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# SPIN

## A PROGRAM FOR MODELING ONE-DIMENSIONAL ROTATING-DISK / STAGNATION-FLOW CHEMICAL VAPOR DEPOSITION REACTORS

**Reaction Design** 

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Reaction Design cautions that some of the material in this manual may be out of date. Updates will be available periodically on Reaction Design's web site. In addition, on-line help is available on the program CD. Sample problem files can also be found on the CD and on our web site at www.ReactionDesign.com.

SPI-036-1

## SPIN: A PROGRAM FOR MODELING ONE-DIMENSIONAL ROTATING-DISK/STAGNATION-FLOW CHEMICAL VAPOR DEPOSITION REACTORS

## ABSTRACT

The SPIN program computes species, temperature and velocity profiles, as well as deposition rates in a steady-state, one-dimensional rotating disk or stagnation-point flow chemical vapor deposition (CVD) reactor. The program accounts for finite-rate gas-phase and surface chemical kinetics and multicomponent molecular transport. The governing differential equations form a two-point boundary value problem. After discretization by a finite difference procedure, the resulting nonlinear algebraic equations are solved by a modified Newton algorithm. The Newton algorithm is implemented in a software package called TWOPNT. SPIN also runs in conjunction with the CHEMKIN, SURFACE CHEMKIN and TRANSPORT Utility software packages that facilitate definition of the gas-phase and surface chemical reaction mechanisms and transport properties. Discussion of an example problem illustrates many of the program's capabilities.

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## NOMENCLATURE

		CGS Units
$a_i$	Scaled radial velocity (V) at the inlet	1/sec
$a_k$	Activity of <i>k</i> th bulk-phase species	none
$A_i$	Pre-exponential factor in the rate constant of the <i>i</i> th reaction	depends on reaction
$c_p$	Specific heat at constant pressure for the gas mixture	ergs∕(g K)
$c_{pk}$	Specific heat at constant pressure for the $k$ th species	ergs/(g K)
$C_{pk}^{o}$	Standard state specific heat at constant pressure of the <i>k</i> th species	ergs/(mole K)
$D_{km}$	Mixture-averaged diffusion coefficient	cm <sup>2</sup> /sec
$D_k^T$	Thermal diffusion coefficient	g/(cm-sec)
$D_{jk}$	Binary diffusion coefficient between species $j$ and $k$	cm²/sec
$E_A$	Activation energy	ergs/mole
G	Bulk growth rate	cm/sec
$h_k$	Specific enthalpy of the <i>k</i> th species	ergs/g
$h_m$	Heat transfer coefficient	gm∕(sec³ K)
i	Reaction index	
Ι	Total number of reactions	
J	Total number of grid points	
$j_k$	Flux of gas-phase species k into the surface	mole/(cm <sup>2</sup> -sec)
k	Species index	
Κ	Total number of species	
$K_b$	Total number of bulk species	
$K_b^f$	Index of the first bulk-phase species in the first bulk phase	
$K_b^l$	Index of the last bulk-phase species in the last bulk phase	
Kg	Total number of gas-phase species	
$K_g^f$	Index of the first gas-phase species	
$K_{g}^{l}$	Index of the last gas-phase species	
$K_s$	Total number of surface species	
$K_s^f$	Index of the first surface-phase species in the first surface phase	
$K_s^l$	Index of the last surface-phase species in the last surface phase	
K <sub>phase</sub>	Vector containing the number of species in each phase	
$K_{ci}$	Equilibrium constant in concentration units for the <i>i</i> th reaction	depends on reaction
$K_{pi}$ M	Equilibrium constant in pressure units for the <i>i</i> th reaction Number of coefficients in polynomial fits to $C_p^o / R$	depends on reaction

