Accuracy of Results

The accuracy of results to the solutions discussed above is a function of time spacing, distance step size, and stability. As was previously mentioned, runs with smaller step sizes will provide more accurate solutions provided stability is maintained. Due to lack of computer time, results with smaller step sizes were not obtained. Stability was checked on each run by monitoring stability moduli for both heat and mass transfer as was discussed in Chapter III. Should any modulus exceed 0.5, the value of the modulus, the iteration, and the station were printed as a warning.

One good method to test accuracy of the numerical solutions is to compare results with those from an analytical solution. Unfortunately, such solutions are not available for this pack cementation problem. However, for very early times, the Arnold solution reported in Bird et al.\(^\text{29}\) can be assumed to approximate results expected from the numerical solutions. In Figure 11, results of Arnold are compared to the multicomponent case and the special case of equal binary diffusivities. If the assumptions are made that at 1900 seconds the multicomponent solution has reached steady state and that the bulk flow term is negligible, a simple analytical solution results. The product of \(\rho_d \text{Vol}\) was fitted to a curve of the form \(a/r^2\) for this solution. Results of the steady state solution and those for the multicomponent case at 1900 seconds are shown in Figure 12.

In the macroscopic sense a test for accuracy is that the product of the radius and coating thickness deposited should be little less than the product of the core radius and the thickness of core material depleted. Results at 1900 seconds for the multicomponent case are \(5.1606 \times 10^{-3}\)
Figure 11. Arnold Solution versus the Multicomponent Solution at Early Times.
Figure 12. Steady State Solution versus the Multicomponent Solution at 1900 Seconds.
mil-inches and $5.4102(10^{-3})$ mil-inches respectively.

Perhaps the most significant measure of the accuracy of results from solutions presented herein concern the values listed in various tables under the heading "TEST." This parameter represents the ratio of the molar concentration gradient as calculated from the Stephan-Maxwell equation to the same gradient as calculated from the numerical solution. Since the Stephan-Maxwell equation is exact, the fact that values for the "TEST" parameters are very close to unity is indicative that the numerical solution is both reasonable and accurate.
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The most important conclusion reached from the work discussed herein is that the model chosen for multicomponent diffusion will provide a successful solution for initial value problems in multicomponent mass transfer. The second important conclusion is that the assumption of equal binary diffusivities will provide a reasonable solution, thus greatly simplifying calculations. And finally, Knudsen diffusion can be a significant contribution to mass transfer in porous medium.

Several areas of further work and development in this area are evident from the results of this thesis. A nested iterative scheme to better calculate the molar concentrations in the porous media when deposition occurs should be developed. Laboratory experiments should be conducted to provide actual data for comparison with the model. And finally, experimental work to better relate porous media properties to transport properties should be conducted.
APPENDIX I

CONTINUITY EQUATION FOR POROUS MATERIAL

Consider a small volume of porous material, $V_e$, composed of substrate particles covered with a thin coating and a gas-filled void. Let the mass of the substrate particle be defined as:

$$m_p = \rho_p V_p$$  \hspace{1cm} (A1-1)

where $V_p$ is the volume of porous media occupied by the substrate particles and $\rho_p$ is the density of the substrate.

and the mass of the coating be defined as:

$$m_c = \rho_c (V_p - V_p')$$  \hspace{1cm} (A1-2)

where $\rho_c$ is the density of the substrate coating and $V_p$ is the volume of the porous media occupied by the solid particles.

The density of the solid composite may be calculated as follows:

$$\rho_P = \frac{m_p + m_c}{V_p}$$  \hspace{1cm} (A1-3)

$$= \frac{\rho_p V_p + \rho_c (V_p - V_p')}{V_p}$$  \hspace{1cm} (A1-4)

$$= \rho_c + \frac{V_p'}{V_p} (\rho_p - \rho_c)$$  \hspace{1cm} (A1-5)

If the porosities of the media are defined as:
\[ \varepsilon_P^e = \frac{V_P^e}{V_t^e} \]  
(A1-6)

and

\[ \varepsilon_P = \frac{V_P}{V} \]  
(A1-7)

where \( V_t^e \) is the total volume of porous media.

Then

\[ \frac{V_P^e}{V_P} = \frac{\varepsilon_P^e}{\varepsilon_P} \]  
(A1-8)

And \( P \) becomes:

\[ P = \rho_c + (\rho_P - \rho_c) \frac{\varepsilon_P^e}{\varepsilon_P} \]  
(A1-9)

Now the continuity equation for a two-phase mixture of solid composite and gas is written as follows:

\[ \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \mathbf{n} = 0 \]  
(A1-10)

where \( \rho \) is the density of the porous medium,

\( \mathbf{n} \) is the mass flux in the porous medium.

But \( \rho \) is \( \varepsilon \rho_c + \varepsilon \rho \), where \( \varepsilon \) is the gas filled volume and \( \rho \) is the density of the gas. Also \( \mathbf{n} = \mathbf{n}_c + \varepsilon \mathbf{n}_e \) where \( \mathbf{n}_e \) is the mass flux of the gas species \( i \). Assuming that the mass flux of the composite, \( \mathbf{n}_P \), is zero, the continuity equation becomes

\[ \frac{\partial \rho}{\partial t} (\varepsilon \rho_c + \varepsilon \rho) + \mathbf{v} \cdot \varepsilon \mathbf{n}_e = 0 \]  
(A1-11)

Now

\[ \varepsilon \rho_P = \varepsilon \rho_c + (\rho_P - \rho_c) \varepsilon \rho \]  
(A1-12)

For a coating with a constant density, the time derivative of \( \varepsilon \rho_P \) will be:
\[
\frac{\partial}{\partial t} (\varepsilon_p \rho_p) = \rho_e \frac{\partial \varepsilon_p}{\partial t}
\]  \hspace{1cm} (A1-13)

And the continuity equation for the porous medium becomes

\[
\frac{\partial}{\partial t} (\varepsilon_p \rho_p) + \rho_e \frac{\partial \varepsilon_p}{\partial x} + \mathbf{v} \cdot \mathbf{n} = 0
\]  \hspace{1cm} (A1-14)
APPENDIX II

BINARY DIFFUSION COEFFICIENT FOR POROUS MEDIA

Evans, Watson, and Mason have proposed a model for the binary diffusion equation in porous media which begins with a modified form of the Stefan-Maxwell equation for constant temperature and pressure.\(^{37}\) Evans et al. proposed their relation in terms of molecules rather than the customary molecular qualities. In addition, these workers have treated the solid particles of the porous medium as large molecules with a zero mole velocity. The general form of this equation is given below.

\[
\sum_{j=1}^{n} \frac{\partial \rho_{ij}^*}{\partial t} D_{ij}^e (\vec{v}_j - \vec{v}_i) = \frac{1}{n} \frac{\partial n_i^e}{\partial z} \tag{A2-1}
\]

where

- \(n_i^e\) is the number of molecules of species \(i\) for the total unit volume of solid and gas
- \(n^e\) is the total number of molecules, solid and gas, for the total unit volume
- \(D_{ij}^e\) is the effective diffusion coefficient
- \(\vec{v}_i\) is mass velocity of species \(i\)
- \(\nu\) is the number of gas and solid \(i\) species.

In this equation, effects of the porous media on the diffusion path are incorporated in the definition of the diffusion coefficient as follows:

\[
D_{ij}^{e'} = \frac{\xi}{\xi} D_{ij}^e \tag{A2-2}
\]
where $\varepsilon'$ is the porosity

$\zeta$ is the tortuosity

$D_{ij}$ is the binary diffusion coefficient.

If the molecular flux of species $i$, $\overline{\jmath}_i$, is defined as the product $n_i \overline{v}_i$, then equation A2-1 may be rearranged to give:

$$\sum_{j \neq i} \left( n_j D_{ij}^e \right) (n_i \overline{\jmath}_j - n_j \overline{\jmath}_i) = \frac{\partial \overline{n}_i}{\partial z} \quad (A2-3)$$

For two gaseous species and one solid species $p$, equation A2-3 becomes:

$$n_i \overline{\jmath}_j - n_j \overline{\jmath}_i \left. \frac{D_{ij}^e}{D_{ij}^p} \right| + n_i \overline{\jmath}_p - n_p \overline{\jmath}_i \left. \frac{D_{ip}^e}{D_{ip}^p} \right| = n_i \frac{\partial \overline{n}_i}{\partial z} \quad (A2-4)$$

Assuming that the solid species $p$ has a zero mass velocity, $\overline{\jmath}_p$ would also be equal to zero. Equation A2-4 could then be arranged to give:

$$\overline{\jmath}_i \left( 1 + \frac{n_p}{n} \frac{D_{ij}^e}{D_{ip}^p} \right) = -\frac{n_i}{n} \left. \frac{D_{ij}^e \partial \overline{n}_i}{\partial z} \right| + \frac{n_i \overline{\jmath}_i}{n} \quad (A2-5)$$

If $\overline{\jmath}_i$ is defined as follows:

$$\overline{\jmath}_i = \left( 1 + \frac{n_p}{n} \frac{D_{ij}^e}{D_{ip}^p} \right)^{-1} \quad (A2-6)$$

Then equation A2-5 may be arranged to give:

$$\overline{\jmath}_i = -D_i^e \frac{\partial \overline{n}_i}{\partial z} + \frac{n_i \partial \overline{\jmath}_i}{n} \quad (A2-7)$$
where

$$D_i^e = \frac{n'}{n} D_{ij}^e \delta_{ij}$$  \hspace{1cm} (A2-8)

and

$$n'D_{ij}^e = \left( \frac{16 \pi \varepsilon}{3 \varepsilon} \left( \frac{m}{\varepsilon RT} \right)^{\frac{1}{2}} m_{ij} Q_{ij} \right)^{-1}$$  \hspace{1cm} (A2-9)

The quantity \(n'D_{ij}^e\) is calculated from a modification of equation A2-9. For a mixture of a gas and solid, the reduced mass \(\bar{m}\) may be approximated by the mass of the gas species, \(m_i\). The collision diameter reduces to the radius of the solid particle and the collision integral becomes \(\left( 1 + \frac{\alpha_i m_i}{\bar{m}} \right)\). The term \(\alpha_i\) is the fraction of species \(i\) diffusely scattered by the solid and for most gases is approximately equal to unit. Therefore, the diffusivity for interaction between the solid and gas is given below:

$$n'D_{ij}^e = \left( \frac{16 \pi \varepsilon}{3 \varepsilon} \left( \frac{m_i}{\varepsilon RT} \right)^{\frac{1}{2}} m_{ij} Q_{ij} \left( 1 + \frac{\alpha_i m_i}{\bar{m}} \right) \right)^{-1}$$  \hspace{1cm} (A2-10)

This equation is used by Evans et al. to represent the effect of Knudsen diffusion.
APPENDIX III

COMPARISON OF VARIOUS FORMS FOR THE BINARY DIFFUSION EQUATION IN POROUS MEDIA

Evans, Watson and Mason have proposed the following equations for the binary diffusion equation in porous media.\(^{37}\)

\[
\vec{N}_i = -D_i^e \frac{\partial n_i}{\partial z} + \frac{n_i}{n} \delta_i \vec{U} \quad (A3-1)
\]

where

\[
D_i^e = \frac{n_i}{n} D_{ij}^e \delta_i \quad (A3-2)
\]

and

\[
\delta_i = \left( 1 + \frac{n_i}{n} \frac{D_{ij}^e}{D_{ij}^e} \right)^{-1} \quad (A3-3)
\]

If the mole fraction of species \(i\), \(X_i\), is defined as the ratio \(\frac{n_i}{n}\), then equation A3-1 may be rearranged to give:

\[
\vec{N}_i = -D_i^e \frac{\partial n_i}{\partial z} \frac{1}{1 - \alpha \delta_i} \quad (A3-4)
\]

where

\[
\alpha = 1 + \frac{\vec{U}}{\vec{N}_i} \quad (A3-5)
\]

Because \(n^' D_{ij}^e\) is equal to \(n D_{ij}^e\), equation A3-2 may be rearranged to
give:

\[
\delta i = \frac{D_i^e}{D_j^e} \tag{A3-6}
\]

Combining this result with equation A3-4 and rearranging yields:

\[
\tilde{\mathcal{N}}_i = \frac{-D_{ij} \frac{\partial n_i^e}{\partial z}}{1 + \frac{D_{ij}}{D_j^e} - \alpha i} \tag{A3-7}
\]

Equation A3-7 is the form suggested by Rothfield\textsuperscript{41} and Scott\textsuperscript{42}.
APPENDIX IV

MULTICOMPONENT DIFFUSION EQUATION FOR POROUS MEDIA

For non-constant pressure and temperature, the Stephan-Maxwell equation written in the terminology of Evans et al. is given as follows:

\[ \sum_{i \neq j} \frac{n_i n_j}{n_t^2} (D_{ij}^{e'})^{-1} (\mathbf{\bar{v}}_{ij} - \mathbf{\bar{v}}_{i}^e) = \mathbf{\nabla} \left( \frac{n_i}{n_t} \right) \]  

(A4-1a)

where

\[ n' = n + n_p \]  

(A4-1b)

\[ n = \sum_{i = 1}^{V} n_i \]  

(A4-1c)

\[ D_{ij}^{e'} = \frac{\varepsilon}{\bar{v}_{ij}} \mathbf{\bar{v}}_{ij}' \]  

(A4-1d)

\[ \mathbf{\bar{v}}_{ij}' = \left( \frac{16}{3} \bar{v}_{ij} \left( \frac{\bar{m}}{2 \pi k T} \right)^{\frac{3}{2}} \frac{\bar{v}_{ij}}{\pi n_t^{\frac{3}{2}}} \mathbf{\bar{v}}_{ij} \right)^{-1} \]  

(A4-1e)

and

\[ n_i \]  

is the molecules per unit total volume of the gas species \( i \)

\[ n_p \]  

is the molecules per unit total volume of the solid species

\[ \mathbf{\bar{v}}_{i}^e \]  

is the apparent molecular average velocity for the gas species \( i \) or the solid species \( p \).

By dividing the number of molecules per unit volume by Avogadro's number
equation A3-1a may be converted to an equation based on the number of moles per unit total volume as follows:

\[ \sum_{i \neq j} \frac{c_i c_j}{c} \left( D_{ij}^e \right) \left( \frac{c_i}{c} - \frac{c_j}{c} \right) = V \left( \frac{c_i}{c} \right) \]  \hspace{1cm} (A4-2)

This equation is further expanded to give:

\[ \sum_{i \neq j} \frac{c_i c_j}{c} \left( D_{ij}^e \right) \left( \frac{c_i}{c} - \frac{c_j}{c} \right) = \frac{1}{c} \lambda c_i c' - \frac{1}{c} \lambda c_i c' \]  \hspace{1cm} (A4-3)

If the molar flux of gas species \( i \) is defined as:

\[ \dot{M}_i^e = c_i \dot{V}_i^e \]  \hspace{1cm} (A4-4)

equation A3-3 becomes:

\[ \sum_{i \neq j} \frac{c_i c_j}{c} \left( D_{ij}^e \right) \left( \frac{c_i}{c} - \frac{c_j}{c} \right) = \frac{1}{c} \lambda c_i c' - \frac{1}{c} \lambda c_i c' \]  \hspace{1cm} (A4-5)

If only one species exists in the solid phase, the term which accounts for the interaction between the solid and the gas species \( i \) may be separated from the summation in equation A3-5 and the mass fraction of the gas species \( i \) substituted for the ratio of \( c_i \) to \( c \) to give:
\[
\sum_{i} \frac{\epsilon_{i}}{c_{i}} (c_{i} \Delta \rho_{i}^{e})^{-1} (x_{i} \Delta \rho_{i}^{e} - x_{i} \Delta \rho_{i}^{e}) - (c_{i} \Delta \rho_{i}^{e})^{-1} (c_{i} \Delta \rho_{i}^{e} - \epsilon_{i} \Delta \rho_{i}^{e}) - (A4-6a)
\]

\[
\frac{\epsilon_{i}}{c_{i}} (\Delta \rho_{i}^{e}) = \frac{\epsilon_{i}}{c_{i}} \nabla x_{i} + \frac{\epsilon_{i}}{c_{i}} \nabla c - \frac{\epsilon_{i}}{c_{i}} \frac{\epsilon_{i}}{c_{i}} \nabla c
\]

where

\[
\kappa_{i} = \frac{\epsilon_{i}}{c_{i}}
\]  \hspace{1cm} (4-6b)

Now \(\Delta c\) equals \(\Delta c\) because the number of solid molecules does not change. In addition, \(\Delta c\) may be factored and canceled to give:

\[
\sum_{i} C_{i} (c_{i} \Delta \rho_{i}^{e}) (x_{i} \Delta \rho_{i}^{e} - x_{i} \Delta \rho_{i}^{e}) + (c_{i} \Delta \rho_{i}^{e}) (c_{i} \Delta \rho_{i}^{e} - \epsilon_{i} \Delta \rho_{i}^{e}) = c_{i} \kappa_{i} + \kappa_{i} (c_{i} - c_{i}) \nabla c
\]  \hspace{1cm} (A4-7)

For most situations \(\frac{\epsilon_{i}}{c_{i}}\) is nearly unity. Thus, equation A4-7 becomes:

\[
\nabla x_{i} = \sum_{i} \frac{c_{i} \Delta \rho_{i}^{e}}{c_{i} \Delta \rho_{i}^{e}} (x_{i} \Delta \rho_{i}^{e} - x_{i} \Delta \rho_{i}^{e}) + (c_{i} \Delta \rho_{i}^{e}) (c_{i} \Delta \rho_{i}^{e} - \epsilon_{i} \Delta \rho_{i}^{e})
\]  \hspace{1cm} (A4-8)
APPENDIX V

MULTICOMPONENT ENERGY CONSERVATION EQUATION
FOR POROUS MEDIA

Neglecting kinetic and potential energy, the equation for energy conservation of a homogeneous mixture is:

$$\frac{\partial}{\partial t} (\rho \hat{H}_\ell) + \nabla \cdot (\rho \vec{v} \hat{H}_\ell) = -\nabla \cdot \vec{q} + \frac{\partial \rho}{\partial t}$$  \hspace{1cm} (A5-1)

where $\hat{H}_\ell$ is the enthalpy of the mixture.

Assuming that the porous medium is a mixture of solid and gases which may be represented by the "dusty gas" model used in previous derivations, equation A5-1 may be modified to give equation A5-2 below. As with other relations based on this model, the velocity of the solid is assumed to be zero. In addition, the solid is assumed to be incompressible so that changes in pressure only occur in the void volume.

$$\frac{\partial}{\partial t} (\rho \hat{H}_\ell) + \frac{\partial}{\partial t} (\rho \hat{H}_p) + \nabla \cdot (\rho \vec{v} \hat{H}_\ell) = -\nabla \cdot \vec{q} + \frac{\partial \rho}{\partial t} (\rho \hat{H}_p)$$  \hspace{1cm} (A5-2)

where $\hat{H}_\ell$ is the enthalpy for the gas mixture
$\hat{H}_p$ is the enthalpy for the solid phase.

Equation A5-2 can be expanded to give:

$$\rho \frac{\partial \hat{H}_\ell}{\partial t} + \frac{\partial (\rho \hat{H}_p)}{\partial t} + \nabla \cdot (\rho \vec{v} \hat{H}_\ell) = -\nabla \cdot \vec{q} + \frac{\partial (\rho \hat{H}_p)}{\partial t}$$  \hspace{1cm} (A5-3)
According to the continuity equation:

$$\frac{\partial}{\partial t}(\varepsilon \rho) + \nabla \cdot \rho \vec{u} = - \frac{\partial}{\partial t}(\varepsilon \rho \rho_c) \tag{A5-4}$$

Inserting this result in equation A5-3 and combining terms yields:

$$\varepsilon \rho \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial t}(\varepsilon \rho_c \rho) - \rho_c \frac{\partial \rho}{\partial t} \rho_c + \rho \vec{u} \cdot \nabla \vec{H} = - \nabla \cdot \vec{Q} + \varepsilon \frac{\partial P}{\partial t} + \rho \frac{\partial \vec{E}}{\partial t} \tag{A5-5}$$

If the solid material is composed of a substate particle and a coating of a single species and if the density of the coating does not change with time, the derivative of the product $\varepsilon \rho$ with respect to time can be represented as shown in equation A5-6. Details of this derivation are shown in Appendix I.

$$\frac{\partial}{\partial t}(\varepsilon \rho \rho_c) = - \rho_c \frac{\partial \varepsilon}{\partial t} \tag{A5-6}$$

Inserting these results into equation A5-5 yields:

$$\varepsilon \rho \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial t}(\varepsilon \rho_c \rho) + \rho_c \frac{\partial \rho}{\partial t} \rho_c = - \rho \vec{u} \cdot \nabla \vec{H} - \nabla \cdot \vec{Q} + \varepsilon \frac{\partial P}{\partial t} + \rho \frac{\partial \vec{E}}{\partial t} \tag{A5-7}$$

In order to express the energy equation in terms of temperature, the following equation is used:

$$A = \sum_{i=1}^{n} \omega_i \dot{A}_i \tag{A5-7a}$$
where
\[ \hat{H}_i = \int_{T_b}^{T} c_{P_i} \, dT + \hat{H}_i^o \quad (A5-7b) \]

and \( \hat{H}_i^o \) is the enthalpy of the gas species \( i \) at the base temperature.

\( T_b \) is the base temperature.

The relation describing the enthalpy of the solid phase can also be expanded to give:

\[ \varepsilon_P \rho_P \hat{H}_P = \varepsilon_P \rho_P \hat{H}_P + (\varepsilon_P - \varepsilon_P^0) \rho_c \hat{H}_c \quad (A5-8a) \]

where
\[ \hat{H}_c = \int_{T_b}^{T} c_P \, dT + \hat{H}_c^o \quad (A5-8b) \]

and
\[ \hat{H}_P = \int_{T_b}^{T} c_{P_i} \, dT + \hat{H}_P^o \quad (A5-8c) \]

Assuming that the density of the solid substrate and of the coating are constant in time, application of these definitions for the individual enthalpies to equation A5-7 results in a conservation of energy equation based on the local temperature of the porous media. This equation is given below:

\[ \frac{\partial}{\partial t} \left( r \epsilon P P \hat{H} \right) + \frac{\partial}{\partial x} \left( \rho c \hat{H} \right) + \frac{\partial}{\partial y} \left( \rho c \hat{H} \right) + \frac{\partial}{\partial z} \left( \rho c \hat{H} \right) + (\varepsilon_P - \varepsilon_P^0) \rho_c \hat{H}_c \quad (A5-9) \]

\[ -\rho c \frac{\partial \hat{H}_c}{\partial x} + \rho c \frac{\partial \hat{H}_c}{\partial y} + \rho c \frac{\partial \hat{H}_c}{\partial z} = -\rho c \cdot \nabla \hat{H} - \nabla \cdot \bar{q} + \varepsilon_P \hat{H} + \rho \frac{\partial \hat{H}}{\partial t} \]

Now the flux of energy into the system, \( \bar{q} \), can be expanded as follows:
Inserting these results into equation A5-9 and combining terms yields the following equation for energy conservation in porous media:

\[
\bar{q} = -k_e \frac{\partial T}{\partial n} + \sum_{i=1}^{N} \mathbf{A}_{i} \mathbf{j}_{i} 
\]

\[
\sum_{i=1}^{N} \frac{\partial}{\partial t} \mathbf{A}_{i} \mathbf{j}_{i} = -\rho \nu e \mathbf{c}_p \cdot \nabla T - \rho \nu e \cdot \sum_{i=1}^{N} \mathbf{A}_{i} \mathbf{v}_{wi}
\]

\[
- \nabla \cdot \sum_{i=1}^{N} \mathbf{A}_{i} \mathbf{j}_{i} + \nabla \cdot k_e \nabla T + \varepsilon \frac{\partial p}{\partial t} + p \frac{\partial}{\partial t} \]
APPENDIX VI

CALCULATION OF THE SUBSURFACE TEMPERATURE

$T(L,t)$ is defined as the temperature of the grid point just inside the shell surface. In the algorithm arranged for solution of this problem, the spacing between this point and the surface can be very much smaller than the spacing for the other grids. As a result, space derivative calculations can be inaccurate. In addition, the value for the surface temperature is specified or experimentally determined. As a result, the value calculated for $T(L,t)$ must be consistent with the value for the heat flux at this point as implied by specification of the surface temperature. In order to provide increased accuracy and to satisfy the constraint on the heat flux, an implicit equation is used to calculate $T(L,t)$. This method is possible at this point because the value of the surface temperature is known at all times. The equation is developed below:

$$T(L,t+\Delta t) = T(L,t) + \frac{\Delta t}{\delta} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \quad (A6-1)$$

where $\frac{\partial T}{\partial t}$ is the time derivative of temperature at time $t$ and $\frac{\partial^2 T}{\partial x^2}$ is the time derivative of temperature at time $t+\Delta t$. The equation for the time derivative of temperature at time $t+\Delta t$ is given below. This equation uses values for all physical and transport properties evaluated at the previous time, $t$. In this respect, the use of this
method is not totally implicit, but the values for these variables will not change significantly in the range of the calculation.

\[
\frac{\partial T}{\partial t} \bigg|_{t+\Delta t} = \left( \frac{2}{\Delta S} \left( \frac{T(s, t+\Delta t)}{\Delta S} + \frac{T(l-1, t+\Delta t)}{\Delta r} \right) - \frac{\partial T}{\partial S} \right) \alpha_S(l, t) \tag{A6-2}
\]

\[
+ \left( \frac{\partial^2}{\partial r^2} + \frac{k_2(l,t)}{E(l)} \right) \frac{1}{\text{Arias}} \left( \left( \frac{\partial}{\partial S} T(s, t+\Delta t) \right) - \frac{\Delta S}{\Delta r} T(l-1, t+\Delta t) \right) \left( \frac{\partial^2}{\partial S^2} - \frac{\Delta S}{\Delta r} T(l, t+\Delta t) \right) \right) \rho(l, t) c_p(l, t)
\]

where \( T(s, t+\Delta t) \) is the temperature at the surface at time \( t+\Delta t \)

\( \alpha_S(l, t) \) is the thermal of diffusivity

\( T(l-1, t+\Delta t) \) is the temperature two points inside the surface at time \( t+\Delta t \)

\( \Delta r \) is the spacing for a normal grid

\( \Delta S \) is the spacing for the last grid point and surface.

and

\[
\frac{\partial k_S}{\partial r} = \left( \frac{\partial}{\partial S} k_S(l, t) \right) - \frac{\Delta S}{\Delta r} k_S(l-1, t) \right) \left( \text{Arias} \right) \cdot k_S(l, t) \frac{\Delta r - \Delta S}{\Delta r \Delta S} \tag{A6-2b}
\]

Application of equation A6-2a and A6-2b to A6-1 yields after rearranging terms:

\[
T(l, t+\Delta t) = \left( T(l, t) + \frac{\Delta t}{2} \frac{\partial T}{\partial t} + \frac{\Delta t}{2} \frac{\partial}{\partial S} \right) \left( \frac{\partial k_S(l, t)}{E(l)} \right) \tag{A6-3}
\]

\[
\frac{\partial}{\partial r} \left( \frac{\rho(l, t) c_p(l, t))}{\text{Arias}} \left( \frac{\partial^2}{\partial S^2} - \frac{\Delta S}{\Delta r} T(l-1, t+\Delta t) \right) \right) + \alpha_S(l, t) \left( \frac{\partial^2}{\partial S^2} T(l, t+\Delta t) \right) \right) \left( 1 + \frac{\Delta t}{2} \frac{\partial^2}{\partial S^2} \right)
\]

\[
\left( \frac{\partial^2}{\partial S^2} - \frac{\Delta S}{\Delta r} T(l-1, t+\Delta t) \right) \right) \left( \frac{\partial^2}{\partial S^2} \right) + \frac{\partial}{\partial S} \left( \frac{\rho(l, t) c_p(l, t))}{\text{Arias}} \left( \frac{\partial^2}{\partial S^2} - \frac{\Delta S}{\Delta r} T(l-1, t+\Delta t) \right) \right) \left( \frac{\partial^2}{\partial S^2} \right)
\]
APPENDIX VII

INTERFACE CONTINUITY EQUATION AND
THICKNESS CALCULATION

Because chemical reaction may consume or deposit solid silicon at
an interface, the distance between the solid surface and the first node
point in the porous medium will vary and a gap will form. As a result,
a special calculation for grid thickness and the continuity equation must
be developed. As was previously stated, storage terms are necessary be­
cause the interface is treated as a volume element in a numerical
solution. The derivations begin with the continuity equation. Dimensions
used in these derivations are shown in Figure 13.

\[ \sum_{\text{area}} \frac{\partial (\rho \phi)}{\partial t} + \frac{\partial (\rho \phi \mathbf{U})}{\partial x} = 0 \]  

Dividing by \( 2\pi R_c L \) yields:

\[ \frac{\partial (\rho \phi \mathbf{U})}{\partial x} = - \frac{R(c_{\text{swp}})}{K_c} \rho \phi \mathbf{U} \]  

But, \( \rho \phi \) is the initial distance from the interface to the node point
just inside the porous media which is constant; so

\[ \sum_{\text{area}} \frac{\partial (\rho \phi \mathbf{U})}{\partial t} + \frac{\partial (\rho \phi \mathbf{U})}{\partial x} = - \frac{R(c_{\text{swp}})}{K_c} \rho \phi \mathbf{U} \]
Figure 13. Schematic Representation of the Porous Media--Core Gap.
Expanding and combining terms yields:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \frac{\partial}{\partial t} \left( \rho \frac{\delta r}{\delta r} \right) + \frac{\partial}{\partial x} \left( \rho \frac{\delta r}{\delta x} \right) + \frac{\partial}{\partial y} \left( \rho \frac{\delta r}{\delta y} \right)
\]

But \( \Delta r = \Delta r - \Delta x \) and \( \Delta r \) is constant so:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \frac{\partial}{\partial t} \left( \rho \frac{\delta r}{\delta r} \right) + \frac{\partial}{\partial x} \left( \rho \frac{\delta r}{\delta x} \right) + \frac{\partial}{\partial y} \left( \rho \frac{\delta r}{\delta y} \right) = - \frac{R(\text{LAMM})}{R_c} \rho \mathbf{v} \]

Combining terms and dividing by \( \Delta x \) gives the final form of the continuity equation used in this work.

\[
\left(1 + \frac{\Delta r}{\Delta x} (e-1) \right) \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} \left( \rho \frac{\Delta x}{\Delta r} \frac{\Delta r}{\Delta x} \right) = - \frac{R(\text{LAMM})}{R_c} \rho \mathbf{v} \]