$\overline{M}$	Mean molecular weight of a mixture	g/mole
$M_k$	Molecular weight of <i>k</i> th species	g/mole
$N_b$	Total number of bulk phases	
$N_b^{f}$	Index of the first bulk phase	
$N_b^l$	Index of the last bulk phase	
$N_s$	Total number surface phases	
$N_s^{f}$	Index of the first surface phase	
$N_s^l$	Index of the last surface phase	
0i	Scaled circumferential velocity (W) at the inlet	1/sec
Р	Pressure	dynes/cm <sup>2</sup>
Ė	Energy source term for heating of surface	ergs/(cm <sup>2</sup> -sec)
$p_m$	Spatially-varying component of pressure in radial momentum eqn.	dynes/cm <sup>2</sup>
Q	Net heat transfer from reactor to ambient	ergs/sec
$\dot{q}$	Total energy deposited into the gas from a heat source	ergs/(cm <sup>2</sup> -sec)
$q_i$	Rate of progress of the <i>i</i> th gas-phase reaction	moles/(cm <sup>3</sup> -sec)
R	Universal gas constant	ergs/(mole K)
r	Radial coordinate	cm
$\dot{s}_k$	Production rate of the <i>k</i> th species due to surface reactions	moles/(cm <sup>2</sup> -sec)
$S_q$	Spatially distributed thermal energy source	ergs/(cm <sup>3</sup> -sec)
t	Time	sec
Т	Temperature	K
$T_0$	Ambient temperature	K
$T_{surf}$	Surface temperature	К
$T_w$	Temperature to which the surface radiates	К
и	Axial velocity	cm/sec
V	Scaled radial velocity	1/sec
V	Volume	cm <sup>3</sup>
$V_c$	Correction velocity	cm/sec
$V_k$	Diffusion velocity of <i>k</i> th species	cm/sec
W	Scaled circumferential velocity	1/sec
$W_k$	Molecular weight of the <i>k</i> th species	g/mole
Ws	Half-width of the distribution of energy source term	cm
$X_k$	Mole fraction of the <i>k</i> th species	
x	Axial coordinate	
$[X_k]$	Molar concentration of the <i>k</i> th species	moles/cm <sup>3</sup>

- $x_s$  Position of the center of the energy source term
- $Y_k$  Mass fraction of the *k*th species
- $Z_k$  Site fractions of the *k*th species at a site

## **GREEK**

		CGS Units
λ	Thermal conductivity	erg/(cm K sec)
ρ	Mass density	g/cm <sup>3</sup>
$V_{ki}$	Stoichiometric coefficients of the <i>k</i> th reaction, $v_{ki} = v''_{ki} - v'_{ki}$	
$v'_{ki}$	Stoichiometric coefficients of the $k$ th reactant species in the $i$ th reaction	
$v_{ki}''$	Stoichiometric coefficients of the <i>k</i> th product species in the <i>i</i> th reaction	
$\dot{\omega}_k$	Chemical production rate of the <i>k</i> th species due to gas-phase reactions	moles/(cm <sup>3</sup> -sec)
$\sigma_k$	Number of surface sites a surface species occupies	
τ	Nominal residence time	sec

cm

10

## 1. INTRODUCTION

In a rotating-disk reactor a heated substrate spins (at typical speeds of 1000 rpm or more) in an enclosure through which the reactants flow. The rotating disk geometry has the important property that in certain operating regimes<sup>2</sup> the species and temperature gradients normal to the disk are equal everywhere on the disk. Thus, such a configuration has great potential for highly uniform chemical vapor deposition (CVD),<sup>3-5</sup> and commercial rotating disk reactors are common, particularly for materials processing in the microelectronics industry.

In certain operating regimes, the equations describing the complex three-dimensional spiral fluid motion can be solved by a separation-of-variables transformation<sup>5, 6</sup> that reduces the equations to a system of ordinary differential equations. Strictly speaking, the transformation is only valid for an unconfined infinite-radius disk and buoyancy-free flow. Furthermore, only some boundary conditions are consistent with the transformation (e.g., temperature, gas-phase composition and approach velocity all specified to be independent of radius at some distance above the disk). Fortunately, however, the transformed equations still provide a very good practical approximation to the flow in a finite-radius reactor over a large fraction of the disk (up to ~90% of the disk radius) when the reactor operating parameters are properly chosen, i.e., high rotation rates.<sup>2</sup>

In the limit of zero rotation rate, the rotating disk flow reduces to a stagnation-point flow, for which a similar separation-of-variables transformation is also available. Such flow configurations ("pedestal reactors") also find use in CVD reactors.

An infinite-radius disk rotating below a fluid medium is a classic problem in fluid mechanics.<sup>6-8</sup> Under these ideal conditions this problem has a solution that is an exact solution of the Navier-Stokes equations. Consequently, the heat and mass transfer near an infinite-radius rotating disk have been extensively studied.<sup>9, 10</sup> For CVD applications, Olander<sup>3</sup> used a rotating disk to study deposition in the germanium-iodide system. Pollard and Newman<sup>5</sup> performed a theoretical study of the deposition of Si from SiCl<sub>4</sub> on a rotating-disk susceptor. They extended the von Karman similarity solution for isothermal flow<sup>6</sup> by adding energy and species equations and incorporating temperature-dependent fluid properties to obtain an ordinary differential equation boundary-value problem for the heat, mass and momentum transfer. Hitchman et al.<sup>4</sup> studied epitaxial Si deposition from SiCl<sub>4</sub> in a rotating-disk reactor and analyzed their results in terms of the infinite-disk solution.