Results of a similar derivation for the other interface are:

\[
\frac{\partial \rho}{\partial t} + \left( \rho \frac{\delta r}{\delta x} \right) = \frac{\partial}{\partial x} \left( \rho \frac{\delta r}{\delta x} \right) + \left( \rho \delta r \frac{1 + \delta r}{\delta r} \right) \frac{\delta r}{\delta r} = - \frac{R(\text{LAMM})}{R_c} \rho \mathbf{v} \]

The thickness of the partial grid between the core and the first node point in the porous medium will change due to depletion of the core.
The thickness of this partial grid is calculated from a mass balance on the species, silicon, in the original grid as follows:

$$t(z_{rr,0} \rightarrow z_{rr,0}) = \frac{\partial}{\partial z} \int_{z_{rr,0}}^{z_{rr,0}^+} \rho \, dz = z_{rr,0} \partial \rho \, dz$$ \hspace{1cm} (A-8)

The last term in equation A7-8 represents the net generation (or depletion) of silicon in the grid of thickness $\Delta \rho$. The other term represents depletion in the porous material and the depletion of the core to form a gap. Dividing by $2\pi R_0$ and expanding terms gives:

$$\Delta \rho \frac{\partial \rho}{\partial t} \bigg|_{z_{rr,0}} = \Delta \rho \, \Delta \rho$$ \hspace{1cm} (A7-9)

But $\epsilon = 1 - \epsilon$, so equation A9-8 becomes:

$$\Delta \rho \frac{\partial \rho}{\partial t} \bigg|_{z_{rr,0}} = \Delta \rho \, \Delta \rho$$ \hspace{1cm} (A7-10)

Solving for $\frac{\partial \rho}{\partial t}$ yields:

$$\frac{\partial \rho}{\partial t} = \frac{\Delta \rho \, \Delta \rho}{\rho}$$ \hspace{1cm} (A7-11)

A similar equation can be derived for the shell interface. The results are shown below:
\[ \frac{\partial \varphi}{\partial x} = - \frac{\Delta \rho \cdot \psi_i + \beta \cdot \Delta \rho \cdot \psi_2}{\beta_i (E - E_0 + 1)} \]
APPENDIX VIII

CALCULATION OF INTERFACE MASS FRACTIONS

BOUNDARY CONDITIONS

In the solution to a differential equation, derivatives of the mass fluxes at the solid boundary must be zero. Also, a boundary has zero thickness so there is no storage term in the mass balance. For a finite difference approximation, a finite volume is used so a storage term and a flux term are needed. For the interface between the core and the porous medium, the following mass balance applies:

\[ \frac{\partial}{\partial t} \left( 2\pi r_c \delta r_p \left( \omega_i \rho_i + \rho_i (\delta r_p - \delta r_p^0) \right) \right) + 2\pi r_c (\omega_{ci} \ell_{ci}) \rho_i \frac{\partial}{\partial z} n_i \bigg|_{\ell_{ci}} = 2\pi r_c \delta r_p \frac{\partial}{\partial r} (\delta r_p) \delta r_p^0 \]

where

- \( R_e \) is the radius of the interface
- \( \ell_{ci} \) is the radius at \( \ell_{ci} \)
- \( \omega_{ci} \) is one point beyond the interface
- \( \delta r_p \) is the thickness of the interval between \( \ell_{ci} \) and \( \ell_{ci} \)
- \( \delta r_p^0 \) is the initial value for \( \delta r_p \)

Equation A8-1 can be expanded to give:

\[ \frac{\partial}{\partial z} (\rho_i \omega_{ci}) + \rho_i \frac{\partial}{\partial r} (\delta r_p \delta r_p^0) \frac{\partial}{\partial z} (\rho_i \omega_{ci}) + \rho_i \frac{\partial}{\partial r} (\delta r_p) \]
In the algorithm for the problem at hand, \( \omega_i(\text{ccw}, t+\Delta t) \) is calculated from a Taylor's series as follows:

\[
\omega_i(\text{ccw}, t+\Delta t) = \omega_i(\text{ccw}, t) + \frac{\Delta t}{2} \left( \frac{\partial^2 \omega_i}{\partial t^2} + \frac{\partial^2 \omega_i}{\partial t \partial \text{rat}} \right) \tag{A8-3}
\]

As with the calculation of the subsurface temperature (see Appendix VI), the fact that \( \Delta r_p \) can be very small, thus producing inaccurate derivatives, warrants the use of an implicit solution for \( \omega_i(\text{ccw}, t+\Delta t) \). The derivative \( \frac{\partial^2 \omega_i}{\partial t^2} \) is obtained from equation A8-2 and is shown in the expanded form below:

\[
\frac{\partial^2 \omega_i}{\partial t^2} \bigg|_{t+\Delta t} = \left( \frac{\Delta r_p}{\Delta r_p} \right) \frac{\partial \text{rat}}{\partial t} - \omega_i(\text{ccw}, t+\Delta t) \left( E(\text{ccw}, t) + \frac{\Delta r_p}{\Delta r_p} - 1 \right) \frac{\partial \text{rat}}{\partial t} \tag{A8-4}
\]

\[
- \rho(\text{ccw}, t+\Delta t) \omega_i(\text{ccw}, t+\Delta t) \left( \frac{\partial E}{\partial t} + \frac{\partial \rho}{\partial \Delta r_p} \frac{\partial \Delta r_p}{\partial \text{rat}} \right) - \frac{\partial E}{\partial \text{rat}} (\text{ccw}, t) \\
\frac{R(\text{ccwp})}{\Delta r_p \, R(\text{ccw})} \left( \frac{\rho(\text{ccwp}, t+\Delta t) \omega_i(\text{ccwp}, t+\Delta t)}{\text{MW} (\text{ccwp}, t+\Delta t)} - \frac{\Delta r_p}{\Delta r_p} \right)
\]

Insertion of equation A8-4 into A8-3 and collecting terms yields the following equation for \( \omega_i(\text{ccw}, t+\Delta t) \):

\[
\omega_i(\text{ccw}, t+\Delta t) = \omega_i(\text{ccw}, t) + \frac{\Delta t}{2} \frac{\partial \omega_i}{\partial t} + \frac{\Delta t}{2} \left( \frac{\Delta r_p}{\Delta r_p} \right) \frac{\partial \text{rat}}{\partial t} \tag{A8-5}
\]

\[+ \frac{R(\text{ccwp})}{R(\text{ccw})} \left( \frac{\rho(\text{ccwp}, t+\Delta t) \omega_i(\text{ccwp}, t+\Delta t)}{\text{MW} (\text{ccwp}, t+\Delta t)} - \frac{\Delta r_p}{\Delta r_p} \right) \]

\[
\left( \omega_i(\text{ccwp}, t+\Delta t) - \omega_i(\text{ccwp}, t+\Delta t) \right) \frac{\Delta r_p}{\Delta r_p} + \frac{\Delta r_p}{\Delta r_p} \omega_i(\text{ccwp}, t+\Delta t) \)
A similar equation can be developed for the interface between the porous medium and the shell. The results are:

\[
\frac{\partial}{\partial t} \left( \frac{\partial \varepsilon}{\partial \rho} \right) + \frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) = \left( \frac{\partial \varepsilon}{\partial \rho} \right) \left( \frac{\partial \varepsilon}{\partial \rho} \right)
\]

\[
\frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) + \frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) = \left( \frac{\partial \varepsilon}{\partial \rho} \right) \left( \frac{\partial \varepsilon}{\partial \rho} \right)
\]

\[
\frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) + \frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) = \left( \frac{\partial \varepsilon}{\partial \rho} \right) \left( \frac{\partial \varepsilon}{\partial \rho} \right)
\]

\[
\frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) + \frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) = \left( \frac{\partial \varepsilon}{\partial \rho} \right) \left( \frac{\partial \varepsilon}{\partial \rho} \right)
\]

\[
\frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) + \frac{\partial}{\partial \rho} \left( \frac{\partial \varepsilon}{\partial \rho} \right) = \left( \frac{\partial \varepsilon}{\partial \rho} \right) \left( \frac{\partial \varepsilon}{\partial \rho} \right)
\]
APPENDIX IX

CALCULATION OF INTERFACE TEMPERATURE

BOUNDARY CONDITIONS

The calculation of the interface boundary condition is based on an energy balance over a portion of the porous section on one side of the interface. To improve the accuracy of the numerical solution, an implicit calculation of the interface temperature values is used. The method used to calculate $T(CA_0w)$, the temperature of the interface between the core and the porous medium, is shown below. Results for a similar derivation are also given for $T(CA_0w)$, the temperature at the other interface. The derivation begins with the following energy balance:

$$\Delta \left[ (E_p - E_r) T - p \Delta T \right] + \frac{2}{\rho_v} \left[ (E_p - E_r) T + \frac{\Delta \rho \Delta T}{\rho_v} \right] + \frac{2}{\Delta \rho} \left[ (E_p - E_r) T + \frac{\Delta \rho \Delta T}{\rho_v} \right] =$$

$$\left( \frac{R(CA_0w)}{R(CA_0w)} \frac{\Delta \rho}{\rho_v} \right) \left( \frac{\rho \Delta \rho}{\rho_v} \right) \left( \frac{\Delta \rho \Delta T}{\rho_v} \right)$$

The first term is the accumulation of internal energy of the gas phase in the partial increment next to the interface. The second term is the accumulation of internal energy of the porous substrate next to the interface. The third term represents the accumulation of internal energy on the core material deposited on the porous substrate. The fourth term is the change in internal energy of the gas in the gap between the core and porous...
medium. The fifth term is the accumulation of internal energy of the core material near the interface. The remaining two terms represent the flux of energy due to diffusion and conduction. For the problem at hand, the density of the solids does not change in time and the internal energy of the solid can be represented in terms of \( \dot{\varepsilon}_p \) so Equation A9-1 becomes:

\[
\frac{\delta}{\partial t} \rho (\dot{\varepsilon}_p \sigma_{p} \dot{U}) + \nabla \cdot (\rho (\dot{\varepsilon}_p \sigma_{p} \dot{U}) \mathbf{v}) + \epsilon_p \sigma_{p} \Delta \rho - \sigma_p \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} \left( \rho c \frac{\partial T}{\partial x} \right) = - \frac{\dot{R}(\dot{\varepsilon}_{\text{cwpi}})}{R_c} \left( \frac{\dot{\varepsilon}_{\text{cwpi}}}{\dot{\varepsilon}_1} \right) \mathbf{f}_{\text{out}}
\]

Substituting the definition for \( \dot{U} \) and expanding and combining terms gives:

\[
\sigma_p \frac{\partial}{\partial x} (\dot{\varepsilon}_p \sigma_{p}) - \sigma_p \frac{\partial}{\partial x} (\epsilon_p \sigma_{p}) + \rho (\dot{\varepsilon}_p \sigma_{p} \mathbf{v}) \frac{\partial }{\partial x} \sigma_{p} + (\dot{\varepsilon}_p \sigma_{p} \mathbf{v}) \frac{\partial }{\partial x} \sigma_{p} + \frac{\partial}{\partial x} \left( \rho c \frac{\partial T}{\partial x} \right) = - \frac{\dot{R}(\dot{\varepsilon}_{\text{cwpi}})}{R_c} \left( \frac{\dot{\varepsilon}_{\text{cwpi}}}{\dot{\varepsilon}_1} \right) \mathbf{f}_{\text{out}}
\]

Application of the definition of \( \dot{H} \) and expansion of terms gives:

\[
\sigma_p \frac{\partial}{\partial x} \dot{H} + \sigma_p \frac{\partial}{\partial x} \sigma_{p} \dot{H} - \sigma_p \frac{\partial}{\partial x} \sigma_{p} \dot{H} + \epsilon_p (\dot{\varepsilon}_p + \frac{\partial}{\partial x} \sigma_{p}) \frac{\partial }{\partial x} \sigma_{p} + (\dot{\varepsilon}_p + \frac{\partial}{\partial x} \sigma_{p}) \frac{\partial }{\partial x} \sigma_{p} + (\epsilon_p \sigma_{p} + \dot{\varepsilon}_p \sigma_{p} \mathbf{v})
\]
\[ + e_R^p \rho_0 \alpha R R_c \frac{\partial \rho}{\partial x} + \frac{(e^p - e_R^p) \rho \alpha R R_c \frac{\partial \rho}{\partial x} + \rho \alpha \rho \alpha R R_c \frac{\partial \rho}{\partial x}}{\rho_0} \quad \text{(A9-4)} \]

Continued

\[ p_R \rho_0 \left( \frac{\hat{p}}{\rho_0^2} \right) \frac{\partial \rho}{\partial x} + p_R \left( \frac{\hat{p}}{\rho_0^2} \right) \frac{\partial \rho}{\partial x} = - \frac{R(\text{ccum})}{R_0^2} \frac{\partial \rho}{\partial x} + R(\text{ccum}) \rho \left( \frac{\partial \rho}{\partial x} \right) \left( \frac{\partial \rho}{\partial x} \right) \]
\[ R \left( \frac{\partial \rho}{\partial x} \right) \frac{\partial \rho}{\partial x} = R \left( \frac{\partial \rho}{\partial x} \right) \frac{\partial \rho}{\partial x} \]

Assuming \( \frac{\partial \rho}{\partial x} \) is \( - \frac{\partial \rho}{\partial x} \) and combining terms based on derivatives yields:

\[ (\alpha_R \rho \rho - \alpha_R \rho \rho - \frac{1}{0.3676}) \frac{\partial \rho}{\partial x} + \alpha_R (\alpha_R \rho \rho - 1.01 \epsilon) - \alpha_R \rho \rho \]
\[ \frac{\partial \rho}{\partial x} + (e \rho \rho - \rho \rho \rho - \frac{1}{0.3676}) \frac{\partial \rho}{\partial x} = - (\alpha_R \rho \rho - 1.01 \epsilon) - \alpha_R \rho \rho \]
\[ \frac{\partial \rho}{\partial x} + (e \rho \rho - \rho \rho \rho - \frac{1}{0.3676}) \frac{\partial \rho}{\partial x} = - (\alpha_R \rho \rho - 1.01 \epsilon) - \alpha_R \rho \rho \]
\[ \frac{\partial \rho}{\partial x} = \frac{R(\text{ccum})}{R_0} \left[ \frac{\partial \rho}{\partial x} \right] + \frac{R(\text{ccum})}{R_0} \frac{\partial \rho}{\partial x} \]
\[ \frac{\partial \rho}{\partial x} = \frac{R(\text{ccum})}{R_0} \left[ \frac{\partial \rho}{\partial x} \right] + \frac{R(\text{ccum})}{R_0} \frac{\partial \rho}{\partial x} \]

For a numerical solution, values for \( \frac{\partial \rho}{\partial x} \) are defined as follows:

\[ \frac{\partial \rho}{\partial x} = - k(\text{ccum}) (T(\text{ccum}) - T(\text{ccum})) / \alpha_R \quad \text{(A9-6)} \]
\[ \frac{\partial \rho}{\partial x} = - k(\text{ccum}) (T(\text{ccum}) - T(\text{ccum})) / \alpha_R \quad \text{(A9-7)} \]

Further, if \( T(\text{ccum}) \) is defined as:

\[ T(\text{ccum}, \text{ccum}) = T(\text{ccum}, \epsilon) + \alpha_R \frac{\partial \rho}{\partial x} \quad \text{(A9-8)} \]

then an implicit numerical solution for \( T(\text{ccum}, \text{ccum}) \) can be found as follows:
\[ T(lcw, t+at) = T(lcw, t) + \frac{\Delta t}{2} \left( -\frac{R(lcw) \frac{\partial}{\partial t} C_{cw}^{\star}(lcw)}{E_{cw}} \right) \]

\[
+ \frac{R(lcw)}{Re \, \alpha r} k(lcw, t+at) T(lcw, t+at) \]

\[
+ \frac{R(lcw)}{Re \, \alpha r} k(lcw, t+at) T(lcw, t+at) - \text{ARGETA} \frac{\partial}{\partial t}
\]

\[
- \text{ARGRNO} \frac{\partial}{\partial t} - \text{ARGRDP} \frac{\partial}{\partial t} \left( \frac{\partial}{\partial t} \right) / \text{ERC}) / \]

\[
(1 + \frac{\Delta t}{2} \left( \frac{R(lcw)}{Re \, \alpha r} k(lcw) + \frac{R(lcw)}{Re \, \alpha r} k(lcw) \right) / \text{ERC})
\]

where

\[ \text{ARGETA} = \alpha r (\hat{P}_{cw}(t+\Delta t)) \rho(lcw, t+at)
\]

\[
\hat{P}_{cw}(t) - \alpha r (\hat{P}_{cw}(t+\Delta t)) \rho(lcw, t+at)
\]

\[ - \frac{1}{0.5676} \]

\[ \text{ARGRNO} = \hat{P}_{cw}(t+\Delta t)(\alpha r + \epsilon(t) \alpha r - \alpha r) \]

\[ \text{ARGRDP} = (\rho(lcw, t+at) \hat{P}_{cw}(t+\Delta t) - \hat{P}_{cw}(t))
\]

\[ (\epsilon(t) + 1) - \rho_{c}(lccwmi, t+at) \hat{P}_{cw}(lccwmi, t+at)
\]

\[ - \frac{1}{0.5676} \]

\[ \text{ERC} = \alpha r \rho (lccwmi, t) \hat{P}_{cw}(lccwmi, t+at)
\]

\[ (\alpha r - \alpha r) + (1-\epsilon_{o}) \rho_{o} \alpha r \hat{P}_{cw}(lccwmi, t+at) +
\]

\[ (\epsilon_{o} - \epsilon_{o}(lccw, t)) \rho_{o} (lccw, t+at) \alpha r \hat{P}_{cw}(lccw, t+at)
\]

\[ + \rho_{c}(lccwmi, t+at) \hat{P}_{cw}(lccwmi, t+at) \alpha r. \]
A similar equation can be derived for the interface between the porous medium and the shell. The results of that derivation are:

\[
T(LPW, t\text{int}) = \left( T(LPW, t) + \frac{\tfrac{\partial P(LPWO)}{\partial t}}{R_p \Delta \rho \rho_0} k(LPWM, t\text{int}) \right) \left( \left( \frac{1}{1 + \frac{R(LPWM)}{R_p \Delta \rho \rho_0} k(LPWM, t\text{int})} \right) \frac{\Delta t}{2} \right) \text{(A9-9)}
\]

where

\[
\text{ARGETA} = \Delta \rho \rho_0 \left( \frac{\partial P(LPW, t\text{int})}{\partial t} \right)
\]

\[
\text{ARGRHO} = \Delta \rho \rho_0 \left( \frac{\partial P(LPW, t\text{int})}{\partial t} \right)
\]

\[
\text{ARGPR} = \Delta \rho \rho_0 \left( \frac{\partial P(LPW, t\text{int})}{\partial t} \right)
\]

\[
\text{ARGP} = \Delta \rho \rho_0 \left( \frac{\partial P(LPW, t\text{int})}{\partial t} \right)
\]

\[
\text{ERC} = \Delta \rho \rho_0 \left( \frac{\partial P(LPW, t\text{int})}{\partial t} \right)
\]
\[ t'at) \Delta x = \rho_{t} \left( \rho_{lw}(t, t') \right) \Delta t \]
APPENDIX X

CALCULATION OF THE OVERALL DIFFUSIVITY
AND OVERALL THERMAL CONDUCTIVITY FOR THE
CORE INTERFACE

Because the interface between the core and the porous medium may recede as a result of depletion of the core material, a special calculation must be made for the diffusivity and the thermal conductivity in the interval just beyond the interface. These calculations are based on a model which treats the intervals as a composite material composed of the gap, formed by recession of the core, and the porous material. The geometry and nomenclature used for this derivation are shown in Figure 13 with as the portion of the increment representing the gap and with as the portion representing the porous medium. The derivation for the diffusivity will be shown first.

If the assumption can be made that for any instant, the molar flux relative to the molar-average velocity in the gap is equal to that in the porous medium just beyond the gap and is only slightly dependent on distance over that interval, an overall diffusivity can be calculated as follows:

\[
-r \left( \frac{\rho}{M_w} \frac{\partial \bar{u}_{im}}{\partial r} \right)_{R_e', \delta_p - \delta_p} = -r \left( \frac{\rho}{M_w} \frac{\partial \bar{u}_{im}}{\partial r} \right)_{R_e', \delta_p} \quad (A10-1)
\]

Upon integration, the following equations result:
\[
\frac{v_i}{R_{c1arp-arp}} - \frac{v_i}{R_c} = - \frac{R_c J_2 e^{e \ln \left( \frac{R_{c1arp-arp}}{R_c} \right)}}{P e^D_m / R_{c1arp-arp}} \quad (A10-2a)
\]

and
\[
\frac{v_i}{R_{c1arp}} - \frac{v_i}{R_{c1arp-arp}} = - \frac{R_c J_2 e^{e \ln \left( \frac{R_{c1arp}}{R_{c1arp-arp}} \right)}}{P e^D_m / R_{c1arp}} \quad (A10-2b)
\]

Adding equations A10-2a and A10-2b and rearranging terms yields:
\[
\frac{v_i}{R_{c1arp}} - \frac{v_i}{R_c} = - \frac{R_c J_2 e^{e \ln \left( \frac{R_{c1arp}}{R_c} \right)}}{P e^D_m / R_{c1arp}} \frac{\ln \left( \frac{R_{c1arp}}{R_c} \right)}{\ln \left( \frac{R_{c1arp-arp}}{R_{c1arp}} \right)} \quad (A10-3)
\]

This equation can be further rearranged to give:
\[
\bar{J}_{2} e^{e} = - \frac{P}{M_u} \left( \ln \left( \frac{R_{c1arp}}{R_c} \right) \right) \left( \frac{R_{c1arp}}{R_c} \right)^{-1} \frac{v_i}{R_{c1arp}} - \frac{v_i}{R_c} \quad (A10-4)
\]

If equation A10-4 is multiplied and divided by the space increment for the interval under consideration, a derivative can be created. If the remaining terms are collected, an overall diffusivity results as shown by equation A10-5a and A10-5b.
\[
\bar{J}_{2} e^{e} = - \frac{P}{M_u} D^e \frac{\partial v_i}{\partial x} \quad (A10-5a)
\]
where

\[
\hat{\kappa}_{\text{eq}} = \left( \frac{\ln \left( \frac{R_{\text{exp}} - a_{\text{exp}}}{R_{\text{exp}}} \right)}{\ln \left( \frac{R_{\text{exp}} - a_{\text{exp}}}{R_{\text{exp}}} \right)} \right)_{a_{\text{exp}}} R_{\text{exp}} \quad (A10-5b)
\]

A similar logic can be used to derive an equation for the overall thermal conductivity for the composite formed from the gap and the porous medium in the interval just beyond the core interface. In this case, the heat flux in the gap is assumed to be independent of distance for the interval and the flux in the gap is assumed to equal that in the porous medium. This relation is represented as follows:

\[
- r_k \frac{dT}{dr} \bigg|_{R_{\text{exp}} - a_{\text{exp}}} = - r_k \frac{dT}{dr} \bigg|_{R_{\text{exp}}} = R_c \overline{q} \quad (A10-6)
\]

Upon integration, the following equations result:

\[
T_{R_{\text{exp}} - a_{\text{exp}}} - T_{R_{\text{exp}}} = R_c \overline{q} \left( \frac{\ln \left( \frac{R_{\text{exp}} - a_{\text{exp}}}{R_{\text{exp}}} \right)}{R_c} \right) \quad (A10-7a)
\]

and

\[
T_{R_{\text{exp}}} - T_{R_{\text{exp}} - a_{\text{exp}}} = R_c \overline{q} \left( \frac{\ln \left( \frac{R_{\text{exp}} - a_{\text{exp}}}{R_{\text{exp}}} \right)}{R_c} \right) \quad (A10-7b)
\]

Adding equation A10-7a and A10-7b yields:
Equation A10-8 can be represented as a derivative equation by multiplying and dividing by \( \Delta \rho \). The overall thermal conductivity is then obtained by collecting terms as follows:

\[
\overline{q} = -\overline{k_e} \frac{\partial T}{\partial r}
\]  

(A10-9a)

where

\[
\overline{k_e} = \left( \frac{\ln \left( \frac{R_e + \Delta \rho}{R_{e1} + \Delta \rho} \right)}{\frac{\Delta \rho}{R_{e1} + \Delta \rho}} + \frac{\ln \left( \frac{R_{e1} + \Delta \rho}{R_e} \right)}{\frac{\Delta \rho}{R_{e1} + \Delta \rho}} \right)^{-1}
\]  

(A10-9b)
APPENDIX XI

COMPUTER PROGRAM

Nomenclature

Program MAIN

Subroutine DIFF
NOMENCLATURE FOR THE COMPUTER PROGRAM

Real Variables:

ALPHAC (I)        Thermal diffusivity for the core material
ALPHAS (I)        Thermal diffusivity for the shell material
ARG              Argument used in time loop limit definition
ARGETA           Argument used in energy equation for either interface
ARGLP            Argument used in space loop limit definition
ARGGP            Argument used in energy equation for either interface
ARGPR            Argument used in energy equation for core interface
ARGRHO           Argument used in energy equation for either interface
ARGRP            Argument used in energy equation for shell interface
ARGX2            Argument used to calculate $y_2$ from equilibrium expression
CAPX (II)        Dimensionless concentration variable used in the Arnold Solution
CCA              Argument used in initial value calculation for the Arnold Solution
CCB              Argument used in initial value calculation for the Arnold Solution
CBO              Interpolation variable used in center line temperature profile calculation
CBI              Same as above
CBI2             Same as above
CID1             Constant for diffusion collision integral calculation
CID2             Same as above
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1V1</td>
<td>Constant for viscosity collision integral calculation</td>
</tr>
<tr>
<td>CLAMB</td>
<td>Argument used in initial value calculation for the Arnold Solution</td>
</tr>
<tr>
<td>COATTH</td>
<td>Coating thickness at the shell-porous medium interface</td>
</tr>
<tr>
<td>COAT1</td>
<td>Coating thickness at the shell-porous medium interface during iteration J</td>
</tr>
<tr>
<td>COLIND (II, JJ)</td>
<td>Collision integral for diffusivity</td>
</tr>
<tr>
<td>COLINV (II)</td>
<td>Collision integral for viscosity</td>
</tr>
<tr>
<td>CONTH</td>
<td>Constant used in pressure calculation equal to</td>
</tr>
<tr>
<td>COREDP</td>
<td>Thickness of core depleted</td>
</tr>
<tr>
<td>CORE1</td>
<td>Thickness of core depleted during iteration J</td>
</tr>
<tr>
<td>CP (I)</td>
<td>Mixture Heat capacity</td>
</tr>
<tr>
<td>CPC</td>
<td>Heat capacity of the core material</td>
</tr>
<tr>
<td>CPC1</td>
<td>Constant for core heat capacity calculation</td>
</tr>
<tr>
<td>CPC2</td>
<td>Same as above</td>
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<tr>
<td>CPC3</td>
<td>Same as above</td>
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<tr>
<td>CPCG (II)</td>
<td>Heat capacity of gas species II</td>
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<tr>
<td>CPCG1 (II)</td>
<td>Constant for gas species II heat capacity calculation</td>
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<tr>
<td>CPCG4 (II)</td>
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</tr>
<tr>
<td>CPCG5 (II)</td>
<td>Same as above</td>
</tr>
<tr>
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<td>Heat capacity of the porous substrate material</td>
</tr>
<tr>
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<td>Constant for porous material heat capacity calculation</td>
</tr>
<tr>
<td>CPP2</td>
<td>Same as above</td>
</tr>
<tr>
<td>CPP3</td>
<td>Same as above</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
</tr>
<tr>
<td>CPP0</td>
<td>Initial value of CPP</td>
</tr>
<tr>
<td>CPS</td>
<td>Heat capacity of shell material</td>
</tr>
<tr>
<td>CPS1</td>
<td>Constant for shell material heat capacity calculation</td>
</tr>
<tr>
<td>CPS2</td>
<td>Same as above</td>
</tr>
<tr>
<td>CPS3</td>
<td>Same as above</td>
</tr>
<tr>
<td>CS0</td>
<td>Interpolation variable used in surface temperature profile calculation</td>
</tr>
<tr>
<td>CS1</td>
<td>Same as above</td>
</tr>
<tr>
<td>CS2</td>
<td>Same as above</td>
</tr>
<tr>
<td>C00</td>
<td>Interpolation variable for centerline and surface temperature profile calculation</td>
</tr>
<tr>
<td>C01</td>
<td>Same as above</td>
</tr>
<tr>
<td>C02</td>
<td>Same as above</td>
</tr>
<tr>
<td>C10</td>
<td>Same as above</td>
</tr>
<tr>
<td>C11</td>
<td>Same as above</td>
</tr>
<tr>
<td>C12</td>
<td>Same as above</td>
</tr>
<tr>
<td>C20</td>
<td>Same as above</td>
</tr>
<tr>
<td>C21</td>
<td>Same as above</td>
</tr>
<tr>
<td>C22</td>
<td>Same as above</td>
</tr>
<tr>
<td>DEGF</td>
<td>Point out variable for temperature</td>
</tr>
<tr>
<td>DELCR</td>
<td>Partial space increment between the last node in the core and the core radius</td>
</tr>
<tr>
<td>DELCRL</td>
<td>Old value of DELCR</td>
</tr>
<tr>
<td>DELCRO</td>
<td>Initial value of DELCR</td>
</tr>
<tr>
<td>DELK (I)</td>
<td>First derivative of K with respect to r</td>
</tr>
<tr>
<td>DELKC (I)</td>
<td>First derivative of KC with respect to r</td>
</tr>
<tr>
<td>DELKS (I)</td>
<td>First derivative of KS with respect to r</td>
</tr>
<tr>
<td>DELKDT</td>
<td>First derivative of the product K(I)*DELT(I) with respect to r at either interface</td>
</tr>
</tbody>
</table>
DELN1E (I)  First derivative of the mass flux of species 1 with respect to r
DELN2E (I)  First derivative of the mass flux of species 2 with respect to r
DELN3E (I)  First derivative of the mass flux of species 3 with respect to r
DELP (I)    First derivative of the pressure with respect to r
DELPR       Partial space increment between the porous medium and the node just inside the porous medium
DELPRL      Old value of DELPR
DELPRO      Initial value of DELPR
DELR        Space increment
DELROV (I)  First derivative of the produce RHO(I)*V(I) with respect to r
DELRP       Partial space increment between the core radius and the node just inside the porous medium
DELRPL      Old value of DELRP
DELRPO      Initial value of DELRP
DELRS       Partial space increment between the porous medium radius and node just inside the shell
DELRSO      Initial value of DELRS
DELS        Space increment variable for the shell energy equation calculation equal to either DELR or DELSR
DELSR       Partial space increment between the last node in the shell and the shell radius
DELSUM (I)  First derivative of the sum of the product AG(II)*V FLUXJI(II) with respect to r
DELT (I)    First derivative of T(t) with respect to r
DELTAU      Time increment
DELVA       Space increment variable for the porous medium calculations equal to either DELR or DELPR
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>DELVAB</td>
<td>Same as above equal to either DELR or DELRP</td>
</tr>
<tr>
<td>DELW1(I)</td>
<td>First derivative of W(I) with respect to r</td>
</tr>
<tr>
<td>DELW2(I)</td>
<td>Same as above</td>
</tr>
<tr>
<td>DELW3(I)</td>
<td>Same as above</td>
</tr>
<tr>
<td>DELX</td>
<td>Space increment variable for the shell energy</td>
</tr>
<tr>
<td></td>
<td>equation calculation equal to either DELRS or DELR</td>
</tr>
<tr>
<td>DELX1(I)</td>
<td>First derivative of X1(I) with respect to r</td>
</tr>
<tr>
<td>DELX2(I)</td>
<td>First derivative of X2(I) with respect to r</td>
</tr>
<tr>
<td>DELX3(I)</td>
<td>First derivative of X3(I) with respect to r</td>
</tr>
<tr>
<td>DG (II, JJ)</td>
<td>Binary diffusivity for the gas pair II, JJ</td>
</tr>
<tr>
<td>DIF (II, JJ)</td>
<td>Argument used in the multicomponent diffusivity calculation</td>
</tr>
<tr>
<td>DIFOPT</td>
<td>Diffusion model option indicator</td>
</tr>
<tr>
<td>DINDEX(I)</td>
<td>Index used to determine whether deposition should occur</td>
</tr>
<tr>
<td>DIST</td>
<td>Printout variable for radius</td>
</tr>
<tr>
<td>DIVN1E(I)</td>
<td>Divergence of N1E(I) with respect to r</td>
</tr>
<tr>
<td>DIVN2E(I)</td>
<td>Divergence of N2E(I) with respect to r</td>
</tr>
<tr>
<td>DIVN3E(I)</td>
<td>Divergence of N3E(I) with respect to r</td>
</tr>
<tr>
<td>DIVROV(I)</td>
<td>Divergence of the product RHO(I)*V(L)</td>
</tr>
<tr>
<td>DK (II)</td>
<td>Knudsen diffusivity for species II</td>
</tr>
<tr>
<td>DM (II, I)</td>
<td>Multicomponent effective diffusivity</td>
</tr>
<tr>
<td>DMO1</td>
<td>Diffusion stability modulus for species 1</td>
</tr>
<tr>
<td>DMO2</td>
<td>Diffusion stability modulus for species 2</td>
</tr>
<tr>
<td>DMO3</td>
<td>Diffusion stability modulus for species 3</td>
</tr>
<tr>
<td>DPRDOT</td>
<td>Change in time of the partial increment DELPR</td>
</tr>
<tr>
<td>DRDS</td>
<td>Ratio of either DELR/DELS or DELX/DELS</td>
</tr>
</tbody>
</table>
DRLIM  Smallest value of the partial increment at the surface accepted equal to 0.01 DELR
DRPDOT  Change in time of the partial increment DELRP
DSDR  Ratio of either DELS/DELX or DELS/DELRI
DTAU10  Variable used in surface and core temperature profile calculation
DTAU20  Variable used in surface and core temperature profile calculation
DTAU21  Variable used in surface and core temperature profile calculation
DTL1  Argument used in shell energy equation calculation
DTL2  Argument used in shell energy equation calculation
DUMM  Dummy variable equal to 1.0/3.0
DX  Sum of mole fractions for normalization
D1M (I)  Multicomponent diffusivity for species 1
D2M (I)  Multicomponent diffusivity for species 2
D3M (I)  Multicomponent diffusivity for species 3
E (II)  Lennard-Jones constant for gas species II
EOVERK(II, JJ)  Lennard-Jones constant for the gas species pair II, JJ
EPS (I)  Emissivity of porous particles
EQUIX (II)  Initial equilibrium concentration of gas species II at the core interface
ERC  Argument used in energy equation calculation for porous medium
ESP  Input value of EPS (I)
ETA (I)  Void fraction or porosity of the porous media
ETADOT (I)  First derivative of ETA (I) with respect to time
ETADTL (I)  Old value of ETADOT (I)
ETALAS (I)  Old value of ETA (I)
ETAO  Initial value of ETA (I)
F (I)  Function used to calculate P (I) equal to ETA(I)*MW(I)*RAD(I)*WBAR1/T(I)
FACTK (I)  Argument used to calculate KE (I)
FLUX  Output variable for the heat flux at the shell interface
FLUXJ1 (I)  Mass flux of gas species 1
FLUXJ2 (I)  Mass flux of gas species 2
FLUXJ3 (I)  Mass flux of gas species 3
GEN1 (I)  Rate of production of species 1, H₂
GEN2 (I)  Rate of production of species 2, HCI
GEN3 (I)  Rate of production of species 3, HSiCl₃
GEN4 (I)  Rate of production of species 4, Si( )
H (I)  Mixture enthalpy
HC (I)  Enthalpy of core material
HC0  Initial value of HC (I)
HEADG2  Input variable for heading
HEADG3  Input variable for heading
HEADG4  Input variable for heading
HEADG5  Input variable for heading
HEADG6  Input variable for heading
HEADG7  Input variable for heading
HG (II0  Enthalpy of gas species II
HGVapo (I)  Heat of vaporization of gas species I at 298° K
HS (I)  Enthalpy of shell
HS0  Initial value of HS (I)
KAPPA (I)  Permeability of porous medium
Thermal conductivity