In Chapter 2 of this manual we describe a model formulation and mathematical analysis of rotating-disk and stagnation-point CVD reactors. Chapter 3 then shows how this analysis approach is implemented in the SPIN program, while Chapters 4 and 5 provide instructions for using the SPIN software. Chapter 6 discusses post-processing options. Finally, Chapter 7 provides an illustrative sample problem. In Chapter 2 we begin with the transformation (which is valid for either the rotating-disk or stagnationpoint flow) derived by Evans and Greif<sup>11</sup> and then extend the analysis to include the coupling of fluid flow with chemical kinetics.<sup>12</sup> In addition to the fluid mechanics, the model formulation includes the production and depletion of species due to reactions in the gas-phase and at the surface, convective and diffusive transport of species in the gas-phase, and transport to the deposition surface. The numerical model predicts deposition rates and gas-phase chemical species density profiles, surface coverages, gas velocities and temperature profiles as a function of process parameters such as susceptor (i.e., the disk) temperature, disk-rotation rate, pressure and flow rates.

The SPIN software depends on several other software packages in the CHEMKIN Collection. The chemical source terms in the governing equations are provided by the CHEMKIN Gas-phase Subroutine Library. The transport properties (viscosities, thermal conductivities, thermal diffusion coefficients and diffusion coefficients) are evaluated with the TRANSPORT Subroutine Library. The surface-reaction chemistry is modeled using the SURFACE CHEMKIN Subroutine Library. The numerical solution algorithm is implemented in the TWOPNT software. Familiarity with these software packages is essential to preparing reaction mechanisms and other input for use in SPIN. The CHEMKIN Collection has associated preprocessor programs, databases and subroutine libraries. Thus, using the SPIN program requires the user to establish certain linkages between all the required modules, as discussed in Chapter 4

The problem formulation and solution technique for the SPIN problem is highly analogous to the approach taken to solve laminar premixed flame problems for combustion applications. The computational approach for these problems is documented in Grcar et al.<sup>13</sup> and in Miller et al.<sup>14</sup> The software implementation of the flame model is documented in the user's manual for PREMIX, which is part of the CHEMKIN Collection. Those familiar with PREMIX will see similarities in the SPIN software.

## 2. ROTATING-DISK/STAGNATION-POINT FLOW EQUATIONS

Consider a solid rotating surface of infinite extent in the r,  $\theta$  plane (Figure 1) separated from a facing, parallel, porous, non-rotating surface by a distance x=L. A forced flow with purely axial velocity emerges from the porous surface and is directed toward the rotating one. The flow at x=L approximates the inlet flow conditions in a cylindrical, rotating-disk CVD reactor. The finite x domain in the present case results in a nonzero value of the radial pressure gradient.

Prior analyses were limited in that there was no flexibility in specifying the inlet velocity. A recent analysis by Evans and Greif<sup>11</sup> combined the stagnation and rotating disk flows for the situation of an infinite-radius, porous, non-rotating disk separated by a distance L from an infinite-radius, nonporous, heated, rotating disk. This combination of flows provides a good approximation to the flow field in a rotating disk reactor. The Evans and Greif analysis forms the foundations for the present model development. However, since predicting details of the chemical kinetics behavior is a main objective here, the present system also incorporates a species conservation equation for each species that occurs in the gas phase.<sup>12</sup> These equations account for convective and diffusive transport of species, as well as production and consumption of species by elementary chemical reactions. The conservation equations defining the boundary-value system that we solve are stated below.

Mixture continuity:

$$\frac{1}{\rho}\frac{\partial\rho}{\partial t} = -\frac{\partial u}{\partial x} - 2V - \frac{u}{\rho}\frac{\partial\rho}{\partial x} = 0$$
(1)

Radial momentum:

$$\rho \frac{\partial V}{\partial t} = \frac{\partial}{\partial x} \left( \mu \frac{\partial V}{\partial x} \right) - \rho u \frac{\partial V}{\partial x} - \rho \left( V^2 - W^2 \right) - \frac{1}{r} \frac{dp_m}{dr} = 0$$
<sup>(2)</sup>

Circumferential momentum:

$$\rho \frac{\partial W}{\partial t} = \frac{\partial}{\partial x} \left( \mu \frac{\partial W}{\partial x} \right) - \rho u \frac{\partial W}{\partial x} - 2\rho V W = 0$$
(3)

Thermal energy:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) - \rho c_p u \frac{\partial T}{\partial x} - \sum_{k=1}^{K_g} \left( c_{pk} \rho Y_k V_k \frac{\partial T}{\partial x} + \dot{\omega}_k h_k \right) + S_q(x) = 0$$
(4)



Figure 1. Sketch of the infinite-radius disk and inlet boundary conditions.