Thermal conductivity of core material

Effective thermal conductivity of porous medium

Equilibrium constant

Constants used to calculate KEQ (I)

Constants used to calculate KEQ (I)

Thermal conductivity of gas species II

Old value of K (I)

Thermal conductivity of the core at station LCW

Mixture thermal conductivity

Thermal conductivity of the porous material

Effective thermal conductivity of the porous material due to radiation

Thermal conductivity due to radiation of the porous material used to calculate KR(I)

Thermal conductivity of the shell

Thermal conductivity of the shell at station LPW

Second derivative of T (I) with respect to r

Natural logarithm of KEQ (I)

Molecular weight of gas species II

Function of M (II) used to calculate D (II, JJ)

Atomic weight of element 1

Atomic weight of element 2

Atomic weight of element 3

Molar flux of gas species I

Molecular weight of porous material

Mixture viscosity of gas species II
MW (I)  Mixture molecular weight
MWO  Initial value of MW (I)
M1  Molecular weight of gas species 1
M2  Molecular weight of gas species 2
M3  Molecular weight of gas species 3
N1E (I)  Mass flux of gas species 1
N2E (I)  Mass flux of gas species 2
N3E (I)  Mass flux of gas species 3
N1ELAS (I)  Old value of N1E (I)
N2ELAS (I)  Old value of N2E (I)
N3ELAS (I)  Old value of N3E (I)
OUTD  Print out value of RAD (I)
OUTTIME  Print out value of TIME
OUTP  Print out value of P (I)
OUTVR  Print out value of V (I)
P (I)  Pressure
PDOT (I)  First derivative of P(T) with respect to t
PARTD  Porous material particle diameter
PHI (I)  Function of molecular weight and viscosity used in mixture property calculation
PI  Constant equal to 3.14159
PLAS (I)  Old value of P (I)
PORER  Porous material pore radius
PO  Initial value of P (I)
R  Universal gas constant
RAD (I)  Radius
RADC  Radius of the core
RADIUS Radius of the shell
RADP Radius of the porous material
RHO (I) Mixture density
RHOC (I) Density of the core
RHOC1 (I) Constant used to calculate RHOC (I)
RHOC2 Constant used to calculate RHOC (I)
RHOC3 Constant used to calculate RHOC (I)
RHODOT (I) Change in time of the mixture density
RHOLAS (I) Old value of RHO (I)
RHOP (I) Density of the porous material
RHOP0 Initial value of RHOP (I)
RHOS (I) Density of the shell
RHOS1 Constant used to calculate RHOS (I)
RHOS2 Constant used to calculate RHOS (I)
RHOS3 Constant used to calculate RHOS (I)
RHOVW (I) Product of RHO (I) and V (I) at the shell interface
RINC Argument used in pressure calculation equal to either 2*DELR or DELR + DEl.RP
RZ (I) Dimensionless space and time variable used in the Arnold Solution
SIG (II) Lennard-Jones constant for gas species II
SIGSQ (II, JJ) Mixture Lennard-Jones constant for the gas species pair II, JJ
SMDIF Argument used to calculate TOT MOF (I)
SUM Argument used to calculate TDOT (I)
SUMDIF (I) Argument used to calculate DM (II, JJ)
SUMGEL (I)  Old value of SUMGEN (I)
SUMGEN (I)  Sum used to determine if all coating has been removed
SUML3 (I)  Old value of SUM3 (I)
SUMXPH  Argument used to calculate mixture physical properties
SUM1 (I)  Argument used to calculate TDOT (I)
SUM2 (I)  Argument used to calculate TDOT (I)
SUM3 (I)  Argument used to calculate TDOT (I)
SUM4C  Argument used to calculate TDOT(I) in the core interface
SUM4S  Argument used to calculate TDOT(I) in the shell interface
SO  Specific surface of porous material
T (I)  Temperature
TAU  Time limit of computer run
TAUO  Value of time used in surface and centerline profile interpolation routine
TAU1  Value of time used in surface and centerline profile interpolation routine
TAU2  Value of time used in surface and centerline profile interpolation routine
TBASE  Base temperature for thermodynamic calculations equal to 70.0°F
TB (J)  Centerline temperature
TBO  Value of TB (I) used in centerline temperature interpolation routine
TB1  Value of TB (I) used in centerline temperature interpolation routine
TB2  Value of TB (I) used in centerline temperature interpolation routine
TCC1  Constant used to calculate KC (I)
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCC2</td>
<td>Constant used to calculate KC (I)</td>
</tr>
<tr>
<td>TCC3</td>
<td>Constant used to calculate KC (I)</td>
</tr>
<tr>
<td>TCP1</td>
<td>Constant used to calculate KP (I)</td>
</tr>
<tr>
<td>TCP2</td>
<td>Constant used to calculate KP (I)</td>
</tr>
<tr>
<td>TCP3</td>
<td>Constant used to calculate KP (I)</td>
</tr>
<tr>
<td>TCS1</td>
<td>Constant used to calculate KS (I)</td>
</tr>
<tr>
<td>TCS2</td>
<td>Constant used to calculate KS (I)</td>
</tr>
<tr>
<td>TCS3</td>
<td>Constant used to calculate KS (I)</td>
</tr>
<tr>
<td>TDOT (I)</td>
<td>Change in time of T (I)</td>
</tr>
<tr>
<td>TEST1 (I)</td>
<td>Ratio of DELX1 to value predicted by Stefan-Maxwell equation</td>
</tr>
<tr>
<td>TEST2 (I)</td>
<td>Ratio of DELX2 to value predicted by Stefan-Maxwell equation</td>
</tr>
<tr>
<td>TEST3 (I)</td>
<td>Ratio of DELX3 to value predicted by Stefan-Maxwell equation</td>
</tr>
<tr>
<td>TIME</td>
<td>Cumulative value of time since calculation began</td>
</tr>
<tr>
<td>TIME 2</td>
<td>Value of time used in surface and centerline temperature equation</td>
</tr>
<tr>
<td>TINIT</td>
<td>Initial value for the temperature profile</td>
</tr>
<tr>
<td>TLAS (I)</td>
<td>Old value of T (I)</td>
</tr>
<tr>
<td>TMOD (I)</td>
<td>Temperature stability modulus</td>
</tr>
<tr>
<td>TOPT</td>
<td>Input data printout option</td>
</tr>
<tr>
<td>TOTMOF (I)</td>
<td>Total mole flux</td>
</tr>
<tr>
<td>TR</td>
<td>Reduced temperature used to calculate DG(I,J)</td>
</tr>
<tr>
<td>TSURF</td>
<td>Surface temperature</td>
</tr>
<tr>
<td>TSO</td>
<td>Value of TSURF used in surface temperature interpolation routine</td>
</tr>
<tr>
<td>TS1</td>
<td>Value of TSURF used in surface temperature interpolation routine</td>
</tr>
</tbody>
</table>
TS2  Value of TSURF used in surface temperature interpolation routine
V (I)  Velocity
VLAS (I)  Old value of V (I)
VRGRDT  Product of V(I)*
W  Sum of mass fractions
W1 (I)  Mass fraction of species 1
W2 (I)  Mass fraction of species 2
W3 (I)  Mass fraction of species 3
W1INIT  Initial value of W1 (I)
W2INIT  Initial value of W2 (I)
W3INIT  Initial value of W3 (I)
WILAS (I)  Old value of W1 (I)
W2LAS (I)  Old value of W2 (I)
W3LAS (I)  Old value of W3 (I)
W1DOT (I)  First derivative of W1 with respect to t
W2DOT (I)  First derivative of W2 with respect to t
W3DOT (I)  First derivative of W3 with respect to t
WBAR1  Elemental mass fraction of gas species 1
W3DT  Old value of W3DOT(I)
X(II,I)  Mole fraction of gas species II
XCPG  Argument used to calculate GP
XHG  Argument used to calculate H
XINIT (II,I)  Initial value of X(II,I)
XK  Argument used to calculate KM (I)
XLAMB  Argument used to calculate initial values for Arnold Solution
XLAS (II,I)  Old value of X(II,I)
XMU  Argument used to calculate MU (I)
XPHI  Argument used to calculate PHI (I)

Integers:

I  Integer used to indicate position
ICT1  Integer used to determine if reaction has occurred
II  Integer used to indicate species
IMINUS  I-1
IPLUS  I+1
IPR  Integer used to indicate station next to shell interface inside the porous medium
IRP  Integer used to indicate station next to core interface inside the porous medium
II  I+1
I2  I+2
J  Integer used to indicate time
JJ  Integer used to indicate species
JJEND  Integer used to indicate end of run
JJJ  Integer used to indicate time
JPLUS  J+1
JPRINT  Integer used in print routine
KK  Integer used to indicate species
KKK  Integer used to indicate species
LC  Integer used to indicate station next to core inside the core
LCPLUS  LC + 1
LCW  Integer used to indicate the core interface
LCUM1  LCW - 1
LCWM2  LCW - 2
LCWP1  LCW + 1
LCWP2  LCW + 2
LMINUS LS - 1
LP  Integer used to indicate the station next to the shell interface inside the porous medium
LPW  Integer used to indicate the shell interface
LPWM1 LPW - 1
LPWM2 LPW - 2
LPWP1 LPW + 1
LPWP2 LPW + 2
LS  Integer used to indicate the surface
N  Integer used to indicate time
NPRINT  Integer used to indicate time in the print routine
NR  LPW + 1
NRE  LS - 1
NT  Integer used to indicate the number of input temperature profile data points.
135

The page contains a table with headers and data entries. The table is divided into several columns with headers such as "STATION," "TEMPERATURE," and "TRACER." The entries include numerical values and units, indicating a scientific context, possibly related to environmental or physical measurements. The table is formatted with specific structures and units, suggesting it is from a technical or research document.