Species continuity:

$$\rho \frac{\partial Y_k}{\partial t} = -\frac{\partial \rho Y_k V_k}{\partial x} - \rho u \frac{\partial Y_k}{\partial x} + M_k \dot{\omega}_k = 0 \quad (k = 1, \dots, K_g)$$
(5)

Equation of state:

$$P = \frac{\rho RT}{\overline{M}} \tag{6}$$

Surface-species conservation:

$$\frac{dZ_k}{dt} = \frac{\dot{s}_k}{\Gamma_n} = 0 \quad (k = 1, \dots, K_s)$$
<sup>(7)</sup>

The objective of the SPIN software is to solve a steady-state problem, not a time-dependent one. Nevertheless, periodically the solution algorithm calls for computing a transient response. Therefore, the governing equations are stated in their transition form, even though we seek the solution when all time derivatives are exactly zero. The solution algorithm is discussed further in the Chapter 3.

In the governing equations the independent variables are *x*, the distance normal to the disk surface, and *t*, time. The dependent variables are the velocities, the temperature *T*, the gas-phase species mass fractions

 $Y_{k}$ , and the surface-species site fractions  $Z_{k}$ . The axial velocity is u, and the radial and circumferential velocities are scaled by the radius as V=w/r and W=w/r, respectively. The mass density is given by  $\rho$  and the specific heats by  $c_{p}$ . The molecular weight and specific enthalpy for species k are given by  $M_{k}$  and  $h_{k}$ . The viscosity and thermal conductivity are given by  $\mu$  and  $\lambda$ . The universal gas constant is R. The chemical production rate of species  $\dot{\omega}_{k}$  by the gas-phase reaction is resumed to result from a system of elementary chemical reactions that proceed according to the law of mass action. The chemical production rate of species by surface reaction is given by  $\dot{s}$ .  $K_{g}$  is the number of gas-phase species and  $K_{s}$  is the number of surface species, not including bulk-phase species. The factor  $\Gamma_{n}$  is the surface site density for site type n. The details of the chemical reaction rate formulation can be found in the users manuals for the CHEMKIN and SURFACE CHEMKIN software, which is part of the CHEMKIN Collection. Details of the transport property (i.e., viscosities, thermal conductivities and diffusion coefficients) formulation can be found in the user's manual for the TRANSPORT program, also part of the CHEMKIN Collection.

The term  $(1/r)(dp_m/dr) \equiv A$  in the radial momentum equation is taken to be constant and its value is computed as an eigenvalue of the problem. The pressure is assumed to be composed of two parts: an average thermodynamic pressure *P* that is taken to be constant, and a spatially varying component  $p_m$  that appears in the radial momentum equation (2) (c.f. Paolucci<sup>15</sup>).

The "surface-species conservation" equation states simply that in steady state the surface composition does not change. In some sense it could be considered a (possibly complex) boundary condition on the gas-phase system. However, because the surface composition is determined as part of the solution, Eq. (7) should be considered part of the system of governing equations.

SPIN makes provisions for dealing with the transport properties at the mixture-averaged (Fickian) level or at the full multicomponent level. At the mixture-averaged level, each species diffusion velocity is calculated in terms of a diffusion coefficient and a species gradient,

$$V_{k} = -\frac{1}{X_{k}} D_{km} \frac{dX_{j}}{dx} - \frac{D_{k}^{T}}{\rho Y_{k}} \frac{1}{T} \frac{dT}{dx} , \qquad (8)$$

where,

$$D_{km} = \frac{1 - Y_k}{\sum_{j \neq k}^{K} \frac{X_j}{D_{jk}}}$$
 (9)

At the multicomponent level, the diffusion velocities are given as

$$V_{k} = \frac{1}{X_{k}\overline{M}} \sum_{j=1}^{K_{g}} M_{j} D_{kj} \frac{dX_{j}}{dx} - \frac{D_{k}^{T}}{\rho Y_{k}} \frac{1}{T} \frac{dT}{dx}.$$
 (10)

Both formulations have an ordinary diffusion component and may have a thermal diffusion (Soret effect) component. In these expressions,  $X_k$  is the mole fraction for the *k*th species,  $D_{jk}$  is the binary diffusion coefficient matrix,  $D_{kj}$  is the matrix of ordinary multicomponent diffusion coefficients, and  $D_k^T$  is the thermal diffusion coefficient for the *k*th species. Thermal diffusion often plays an important role in CVD problems. In the presence of strong temperature gradients, thermal diffusion causes high molecular-weight species in a low molecular-weight carrier to diffuse rapidly toward the low-temperature region.<sup>16</sup> The multicomponent and mixture transport properties are evaluated from the pure species properties using the averaging procedures given by Dixon-Lewis<sup>17</sup> computed with the TRANSPORT package of FORTRAN subroutines.

Mass conservation requires that  $\sum_{k=1}^{K_s} Y_k V_k = 0$ . However, a consequence of using the Fickian mixtureaveraged diffusion coefficient defined in Eq. (9) to define a diffusion velocity in Eq. (8) is that mass is not always conserved, i.e.,  $\sum_{k=1}^{K_s} Y_k V_k \neq 0$ . Therefore, at this level of closure of the transport formulation, some corrective measures must be taken. The user of SPIN has several options. One is for the program to apply an ad hoc correction velocity, defined as

$$V_c = -\sum_{k=1}^{K} Y_k V_k . (11)$$

When this correction velocity (independent of species k) is added to all the species diffusion velocities as computed from Eq. (8), mass conservation is assured.

Another option in SPIN is to account for the deficiencies of the mixture-averaged closure of the multicomponent transport problem and to assure mass conservation is to solve only  $K_g$ -1 gas-phase species conservation equations and determine the remaining mass fraction by requiring  $\sum_{k=1}^{K_g} Y_k = 1$ . (The mixture-averaged transport closure is asymptotically correct in the trace-species limit.) In cases where one species is present in large excess (such as a carrier gas in a CVD reactor), this is a reasonable option. The carrier gas composition is conventionally determined as

$$Y_{K_g} = 1 - \sum_{k=1}^{K_g - 1} Y_k \ .$$

The default for this option is to consider the last-named gas-phase species in the CHEMKIN input ( $K_g$ ) as the species for which a conservation equation is not solved. SPIN also provides for dynamically determining the largest species concentration at each mesh point and removing its conservation equation from the system of equations. Invoking any of these options is accomplished by using combinations of the keywords described in Chapter 5.

The source term in the thermal energy equation  $S_q(x)$  is a spatially distributed thermal energy source tat we assume is in the form of a Gaussian:

$$S_q(x) = \dot{q} \frac{1}{w_s} \sqrt{\frac{3}{\pi}} \exp\left[\frac{-3(x-x_s)^2}{w_s^2}\right].$$
 (12)

To use this expression, the user is expected to specify three parameters:  $\dot{q}$ ,  $w_s$  and  $x_s$ . The parameter  $\dot{q}$  is the total energy integrated over its full spatial extent. Implicit in Eq. (12) is the fact that

$$\dot{q} = \int_{-\infty}^{\infty} S_q(x) dx \,. \tag{13}$$

The distribution is centered at  $x=x_s$  and  $w_s$  is the  $2\sigma$  half-width of the distribution. (The integral of  $S_q(x)$  from  $-w_s$  to  $w_s$  includes 95% of the total added energy  $\dot{q}$ .)

The disk boundary condition becomes relatively complex in the presence of heterogeneous surface reactions. The gas-phase mass flux of each species to the surface  $j_k$  is balanced by the creation or depletion of that species by surface reactions, i.e.,

$$j_k = \dot{s}_k M_k \quad (k = 1, \dots, K_g).$$
 (14)

The gas-phase mass flux of species *k* at the surface is a combination of diffusive and convective processes,

$$j_{k} = \rho Y_{k} u + \rho Y_{k} V_{k} \quad (k = 1, \dots, K_{g}),$$
 (15)

where *u* is the bulk normal fluid velocity at the surface and  $V_k$  is the diffusion velocity of the *k*th species. The bulk normal fluid velocity at the surface is computed from the surface reaction rates summed over all the gas-phase species  $K_{g}$ ,

$$u = \sum_{k=1}^{K_g} \frac{\dot{s}_k M_k}{\rho} \,. \tag{16}$$

Even though the susceptor surface is solid, there is a bulk fluid velocity into the surface (the Stefan velocity) that accounts for the mass of solids deposited. This bulk velocity at the surface is usually small, and thus the boundary movement due to the deposition is neglected. That is, the problem is solved in a

fixed spatial domain. While SPIN predicts the surface growth rate, it does not adjust the computational domain to account for small changes resulting from surface growth.