The page also includes a note at the bottom that indicates it is page 135 and mentions that the page is not the start of a program. This note is typically found in technical documents to inform the reader about the context of the page within a larger document.
C********** ELEMENT 1 **********

C 110 WRITE(6,51)
C
C READ NUMBER OF INPUT POINTS, PRINT FACTOR, NUMBER OF SPECIES
C PRINT OPTION AND DIFFUSIVITY OPTION
C
C 110 READS,*INT,APRINT,KK,OPT,DIFOPT
C
C CHECK FOR END OF RUN
C
C 120 IF(INLE.0)GO TO 300
C
C READ AND WRITE OTHER INPUT RATE
C
C READ(4,2)HEA0D1,HEA0D2,HEA0D3,HEA0D4,HEA0D5,HEA0D6,HEA0D7
WRITE(6,52)HEA0D6,HEA0D2,HEA0D3,HEA0D4,HEA0D5,HEA0D6,HEA0D7
IF(DIFOPT.1I.125.125.125)
125 WRITE(6,99)GO TO 129
126 WRITE(6,101)GO TO 129
127 WRITE(6,99)
130 CONTINUE
C
C IF TC=T-0 CONTINUE
WRITE(6,38)CONTINUE
C FOR COMPLETE INPUT PR0DUCT, TOPT MUST EQUAL 1
C WRITE(6,140)140,141
C
140 CONTINUE
C
C WRITE(6,94)C01,C02,CIV,CIV2
C WRITE(6,253)C01,K02
C WRITE(6,70)HCC1,HCC2,HCO1,HCO2,HOS1,HOS2,HOS3,HOS4,HCE,HSO,TBASE
WRITE(6,83)M1,M2,M3
C WRITE(6,61)M1,M2,M3
C WRITE(6,55)TCC1,TCC2,TCC3,TPC1,TPC2,TPC3,TCS1,TCS2,TCS3
WRITE(6,56)E1,SIG1,SIG2,SIG3,SIG4
C WRITE(6,60)C01,C02,C03,C04,C05,C06,C07
1 CGF(1),CGF(2),CGF(3),CGF(4),CGF(5),CGF(6),CGF(7)
2 CGF(8),CGF(9),CGF(10),CGF(11),CGF(12)
3 CGF(13),CGF(14),CGF(15),CGF(16),CGF(17),CGF(18),CGF(19),CGF(20),CGF(21)
140 CONTINUE
C
READ5.11)TAU0.TS0
READ(5.11)TAU1.TS1
READ(5.11)TAU2.TS2

C CONVET TIME UNITS FROM SECONDS TO HOURS

TAU=TAU/3600.0
DELTAU=DELTAU/3600.0
TAU=TAU/3600.0
TAU2=TAU2/3600.0

C CONVERT DISTANCE UNITS FROM INCHES TO FEET

RADIUS=RADIUS/12.0
RADC=RADC/12.0
DELPH=DELPH/12.0

C CONVERT TEMPERATURE UNITS FROM FAHRENHEIT TO RANKINE

TBASE=TBASE+49.6
TINIT=TINIT+49.6
TS1=TS1+49.6
TS2=TS2+49.6

C COMPUTE LIMIT OF RADIUS AND TOTAL NUMBER OF DISTANCE STATIONS

DLIP=5.0, D1=DELP
LS=IFIX(RADIUS/DELPH)
LS2=RADIUS-FLOAT(LS)*DELPH
200 IF(C.G.ELSR-DLIM)210,210,220
210 DELPH=CELS*-DELPH
LS=LS+1
GO TO 230
220 LS=LS+2
230 LS=LS+2

LC=IXECH+DPS/DLPS
DELC=RADE-FLOAT(LC)*DLFR
DELC=DELFR
LC=LC+1
RGLF=(RGLF+RANG-RADC)
LP=FIXEPGLP/CFLP+LC
DELFR=RADE-FLOAT(LP)*DELFR+DELFR
DELFR=DELFR-DELFR
DELPS=DELPS+DELFR
DELPS=DELPS
LP=LP+1
LP=LP+1
LC=LC+1
WRITE(6,93)LC,LP,LS,LCW,LPW

C READ TIME AND SURFACE TEMPERATURES FOR FIRST INTERVAL
RAO(I) = 0.0

NC, CTL, I = 2, L,C

1 = INTUS
RAO(I) = -AD(LC) + FLOAT(I-LCW)*DEL

231 CONTINUE

RAO(LCH) = HAC

NP = LCH + 1

GO TO 232

RAO(I) = RAO(LC)+FLOAT(LC-LCH)*DEL

232 CONTINUE

RAO(LFH) = PAF

NP = LCH + 1

NP = LCH + 1

GO TO 233

RAO(I) = RAO(LP)+FLOAT(I-LPH)*DEL

233 CONTINUE

RAO(LS) = INTUS

NP = LCH + 1

TLAS(I) = INT

RHOC(I) = 0.0

IF(LC-LC) = 0, 250, 240

253 KLAS(I) = TG1+TG2/TLAS(I)+TG3*TLAS(I)

GO TO 360

260 IF(T-LPH) = 0, 150

270 KLAS(I) = TC1+TC2/TLAS(I)+TC3*TLAS(I)

GO TO 360

283 KLAS(I) = TCS1+TCS2/TLAS(I)+TCS3*TLAS(I)

GO TO 360

290 CONTINUE

KSLF = KLAS(LFH)

C

CALCULATE PORE FRACTIONS

MWL = 1.0/(M1*INIT/M2*2INIT/M3*3INIT/M4)

XINIT(1) = M1*INIT/MWD

XINIT(2) = M2*INIT/MWD

XINIT(3) = M3*INIT/MWD

OX = XINIT(1) + XINIT(2) + XINIT(3)

XINIT(1) = XINIT(1)/OX

XINIT(2) = XINIT(2)/OX

XINIT(3) = XINIT(3)/OX

WRITE(6, 66) XINIT(1), XINIT(2), XINIT(3)

C

INITIALIZE VARIABLES

DELPR = DELR = 0

DELPL = DELP = 0

DELP = DEL = 0

DFACT = 0.0

DFACT = 0.0

DO 305 I = LCW, LCH

305 STAAS(I) = TAO

VLAS(I) = 0.0

WLAS(I) = INIT

WLAS(I) = INIT

WLAS(I) = INIT

MW(I) = MWL
PLAS(1) = 1.0
XLAS(1,1) = XINIT(1)
XLAS(2,1) = XINIT(2)
XLAS(3,1) = XINIT(3)
SUNL(J1) = 0.0
NL = 0.7302
EMOLAS(I) = PLAS(I)*MN(I)/RTLAS(I)
M2LAS(I) = 0.0
M2FLAS(I) = 0.0
H3ELAS(I) = 0.0
H3FLAS(I) = 0.0
H2MOL(I) = 0.0
H2FOL(I) = 0.0
GEN3(I) = 0.0
GEN4(I) = 0.0
ETADTL(I) = 0.0
PHDOL(I) = 0.0
SURGE(I) = 0.0
ICT4(I) = 0.0
105 CONTINUE
C C008 = C008 + C02*INIT-C02*INIT**2.0
C C CALCULATE THE MULTICOMPONENT CONSTANTS
C M1(1) = 1
M2(1) = 2
M3 = 3
II = 0
350 DO 400 IT=1,400
JJ = 0
DO 360 JJ = 1,400
SIGS0(I,J,J) = (SIG(I,J) + SIG(J,J))**2.0
460 SIGS0(I,J,J) = (SIG(I,J) + SIG(J,J))**2.0
SIGS0(I,J,J) = (SIG(I,J) + SIG(J,J))**2.0
360 CONTINUE
400 CONTINUE
C C SET REAL TIME COUNTERS AND INTEGERS
C JJECOUNT = 0
JPRINT = NPRINT
APG = TAU/GEFTAU
AM = INIT(GEF)
IF(NPRINT .GT. 0) GO TO 330
J = A + JPRINT
J = A + JPRINT
IF(J-J) 310, 370, 320
310 N = J + NPRINT
GO TO 330
320 N = J
330 CONTINUE
TIME = 0.0
TIME = 0.0
JJJ = 2
CALCULATE THE INITIAL SURFACE TEMPERATURE

\[
\begin{align*}
\text{DTAU0} &= \text{TAU1} - \text{TAU0} \\
\text{DTAU2} &= \text{TAU3} - \text{TAU2} \\
\text{DTAU1} &= \text{TAU2} - \text{TAU1} \\
\text{C1} &= \frac{\text{DTAU1}}{\text{DTAU2}} - \text{TAU0} \\
\text{C2} &= \frac{\text{DTAU1}}{\text{DTAU0}} \\
\text{C1} &= \frac{\text{C2}}{\text{C1}} \\
\text{C2} &= \frac{\text{C1}}{\text{C2}} \\
\text{C1} &= \frac{\text{C2}}{\text{C1}} \\
\text{C2} &= \frac{\text{C1}}{\text{C2}} \\
\text{C1} &= \frac{\text{C2}}{\text{C1}} \\
\text{C2} &= \frac{\text{C1}}{\text{C2}} \\
\text{C1} &= \frac{\text{C2}}{\text{C1}} \\
\text{C2} &= \frac{\text{C1}}{\text{C2}} \\
\end{align*}
\]

\[ P = 0.7302 \]

\[ P0 = 1.3 \]

\[ \text{WEARI} = \text{HE1}/\text{H2} \times (\text{IN1}+2.0) \times \text{HE1}/\text{H1} \times (\text{H1}+2.0) \times \text{WEI} \]

\[ \text{GTAI} = \text{TAU0}/(\text{H2}+3) \times (\text{H2}+3) \times \text{WEI} \]

BEGIN FORWARD MARCHING IN TIME

\[
\begin{align*}
\text{K} &= 1.0 \times 10^6 \\
\text{TP} &= \text{TIME} + \text{DELTAU} \\
\text{IF} &= \text{TAU2} - \text{TAU1} \\
\text{II} &= \text{TAU2} + \text{TAU1} \\
\text{TAU} &= \text{TAU1} + \text{TAU2} \\
\text{TS0} &= \text{TS1} \\
\text{TS1} &= \text{TS2} \\
\text{TS2} &= \text{TS0} \\
\text{TS0} &= \text{TSL} \\
\text{TSL} &= \text{TS0} + \text{DTAU2} \\
\text{TS0} &= \text{TS1} \\
\text{TS1} &= \text{TS2} \\
\text{TAU0} &= \text{DTAU1} \\
\text{TAU1} &= \text{TAU0} \\
\text{TAU2} &= \text{TAU1} + \text{DTAU1} \\
\text{TAU3} &= \text{TAU1} + \text{DTAU1} \\
\text{TAU4} &= \text{TAU1} + \text{DTAU1} \\
\end{align*}
\]

UPDATE INPUT SURFACE TEMPERATURE PROFILE

\[
\begin{align*}
\text{TS0} &= \text{TAU1} + \text{DTAU1} \\
\text{TS0} &= \text{TAU2} + \text{DTAU1} \\
\text{TS0} &= \text{TAU3} + \text{DTAU1} \\
\text{TAU4} &= \text{TAU3} + \text{DTAU1} \\
\text{TAU5} &= \text{TAU4} + \text{DTAU1} \\
\text{TAU6} &= \text{TAU5} + \text{DTAU1} \\
\text{TAU7} &= \text{TAU6} + \text{DTAU1} \\
\text{TAU8} &= \text{TAU7} + \text{DTAU1} \\
\end{align*}
\]
C21 = l.~G/"'rTA':in»OTAfj26)~
C 21  = 1 ,
C2£ = t.9/fcfA*;?G*5riuii)
.._'. ClO  = C20*(.TaUl •!A..
,!
Cli  =  C2i*(Ta
Cir=c<2.2*  f i •lU^tiAUi*
C0G=C20»TAUi»TAU2
C_0 i =  c 21 *.LM-' -IlIAil'
C02  = C22*TAUi*TA!JC
CSl  = ClJ*TSG*-Ci2*TS2-Cli»TSi
CS2 = C2 0MSC+C2JLl
500  TLAS(LS)=TS!]KF
TSLPF = CS0 + Tiy£2MCS2MIM'

C

********** ELEMENT 2 **************
C
C SOLVE EQUATION FOR CORE MATERIAL
C
C 0.600  I=2.1,C
IPLUSX=1,
IMINUS=1-1,
CPC(C)=CPS*(DELTA/(DELTA+1))
KCL0=KCL0+1*
1 (KLSL0-KLAS(MINUS))*DELV/A/DELV/DELV/A
GTOL 5.0,

C

********** ELEMENT 1 **************
C
C SOLVE TRANSPORT EQUATIONS FOR POROUS SECTION
C
C IPR=DELCH+1
IF(D=LPW-1

********** ELEMENT 2 **************
C
C SOLVE EQUATION FOR CORE MATERIAL
C
C 0.600  I=2.1,C
IPLUSX=1,
IMINUS=1-1,
CPC(C)=CPS*(DELTA/(DELTA+1))
KCL0=KCL0+1*
1 (KLSL0-KLAS(MINUS))*DELV/A/DELV/DELV/A
GTOL 5.0,

C

********** ELEMENT 1 **************
C
C SOLVE TRANSPORT EQUATIONS FOR POROUS SECTION
C
C IPR=DELCH+1
IF(D=LPW-1

********** ELEMENT 2 **************
C
C SOLVE EQUATION FOR CORE MATERIAL
C
C 0.600  I=2.1,C
IPLUSX=1,
IMINUS=1-1,
CPC(C)=CPS*(DELTA/(DELTA+1))
KCL0=KCL0+1*
1 (KLSL0-KLAS(MINUS))*DELV/A/DELV/DELV/A
GTOL 5.0,

C

********** ELEMENT 1 **************
C
C SOLVE TRANSPORT EQUATIONS FOR POROUS SECTION
C
C IPR=DELCH+1
IF(D=LPW-1

********** ELEMENT 2 **************
C
C SOLVE EQUATION FOR CORE MATERIAL
C
C 0.600  I=2.1,C
IPLUSX=1,
IMINUS=1-1,
C  CALCULATE _SPACc_DERIVATIVES_

C

C

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C
SOLVE SPECIES CONSERVATION EQUATIONS

CALL EFF

CALL CIFF

CHECK ACCURACY OF THE DIFFUSION EQUATION

IF (ABS(TCTMF(II))<0.01830,670,631

630 TEST(I)=1.0

631 CONTINUE

GO TO 636

633 NIF(II,JI)=(XLAS(II,JI)*MCFI.X(JJ,II)-XLAS(JJ,II)*MCFI.X(II,JI))

634 SUMDIF(II,JI)=SUMDIF(II,JI)+NIF(II,JI)

635 CONTINUE

CALCULATE PHYSICAL PROPERTIES

GO 620 KK=1,3

XLAS(II)=FLAS(II)/1.4
$T_{HAS} = T_{AS}/P_{1.0}$

$1 + CGF (KK) \cdot T_{LAS} (1)^{**3.3} \cdot CFG 5 (KK) / T_{LAS} (1)^{**2.0}$

$M (KK) = CGF (KK) \cdot T_{LAS} (1)^{**} \cdot CGF 2 (KK) \cdot T_{LAS} (1)^{**} \cdot T_{BASE} ** 2.0$

$2 \cdot T_{1} + CGF (KK) \cdot T_{LAS} (1)^{**} \cdot T_{BASE} ** 3.0 \cdot T_{HAS} (1)^{**} \cdot P_{GVFAP (KK)}$

$0 \cdot CGF (KK) \cdot T_{LAS} (1)^{**} \cdot T_{BASE} ** 3.0 \cdot T_{HAS} (1)^{**} \cdot P_{GVFAP (KK)}$