SPIN provides two options for treating the thermal-energy boundary condition on the deposition surface. The first is to simply specify the surface temperature. If the temperature is controlled or measured directly, this option is usually the one of choice. However, some problems require that the surface temperature be predicted as part of the solution. The appropriate boundary condition is derived from a surface energy balance. Exothermicity (or endothermicity) of surface reactions contributes to the energy balance at an interface. Diffusive and convective fluxes in the gas-phase are balanced by thermal radiative and chemical heat release at the surface. This balance is stated as

$$\lambda \frac{\partial T}{\partial x} - \sum_{k=1}^{K_g} \rho Y_k \left( V_k + u \right) h_k = \sigma \varepsilon \left( T^4 - T_w^4 \right) + \sum_{k=K_s^f}^{K_b^f} \dot{s}_k M_k h_k + \dot{P} \,. \tag{17}$$

In the radiation term,  $\sigma$  is the Stefan-Boltzmann constant,  $\varepsilon$  is the surface emissivity, and  $T_w$  is the temperature to which the surface radiates. The summation on the right-hand side runs over all surface and bulk species.  $K_s^f$  and  $K_b^l$  are the SURFACE CHEMKIN notations for the indices that identify the first surface species and the last bulk species. By substituting Eqs. (14) and (15) into Eq. (17), the energy balance can be written in a more compact form as

$$\lambda \frac{\partial T}{\partial x} = \sigma \varepsilon \left( T^4 - T_w^4 \right) + \sum_{k=1}^K \dot{s}_k M_k h_k + \dot{P} .$$
<sup>(18)</sup>

The reaction-rate summation on the right-hand side runs over all species, including the gas-phase species. The term  $\dot{P}$  represents an energy source in the surface itself, such as might be generated by resistance heating.

The SURFACE CHEMKIN package requires as input the mass densities  $\rho_k$  of the bulk species. The SPIN application uses these densities to convert the rate of production of a bulk species (in moles/cm<sup>2</sup>/sec) into a thickness growth rate *G* (in cm/sec). The needed relationship is

$$G = \sum_{k=K_b^f}^{K_b^f} \frac{\dot{s}_k M_k}{\rho_k} \,.$$
(19)

When solving for the flow induced by the rotation of a disk in an infinite, otherwise quiescent fluid, the axial velocity u at x=L is part of the solution. However, for the case corresponding to injection of the gas through a non-rotating porous surface, u is the specified inlet velocity at height x=L. This gives us the flexibility of either "forcing" or "starving" the inlet flow compared to the natural flow induced by the

spinning disk itself. It is always necessary to specify the inlet velocity in the case of a stagnation-point flow.

The other boundary conditions on the fluid flow fields are relatively simple. The temperature at x=L (the reactor inlet) is specified. Normally, the radial and circumferential velocities are zero at x=L. However, SPIN makes the provision for a linearly varying radial velocity or a specified spin rate at x=L. In these cases,  $V=v/r=a_i$  or  $W=w/r=o_i$ , where  $a_i$  and  $o_i$  are specified parameters. The radial velocity on the disk is zero, and the circumferential velocity is determined from the spinning rate  $W=\Omega$ . For the species composition at the inlet boundary, the default formulation is for SPIN to solve the following flux balance:

$$\rho u \varepsilon_k = \rho u Y_k + \rho Y_k V_k \tag{20}$$

where  $\varepsilon_k$  is the species mass fraction specified for the inflow. The user may also opt to fix the species composition (i.e.,  $Y_k = \varepsilon_k$ ), by including the keyword COMP.

## 3. NUMERICAL SOLUTION METHOD

The TWOPNT software provides the implementation of the hybrid Newton/time-step algorithm that we use to solve the governing equations in SPIN. In this section we only summarize the salient features of the algorithm and refer to the TWOPNT manual for more detail.

The numerical solution procedure begins by making finite difference approximations to reduce the ordinary differential equation boundary value problem to a system of algebraic equations. The initial approximations are usually on a coarse mesh that may have as few as five or six points. After obtaining a solution on the coarse mesh, new mesh points are added in regions where the solution or its gradients change rapidly. An initial guess for the solution on the finer mesh is obtained by interpolating the coarse mesh solution. This procedure continues until no new mesh points are needed to resolve the solution to the degree specified by the user. This continuation from coarse to fine meshes significantly enhances the efficiency of the algorithm. The damped modified Newton algorithm first attempts a solution to the system of algebraic equations. However, if the Newton algorithm fails to converge, then the solution estimate is conditioned by time integration. This provides a new starting point for the Newton algorithm that is closer to the solution, and thus more likely to be in the domain of convergence for Newton's method. As the mesh becomes finer, the estimate interpolated from the previous mesh is likely to be within the domain of convergence of Newton's method.

There are many controls that can be used to influence the course of the Newton search and the time evolution. Most have default values that need not be changed for most problems. However, for difficult problems, the user may need to consult Keyword Sections 5.3 or 5.4 to help TWOPNT cope with convergence difficulties.

### 3.1 Finite Difference Approximations

The first task in solving the deposition problem is to discretize the governing conservation equations. We use finite difference approximations on a non-uniform grid with points numbered by j from 1 at the disk boundary to J at the inlet boundary.

The "convective" terms, such as  $\rho u \partial V / \partial x$  in Eq. (2) are approximated by first-order upwind formulas, as

$$\rho u \frac{\partial V}{\partial x} \approx \rho_j u_j \left( \frac{V_{j+1} - V_j}{x_{j+1} - x_j} \right).$$
(21)

The *u* velocity is always negative in these problems (flowing from the inlet at large values of *x* toward the substrate at x=0), so the upwind differencing calls for the derivative to be formed between j+1 and j. Upwind differences cause substantial artificial diffusion, especially on coarse mesh networks. However, we have found that they lead to much more reliable convergence on coarse meshes early in the iteration procedure. Ultimately, because the meshes are adaptively refined, the artificial diffusion is very small in the final solution.

The first derivative in the summation term in the energy equation (4) is always approximated by a central difference formula,

$$\left(\frac{\partial T}{\partial x}\right)_{j} \approx \left(\frac{h_{j-1}}{h_{j}(h_{j}+h_{j-1})}T_{j+1} + \frac{h_{j}-h_{j-1}}{h_{j}h_{j-1}}T_{j} - \frac{h_{j}}{h_{j-1}(h_{j}+h_{j-1})}T_{j-1}\right),\tag{22}$$

where the mesh intervals  $h_j = x_{j+1} - x_j$ . The coefficients in the summation are evaluated at *j*.

The second-derivative diffusion terms, such as that in the energy equation, are approximated by the following second order central difference:

$$\frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right)_{j} \approx \left( \frac{2}{x_{j+1} - x_{j-1}} \right) \left[ \lambda \left( \frac{T_{j+1} - T_{j}}{x_{j+1} - x_{j}} \right) - \lambda \left( \frac{T_{j} - T_{j-1}}{x_{j} - x_{j-1}} \right) \right].$$
(23)

The coefficient  $\lambda$  in this formula (at  $j \pm 1/2$ ) are evaluated using the averages of the dependent variables between mesh points.

The diffusive terms in the species conservation equations are analogous to the diffusive term in the energy equation. However, because we express them in terms of diffusion velocities, they at first appear different. In Eq. (5), the diffusive term is approximated as

$$\frac{\partial \rho Y_k V_k}{\partial x} \approx \frac{\rho_{j+1/2} Y_{k,j+1/2} V_{k,j+1/2} - \rho_{j-1/2} Y_{k,j-1/2} V_{k,j-1/2}}{x_{j+1/2} - x_{j-1/2}}.$$
(24)

The ordinary multicomponent diffusion and thermal diffusion fluxes (Eq. 10) are approximated at the  $j \pm \frac{1}{2}$  positions as illustrated by

$$(\rho Y_k V_k)_{j+1/2} = \left(\frac{\rho M_k}{\overline{M}^2}\right)_{j+1/2} \sum_{l=1}^{K_k} (M_l D_{k,l})_{j+1/2} \left(\frac{X_{l,j+1} - X_{l,j}}{x_{j+1} - x_j}\right) + \left(\frac{D_k^T}{\rho Y_k T}\right)_{j+1/2} \left(\frac{T_{j+1} - T_j}{x_{j+1} - x_j}\right).$$
(25)

An analogous finite-difference expression is used for the mixture-averaged approximation to the diffusion fluxes. Since the mole fraction of a species can be zero, we avoid difficulties by forming  $\rho YkVk$ , which is the expression needed in Eq. (4), rather than  $V_k$  itself ( $Y_k = X_k M_k / \overline{M}$ ).

All the non-differentiated terms, such as the chemical production rate terms, are evaluated at the mesh points *j*. Coefficients not appearing within derivatives are also evaluated at the mesh points.