$T_{HAS} = T_{BASE} ** 2.0$

$T_{AS} = T_{AS} (II)/P_{1.0}$

$T_{LAS} (II) = T_{LAS} (II) ** P_{1.0}$

$MUG (KK) = 2.652 \cdot T_{LAS} (II) / 10.0 \cdot T_{LAS} (1)^{**} \cdot T_{LAS} (II) / 10.0 \cdot T_{HAS} (II) ** 2.0$

$1 \cdot CGIMV (KK)$

$P_{1.0} \cdot K_{G (KK)} = T_{LAS} (II) / P_{1.0} \cdot K_{G (KK)}$

$MUG (KK) = T_{LAS} (II) / (M (KK) \cdot T_{BASE} ** 2.0) \cdot T_{HAS} (II) ** 2.0$
K(I) = KE(I)

C SOLVE ENERGY EQUATION
C

SUP1(I) = H(I) * IDOT(I) + H(G) * IDOT(I) + H(2) * IDOT(I)
SUP2(I) = H(I) * IDOT(I) + H(2) * DELH2(I) + H(3) * DELH3(I)
SUP3(I) = H(I) * FLUXJ3(I) + H(G) * FLUXJ3(I) + H(2) * FLUXJ3(I)
IF(I, EQU) SUP4 = H(I) * MFW(I) + H(F) * MFW(I)
IF(I, EQU) SUMS = H(I) * MFW(I) + H(F) * MFW(I)

ERC = TALAS(I) + PHO(I) + CP(I) + ETA(I) + PHOC(I)
1 + ETA(I) = TALAS(I) + CP(I) + ETA(I) + PHOC(I)

TOM(I) = (PHOC(I) * MFW(I) - H(G) + PLAS(I) / 0.3676) * EXP(I) -
1 + ETA(I) = MFW(I) * CP(I) * MFW(I) * PLAS(I) * DELT(I) -
2 * PHOC(I) * MFW(I) * MFW(I) * DELT(I) * PLAS(I) * DELT(I) -
3 * K(I) * PLAS(I) * DELT(I) * DELT(I) * PLAS(I) * ETA(I) * ETA(I)

C CALCULATE EQUILIBRIUM CONSTANT
C

LOGKE(I) = KE1 + KE2 * T(I) / 1.9
KEOC(I) = EXP(LOGKE(I) + 2.303)

C DETERMINE WHETHER DEPOSITION HAS OCCURRED
C

DO 100 I = 1, N, 10
100 CONTINUE

C SOLVE SIMULTANEOUS EQUATIONS FOR MOLF FRACTIONS.
C

W1(I) = H1DOT(I) + DETAU + XLAS(I)
W2(I) = H1DOT(I) + M1 + M2 + M3
W3(I) = H1DOT(I) + DETAU + XLAS(I)
W4(I) = N1DOT(I) + M1 + M2 + M3
W5(I) = X1(I) + X1(I) * X1(I) + KE0(I) / PLAS(I)

IFIC(I) = 1.0
GO TO 675

675 X1(I) = - (X1(I) * X1(I) + X1(I) + X1(I) + X1(I)) / DUMMY

676 DX = X1(I) + X2(I) + X3(I) + X4(I)
X1(I) = X1(I) + DX
X2(I) = X2(I) + CX
X3(I) = X3(I) + CX
X4(I) = X4(I) + CX
W1(I) = X1(I) + M1 + M2 + M3
W2(I) = X2(I) + M2 + M3
W3(I) = X3(I) + M3
W5(I) = X4(I) + M2 + M3
W6(I) = X5(I) + M2 + M3
W7(I) = X6(I) + M3

C CALCULATE THE DEPOSITION RATE
C

AND THE NEW POROSITY
M3CT = (W1(I) - W2LAS(I) * NT / CN3(I))

G34(I) = -(G3/3 + G3N3(I))

GNU(I) = 1.0 / (M2 + GEN4(I))

GEN2(I) = GEN2(I) + GEN3(I) - GEN4(I)

ETA(I) = ETA(I)* = TAU(I) + ETA(I)

GO TO 685

NO REACTION HAS OCCURRED, CONTINUE

W1(I) = W2LAS(I) + W1DOT(I)* OELTAU

W2(I) = W2LAS(I) + W2DOT(I) * DELTAU

F(I) = W2(I) + W2(I)

F(I) = W2(I) + W2(I)

W1(I) = W1(I) / M1

W2(I) = W2(I) / M2

W3(I) = W3(I) / M3

X(1, I) = W1(I)* ECTC(I) / M1

X(2, I) = W2(I)* ECTC(I) / M2

X(3, I) = W3(I)* ECTC(I) / M3

GEM(I) = 0.0

GEN2(I) = 0.0

ETA(I) = ETA(I)

GO TO 685

CALCULATE THE FUNCTIONS FOR PRESSURE INTEGRATION

W11 = 2.0*W1(I) / M1 + W2(I) / M2 + W3(I) / M3

F(I) = EXP(I) * W11(I) * WPAR(I) / T(I)

GO CONTINUE

************ ELEMENT 4 ************

SOLVE EQUATIONS FOR THE CORE INTERFACE

I = LCW

LCWPI = LCW + 2

LCW1 = LCW + 1

LCW2 = LCW - 2

LCW1 = LCW - 1
**ETALAS**

**CALCULATE SPACE DERIVATIVES**

\[
\text{DELX}_i(I) = \frac{\text{WLAS}(LCP_1) - \text{WLAS}(I)}{\text{DELX}_i}
\]

\[
\text{DELX}_j(I) = \frac{\text{KLAS}(LCP_1) - \text{KLAS}(I)}{\text{DELX}_j}
\]

\[
\text{DELX}_k(I) = \frac{\text{XLAS}(LCP_1) - \text{XLAS}(I)}{\text{DELX}_k}
\]

\[
\text{DELX}_l(I) = \frac{\text{YLAS}(LCP_1) - \text{YLAS}(I)}{\text{DELX}_l}
\]

**CALCULATE DENSITY AND VELOCITY**

\[
\rho(I) = \frac{\text{VLAS}(LCP_1) \times \text{VLAS}(LCW)}{\text{RHO}(I)}
\]

\[
\text{RHO}(I) = \frac{\text{VLAS}(I) \times \text{RHO}(I)}{\text{VLAS}(LCP_1)}
\]

**CALCULATE FLUXES FROM OLD VALUES**

\[
\text{MCFLX}(I) = \text{FMCFLX}(I) \times \text{FMCFLX}(I)
\]

\[
\text{NCFLX}(I) = \text{XFLAS}(I) \times \text{XFLAS}(I)
\]

\[
\text{MCFLX}(I) = \text{FMCFLX}(I) \times \text{FMCFLX}(I)
\]

**CHECK ACCURACY OF THE DIFFUSION EQUATION**

\[
\text{TEST1}(I) = 1.0
\]

\[
\text{TEST2}(I) = 0.0
\]

\[
\text{GO TO 736}
\]

\[
\text{GO TO 734}
\]

\[
\text{IF}(I,J) = \text{XLAS}(I,J) \times \text{XLAS}(I,J) \times \text{MCFLX}(I,J)
\]

\[
\text{FMCFLX}(I,J) = \text{MCFLX}(I,J) \times \text{MCFLX}(I,J)
\]

\[
\text{MCFLX}(I,J) = \text{FMCFLX}(I,J) \times \text{FMCFLX}(I,J)
\]

\[
\text{GO TO 734}
\]

\[
\text{GO TO 735}
\]
734 CONTINUE

C

C   ...SOLVE_SPECIES_I_CONSERVATION_EQUATIONS...
C

C   FMCCT(I) = (-AF(LCFL) +4AC(I) +2M(LCFW) +4LCW1(I)/DETPE
1   - (MKAC(I) - DMHC(I)) +DFPOT/DELPE - (MKAC(I) - FMCCT(I)) * TFATL(I))
2   /1.0*DELPE/CELPF*(ETALAS(I)-1.0))

C   NWCT(I) = (GEA(I) *DELPP/DELPC-HLASF(I)*(ETALAS(I)-DELPF)
1   /CELPC(I)-1.0) *MHODT(I) - HOD2(I) *HLASF(I) *(ETATOL(I) + DELPQT
2   /DELPE(I) -1.0*LCFW2(I)/PAN2(I)/DELFL(I))
3   /FMCCT(I) *ETALAS(I) -1.0*DELPP/DELPE)

C   NWODT(I) = (KEPL(I) *DELPP/DELPC-HLASF(I) *(ETALAS(I)-DELPF)
1   /CELPC(I)-1.0) *MHODT(I) - HOD2(I) *HLASF(I) *(ETATOL(I) + DELPQT
2   /DELPE(I) -1.0*LCFW2(I)/PAN2(I)/DELFL(I))
3   /FMCCT(I) *ETALAS(I) -1.0*DELPP/DELPE)

C   CALCULATE_PHYSICAL_PROPERTIES
C

C   HOD2(I) = PH023
FMCCT(I) = FMCCT(I) + HOD2(I) * HLASF(I) + HOD2(I) * HLASF(I) **2.0
CFC(I) = CCL + CFP2 + HLASF(I) + CFP2 / HLASF(I)**2.0

C   1   CFC(I) = (1.0*HLASF(I) -1.0)*TEASP + HOD2
C   2   /CFC(I) = CF2 + CFP2 + HLASF(I) * CFP2 / HLASF(I)**2.0

C   DO 7660 KK=1,KKK

C   TALSAS(I) = TALSAS(I)/1.0

C   TRASF = TRAS2/I.

C   CPF2(I) = CPF2(I) + CPF2(I) * HLC(I) * CFP2(I) * CFL(I)**2.0
C   AC0P4 = CPF2(I) * TALSAS(I)**3.0* CFL(I)**2.0
HC2(I) = CPF2(I) * TALSAS(I)**2.0
HLC(I) = CPF2(I) * TALSAS(I)**2.0
HKG = CPF2(I) * TALSAS(I)**2.0
HKG = CPF2(I) * TALSAS(I)**2.0
HLC(I) = CPF2(I) * TALSAS(I)**2.0

C   3.0/2.0*TALSAS(I) -1.0/2.0

C   TRASF = TRASF - I.

C   TALSA(I) = KGK
GCLVI(VK) = 1.0*(1.0 + CIV1*(1.0 + CIV2*ALOG(T))))

TALSAS(I) = TALSAS(I)**2.0

C   1.0*CCL + CCL

C   P = 1.0

C   KG(KK) = CPF2(KK) + CPF2(KK)**1.25*I

C   7649 CONTINUE

C   MK(I) = 0.0
CP(I) = 0.0
MK(I) = 0.0
HI(I) = 0.0

C   DO 7669 II=1,KKK
C
CALCULATE THE EQUILIBRIUM CONSTANT AND THE
C DEPOSITION INDEX
C
LOCKED(I) = KEN1*FACT(I)/FACT(I)/1.8
KED(I) = KEN1*2.03*LOCKED(I)
C
CALCULATE THE NEW CONCENTRATIONS
C
DIAGK(I) = 1.0/(XLAS(1,1)*XLAS(3,1)/XLAS(2,1)**2.0*PLAS(I))
C
IF(J.GT.1) GO TO 7740
CUP = 3.0*XLAS(2,1)
CUC=19.0*XLAS(1,1)+XLAS(7,1)-XLAS(1,1)*XLAS(3,1)
1 + 19.0*XLAS(1,1)**2.0*PLAS(I)/KEQ(I)/
2 (27.0*PLAS(I)/KEQ(I)-1.0)
CUD=27.0*XLAS(1,1)*PLAS(I)/KEQ(I)
CUP=CUC/CUD+2.0*XLAS(1,1)**2.0
CUC=CUC/2.0+CUP**0.5
CUP=CUP/2.0+CUP**0.5
IF(CUP.LT.0.0) GO TO 7741
CCP=CLP1**0.0
GO TO 7742
7741 CCP=-CUC**0.0**0.0
7742 IF(CUP.CE.1.0) GO TO 7743
CCP=CUC**0.0**0.0
GO TO 7744
7743 CCP=-CUC**0.0**0.0
7744 CLAP=CCP+CCP
XLAS=XLAS(3,1)+XLAS(2,1)*XLAS(3,1)
XAP=XLAS(2,1)*XLAS(3,1)
GO TO 7745
7745 W(I) = (XLAS(I)+DIELAU/2.0*W(I))+DIELAU/2.0*(GEN1(I)
1 +DIELAP/DIELAP+DIELAU/DIELAU)*PLAS(I)
2 CLP1=PLAP1+DIELAP/DIELAP*PLAP1
3 X(1,1)+XAPS1)**CILP3=X(1,1)*XAPS1)**CILP3
4 *X(1,1)**CILP3=0.03**ETLAS(I)*ETLAS(I)*ETLAS(I)
5 +CLAP/CLAP1 =DIELAU/2.0*W(I)+DIELAU/2.0*W(I)
6 /ACD1**P00(C1P1)+DIELAP1/XM(C1P1)*ETLAS(I)*ETLAS(I)
7 /CILP4=DIELAP/DIELAP**W(I)/DIELAP/DIELAP**W(I)*DIELAU/DIELAU
8 /DIELAF=DIELAU/DIELAU**W(I)+DIELAU/DIELAU**W(I)
9 +DIELB(DIELB1)**ETLAS(I)**ETLAS(I)**ETLAS(I)
X(I,1)+W(I)*M(I)
10 XAPS1=XAPS1-XAPS1**((XAPS1/2.0)*W(I))**2.0*(GEN1(I)
1 +DIELP/DIELP+DIELP/DIELP)**PLAS(I)
2 CLP1=PLAP1+DIELP/DIELP*PLAP1
3 X(1,1)+XAPS1)**CILP3=X(1,1)*XAPS1)**CILP3
4 *X(1,1)**CILP3=0.03**ETLAS(I)*ETLAS(I)*ETLAS(I)
5 +CLAP/CLAP1 =DIELAU/2.0*W(I)+DIELAU/2.0*W(I)
6 /ACD1**P00(C1P1)+DIELAP1/XM(C1P1)*ETLAS(I)*ETLAS(I)
7 /CILP4=DIELAP/DIELAP**W(I)/DIELAP/DIELAP**W(I)*DIELAU/DIELAU
8 /DIELAF=DIELAU/DIELAU**W(I)+DIELAU/DIELAU**W(I)
9 +DIELB(DIELB1)**ETLAS(I)**ETLAS(I)**ETLAS(I)
X(I,1)+W(I)*M(I)
C SOLVE THE EQUATIONS FOR THE SHELL INTERFACE

C

C ELEMENT 6

C SOLVE THE EQUATIONS FOR THE SHELL INTERFACE

C

C CALCULATE SPACE DERIVATIVES

C

DELX1(I) = (N(1) - L(1)) / DELX10(I)
DELX2(I) = (L(1) - N(1)) / DELX10(I)
DELX3(I) = (L(3) - L(2)) / DELX10(I)
DELX4(I) = (N(1) - L(3)) / DELX10(I)
DELX5(I) = (L(3) - N(1)) / DELX10(I)
DELX6(I) = (L(2) - L(3)) / DELX10(I)
DELX7(I) = (N(1) - L(2)) / DELX10(I)
**Calculate Density and Velocity**

\[ \rho(I) = \rho(I) \cdot \frac{\Delta T}{\Delta P} \]

**Calculate Fluxes from Old Values**

\[ \frac{\partial \rho}{\partial t} = \frac{\partial (\rho \cdot \frac{\partial \rho}{\partial t})}{\partial t} \]

**Check Accuracy of the Diffusion Equation**

\[ \text{IF } \rho(I) > \text{TEST} \rightarrow \text{CONTINUE} \]
\[ \text{IF } \rho(I) < \text{TEST} \rightarrow \text{CONTINUE} \]

**Solve Species Conservation Equations**

\[ \frac{\partial \rho}{\partial t} = \frac{\partial (\rho \cdot \frac{\partial \rho}{\partial t})}{\partial t} \]

**Compute Density and Velocity**

\[ \rho(I) = \rho(I) \cdot \frac{\Delta T}{\Delta P} \]

**Calculate Fluxes from Old Values**

\[ \frac{\partial \rho}{\partial t} = \frac{\partial (\rho \cdot \frac{\partial \rho}{\partial t})}{\partial t} \]

**Check Accuracy of the Diffusion Equation**

\[ \text{IF } \rho(I) > \text{TEST} \rightarrow \text{CONTINUE} \]
\[ \text{IF } \rho(I) < \text{TEST} \rightarrow \text{CONTINUE} \]

**Solve Species Conservation Equations**

\[ \frac{\partial \rho}{\partial t} = \frac{\partial (\rho \cdot \frac{\partial \rho}{\partial t})}{\partial t} \]
```
C CALCULATE PHYSICAL PROPERTIES

CFF(KK) = CFF1 + CFF2 * TLA5(KK) * CFF3
CFF(KK) = CFF1 + CFF2 * TLA5(KK) * CFF3
MC(KK) = MC(KK) * TLA5(KK) * BASE + MC(KK) * TLA5(KK) * BASE
C(KK) = C(KK) * TLA5(KK) * BASE + C(KK) * TLA5(KK) * BASE
PHOC(KK) = PHOC(KK) * TLA5(KK) * BASE + PHOC(KK) * TLA5(KK) * BASE

CONTINUE:
C IN
IC = IC + 1
DO 0 IC = 1, IC
```

\[ \text{SUP} = \text{X} = \text{H} = \text{L}(\text{II}) \]

\[ \text{865 CONTINUE} \]

\[ \text{X} = \text{XS} = \text{X} = \text{L}(\text{II}) \]

\[ \text{X} = \text{CF} = \text{X} = \text{S} = \text{C} = \text{H}(\text{II}) \]

\[ \text{K}(\text{I}) = \text{X} = \text{K} = \text{M}(\text{II}) \]

\[ \text{HG}(\text{II}) = \text{X} = \text{G} = \text{H}(\text{II}) \]

\[ \text{SUM} = \text{K} = \text{G} = \text{M}(\text{II}) \]

\[ \text{HG}(\text{II}) = \text{X} = \text{H} = \text{G}(\text{II}) \]

\[ \text{CF} = \text{X} = \text{CF} = \text{C} \]

\[ \text{H} = \text{X} = \text{H} = \text{M}(\text{II}) \]

\[ \text{HG} = \text{H} = \text{G}(\text{II}) \]

\[ \text{SUP} = \text{S} = \text{X} = \text{H} = \text{X} = \text{M}(\text{II}) \]

\[ \text{CF} = \text{X} = \text{CF} = \text{C} \]

\[ \text{H} = \text{X} = \text{H} = \text{M}(\text{II}) \]

\[ \text{HG} = \text{H} = \text{G}(\text{II}) \]

\[ \text{SUP} = \text{S} = \text{X} = \text{H} = \text{X} = \text{M}(\text{II}) \]
C SOLVE SIMULTANEOUS EQUATIONS FOR MOLE FRACTIONS
C AND CALCULATE THE NEW DENSITY
C
156
D1C3EX111 = (XSLAS(I,I)*XSLAS(I,I)*XSLAS(I,I))/XSLAS(I,I)
157
1.CT(I) = (1.E0+X0.40)*970.970.973
C
876 CONTINUE
ICT1(I) =
C
P = L72.72
DI.CEX111 = (XSLAS(I,I)*XSLAS(I,I)*XSLAS(I,I))/XSLAS(I,I)
1.CT(I) = (1.E0+X0.40)*970.970.973
C
876 CONTINUE
ICT1(I) =
GEN(I) = GEN2(I) + GEN3(I) + GEN4(I)
ETA(I) = ETAL(I)
ETA(I) = ETA(I)
ETA(I) = ETA(I)
ETA(I) = ETA(I)
ETA(I) = ETA(I)
ETA(I) = ETA(I)
ETA(I) = ETA(I)
ETA(I) = ETA(I)
CONTINUE

IF (I - LCW) < 3.0, 68, 688

IF(I = LCW) * 444.6844, 6889
GO TO 6865

6865 R1=2.0*DELFA
6866 CONTINUE

SUM=SL+RINC/5.0*(F(I)+F(I+12)+F(I+24)+F(I+36))
IF(I)%L>15.0%599=0.
6867 CONTINUE

SUM=SUM*(F(I)+F(I+24))/2.0*DELFA
6868 CONTINUE

DO 6590 I=L1C,LP4
IF(I)=CONT*12.0*SI*SUM
6869 CONTINUE

POD=(FLPH-FLAS(LPW))/16.0/6.0/3.375
C
C CALCULATE DEPOSITION RATE, COATING DEPOSITION.
C COFF DEPLETED. AND HEAT FLUX ALL AT THE WALL.
C
FLUX=K(I)*+CTALPH(I)
POD=G0(M(I))
G0=FLPH(I)-DELT(I-DELPH(I))
G0=G0+FLPH(I)-DELT(I-DELPH(I))
CONT=FLPH(I)-DELT(I-DELPH(I))
CONT=FLPH(I)-DELT(I-DELPH(I))

G0=G0/DELPH(I)

DO 6590 I=L1C,LP4
IF(I)=CONT*12.0*SI*SUM
6869 CONTINUE

POD=(FLPH-FLAS(LPW))/16.0/6.0/3.375
C
C CALCULATE DATA FOR THE APHOLD SOLUTION.
C
DO 6311 I=L1C,LP4
C0E(I,I)=X(I,I)-XUJ(I,I)/(ABS(X(I,I)-XINIT(I,I))
6872 CONTINUE
C
C ESTABLISH OLD PROPERTIES.
C
KSL=KSL(I)

6485 I=1+11*
USLAS(I)=USL(
N2LAS(I)=N2L(I)
N2LAS(I)=N2L(I)
FLAS(I)=FLAS(I)
ETALAS(I)=ETALAS(I)
RHOLAS(I)=RHOLAS(I)
MLAS(I)=MLAS(I)
MLAS(I)=MLAS(I)
XLAS(I)=XLAS(I)
XLAS(I)=XLAS(I)
XLAS(I)=XLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)
VLAS(I)=VLAS(I)

6885 CONTINUE
SUBROUTINE DIFF

C ALGORITHM FOR N-DIMENSIONAL DIFFUSIVITY CALCULATION

C

DATA E/3.14159/

DO 620 II=1,KK

R=II**4.7

TLAS(I)=TLAS(I)/1.9

OK(I,I)=.6625-X**2*(R**2-TLAS(I)/M(I,I)/M(I)**.5)

TLAS(I1)=TLAS(I1)*1.9

II=0

IF(II-JJ)66,669,669

II=II+JJ

GO TO 611

II=II-JJ

GO TO 611

C CONTINUE

TLAS(I)=TLAS(I)/1.9

IP=TLAS(I)/SQRT(I1,I,J)

COLMN(I,J)=0.5*(C12*(L1+1)+C10)*LOG(T)

OK(I,I)=.9553**4*(TLAS(I)**2.5*D2P(I,J,J)**.5/TLAS(I)**

2 SIGSQ(I,J)+COLMN(I,J,J))

TLAS(I1)=TLAS(I1)*1.9

OK(I,J)=.95(I,J)**1.375*TLAS(I1)**2.6

IF(CIFOPF=1,1)DP(I,J,J)=66(1,2)

IF(CIFOPF=1,2)DP(I,J,J)=66(1,2)

611 CONTINUE

620 CONTINUE

IF(II=I0KOF(I1)-0.1)636,638,639

II=II+K

IF(II=I0KOF(I1))64,643,646

II=II-K

IF(II=I0KOF(I1))64,643,646

II=II-JJ

GO TO 634

II=II+JJ

GO TO 634

636 CONTINUE

638 CONTINUE

639 CONTINUE

64 CONTINUE
6376    DD 6377  II=1,KKK
  2Cn=10CFLX(III,II)-XLAS(III,II)*TOTALF(II)/SUMCEF(III,II)
  QM(II,II)=DEL5F=2DLILCCH)/(BLOG((2DLILCCH)+DELSP+DELRP))
  1/2CFL(LP1)/C3*XLAS(II,II)*(2DLILCCH)+DELPR)/(2DLILCCH)+3
  2DEL=(2FLRQII)/QM(II,II)

6377    CONTINUE
  GO TO 641

6380  DD 700  II=1,KKK
  DD 649  II=1,KKK
  DD 649  JJ=1,KKK
  IF (II=JJ) 654,677,638

6387  DD 6IF(II,JJ)=0.0
  GO TO 639

6394  DD 6IF(II, JJ)=XLAS(JJ, II)/QM(II, JJ)

6395  DD SUMCEF(II, II)=CEF(II, II)+SUMCEF(II, I)

6404  DD QM(II, II)=(2.0-XLAS(II, II))/SUMCEF(II, II)

6413    CONTINUE
  DD 642  II=1,KKK

6420  DD FLRQII=QM(II, II)*(LH+0E-35)/(QM(II, II)+1.0E-35)
  DD 2M(II)=QM(II, II)

       RETURN

       END
APPENDIX XII

PROPERTIES FOR GAS PHASE SPECIES

<table>
<thead>
<tr>
<th>Species</th>
<th>A</th>
<th>Bx(10²)</th>
<th>Cx(10)</th>
<th>Dx(10³)</th>
<th>Ex(10⁻⁴)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>6.952</td>
<td>-0.04576</td>
<td>0.09563</td>
<td>-0.2079</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCl</td>
<td>7.244</td>
<td>-0.1820</td>
<td>0.3170</td>
<td>-1.036</td>
<td>0</td>
<td>-22.063</td>
</tr>
<tr>
<td>HSCl₃</td>
<td>21.514</td>
<td>0.2325</td>
<td>0</td>
<td>0</td>
<td>-29.4</td>
<td>-123.7</td>
</tr>
</tbody>
</table>

VALUES FOR THE CRITICAL CONSTANTS

<table>
<thead>
<tr>
<th>Species</th>
<th>Vᵣ(cc/mole)</th>
<th>Tcᵣ(°K)</th>
<th>(e/k)ᵣ(°K)</th>
<th>a₁(A°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>64.5</td>
<td>33.26</td>
<td>25.61</td>
<td>3.372</td>
</tr>
<tr>
<td>HCl</td>
<td>86.9</td>
<td>324.56</td>
<td>249.91</td>
<td>3.725</td>
</tr>
<tr>
<td>HSCl₃</td>
<td>254.0</td>
<td>495.0</td>
<td>381.0</td>
<td>6.33</td>
</tr>
</tbody>
</table>

COEFFICIENTS FOR THE EQUILIBRIUM CONSTANT

<table>
<thead>
<tr>
<th>Species</th>
<th>A</th>
<th>-B(10⁻⁴)</th>
<th>Range</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSCl₃</td>
<td>6.85675</td>
<td>0.99496</td>
<td>200-1500 °K</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX XIII

PROPERTIES FOR SOLID SPECIES

VALUES FOR THE THERMAL CONDUCTIVITY AND DENSITY

<table>
<thead>
<tr>
<th>Species</th>
<th>A(BTU/ft hr°C)</th>
<th>B(BTU/ft hr°C²)</th>
<th>(#m/ft³)</th>
<th>(in/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>84.6125</td>
<td>0</td>
<td>145.314</td>
<td>2.33</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-1.35239</td>
<td>1.1498E4</td>
<td>248.432</td>
<td>2.61</td>
</tr>
<tr>
<td>Al₂O₃ (80%)</td>
<td>-1.23226</td>
<td>6.1728E3</td>
<td>198.746</td>
<td>-</td>
</tr>
</tbody>
</table>
APPENDIX XIV

CALCULATION OF THE AVERAGE PRESSURE

For the problem chosen for this thesis, the pressure of the system is assumed to be independent of position within the porous medium. However, the pressure will change with time because solid silicon is either deposited or depleted within a closed container. For the reaction system chosen, the quantity of the element hydrogen will remain constant for all time. With this fact, the value for the pressure at any time can be calculated as follows.

In an incremental volume of porous medium, $edV$, the amount of elemental hydrogen, $dX$, is calculated from the following equation.

$$\rho \bar{ω}_H \, edV = dX \tag{A13-1}$$

where

$$dV = \pi L_0 \, rdr \tag{A13-2}$$

and $L_0$ is the length of the cylinder.

The term $\bar{ω}_H$ can be calculated from the following equation:

$$\bar{ω}_H = \frac{ω_{HCl}}{M_{HCl}} + \frac{ω_{H_2}}{M_{H_2}} + \frac{ω_{SiCl_4}}{M_{SiCl_4}} \tag{A13-3}$$

Inserting the ideal gas law and the last two equations into equation A13-1 gives:

$$\frac{PM_{H_2}}{RT} \left( \frac{ω_{HCl}}{M_{HCl}} + \frac{ω_{H_2}}{M_{H_2}} + \frac{ω_{SiCl_4}}{M_{SiCl_4}} \right) \pi r L_0 \, dr = dX \tag{A13-4}$$
If the pressure is assumed to be independent of position, the total amount of elemental hydrogen can be obtained by integrating equation A13-4 over the limits of the radii bounding the porous medium as follows:

\[ X = \bar{P} \frac{2\pi L_0}{R} \int_{R_e}^{R_p} \frac{\varepsilon M_w}{T} \left( \frac{\omega_{H_2}}{M_{H_2}} + \frac{\omega_{H_2}}{M_{H_2}} \right) r \, dr \]  

(A-13-5)

where \( \bar{P} \) is the average pressure at time \( t \).

In the problem at hand, all quantities within the integral are constant with respect to position so \( \frac{X}{L_0} \) can be obtained as follows:

\[ \frac{X}{L_0} = \frac{\varepsilon_0 \rho_0 M_w}{R T_0} \bar{\omega}_o \pi \left( R_p^2 - R_e^2 \right) \]  

(A-13-6)

Equation A13-5 can be rearranged to calculate the average pressure at any time.

\[ \bar{P} = \frac{X}{L_0} \frac{R}{2\pi} \int_{R_e}^{R_p} \frac{\varepsilon M_w}{T} \left( \frac{\omega_{H_2}}{M_{H_2}} + \frac{\omega_{H_2}}{M_{H_2}} \right) r \, dr \]  

(A-13-7)
LITERATURE CITED


VITA

Allen Charles Merritt was born October 19, 1945 in Fort Collins, Colorado. The author attended the United States Military Academy and the Georgia Institute of Technology from which he received a Bachelor of Chemical Engineering degree in 1967.

The author was employed by the Proctor and Gamble Company as a summer engineer for two summers, served as a Lieutenant in the Air Defense Artillery of the United States Army, and was then employed as an Assistant Research Engineer with the Engineering Experiment Station. During this period the Master of Science in Chemical Engineering was completed at the Georgia Institute of Technology in 1969. The author has served as Manager of Technical Services for Gold Kist Incorporated since 1972.