#### 3.2 Starting Estimates

SPIN needs a starting estimate of the solution from which to begin its iteration. The general form of this estimate is shown in Figure 2. The estimate assumes there is a reaction zone in which the inlet gas composition changes to the product composition. The user estimates the location and thickness of this reaction zone and the composition of the products. Within the reaction zone the program uses linear interpolation between the initial and final values for the reactants and products. On the inlet side of the reaction zone the reactant species profiles are flat at the inlet values. On the disk side, the product species are flat at the estimated product values. Note that a species can be both reactants and products in a silicon deposition system. Species can also be identified as "intermediates". Intermediates, such as short-lived radical species, are assumed to have a Gaussian profile that peaks in the center of the reaction zone. The peak height is specified in the input to the program, and the Gaussian's width is such that the profile is at 1/10 of its peak value at the edges of the reaction zone.

We find that the shape of the assumed initial species profiles is not too important. Smoother shapes have no apparent effect on the convergence properties of the method. Moreover, since the starting profiles are typically evaluated on a very coarse mesh, it makes little difference whether the underlying functions are smooth or not.



Figure 2. The general form of the starting estimate.

### 3.3 Continuation Start-up Procedure and User-Specified Temperature Profile

It is sometimes preferred to model the deposition using a known temperature profile. For example, temperature data may be available experimentally and using them may facilitate interpreting chemistry data from the reactor. If a specified temperature profile is used the energy equation is not solved. There are computational advantages to using a known temperature profile. The most severe non-linearities in chemical kinetics come from the exponential dependence on temperature of the reaction rates. Thus, eliminating temperature from the iteration makes the problem considerably easier to solve.

We find that even if the energy equation is to be solved for the temperature distribution, the iteration often converges more reliably if the species profiles are first computed using a fixed temperature profile. SPIN therefore provides for the following three-stage procedure to solve the fully coupled problem. However, either or both the first two stages can be skipped by using appropriate Keywords.

The program solves for just the velocity fields (and temperature, if not specified as fixed using the TEMP and TGIV Keywords), neglecting all chemistry and species equations. For chemical vapor deposition problems where there is a large non-reacting carrier gas concentration, the non-reacting problem provides a good approximation of the temperature and velocity fields. This stage may be bypassed by using the NONR Keyword.

The full set of species and flow equations is solved, using the temperature field from the first step and ignoring the energy equation. Especially for problems with large carrier-gas concentrations, the temperature profile from step one is usually quite close to the final profile, and omitting the energy equation at this point eases solution by eliminating a strong non-linearity (due to the Arrhenius form of the rate expressions). If the TGIV Keyword is used, the temperature profile used at this stage is the one specified through the TEMP Keywords. This stage can be bypassed by using the NOFT Keyword.

The energy equation is included and the fully coupled problem is solved, using the output from stage two as the initial guess. If the temperature profile was specified using the TGIV, TEMP combination, this stage is skipped because stage 2 completes the calculation. This multi-stage continuation procedure is usually more efficient than attempting to solve the fully coupled problem directly.

The user input for the temperature profiles is in the form of position-temperature pairs. In general, the mesh used by the SPIN program will not be the same as the one on which the given temperature estimate is defined. The program uses a linear interpolation of the given temperatures onto the current mesh. Thus, especially in the case where the energy equation is not included, it is important for the user to provide enough temperature points that the profile is well resolved and relatively smooth.

#### 3.4 Modified Damped Newton's Method

The TWOPNT software implements the computational algorithms, which are documented completely in the TWOPNT users manual. In this and the following sections, the solution method is introduced briefly – mainly to establish some nomenclature for the keywords and the sensitivity analysis.

After discretization on a given mesh, we have a system of nonlinear algebraic equations that we attempt to solve by a damped Newton's method. Newton's method determines a sequence of iterations or approximate solutions that approach the true solution. For the sake of notational ease we call these approximate solution vectors  $\phi$ . When any arbitrary  $\phi$  is substituted into the finite difference analog of Eqs. (1-7), they do not equal zero as they would if the true solution were substituted; in general they equal a residual vector that we will call *F*. Thus our purpose is to find a vector  $\phi$  that satisfies

$$F(\phi) = 0. \tag{26}$$

In our case the vector  $\phi$  is composed as follows:

$$\phi = (z, u_1, V_1, W_1, T_1, \Lambda_1, Y_{1,1}, \dots, u_J, V_J, W_J, T_J, \Lambda_J, Y_{1,J})^T .$$
(27)

The corresponding *F* vector is composed of the residuals of the surface species equations, energy equation, the velocity equations, the gas-phase species equations, and the pressure eigenvalue equation. The ordering of the *F* vector corresponds to the order of the  $\phi$  vector; it begins with the residuals of the surface species, then the residuals at the first node (the disk), followed by the residuals at the interior mesh points, and finally the residuals at the inlet boundary, *j*=*J*.

If the initial estimate  $\phi^{(n)}$  of the solution is sufficiently good, then Newton's method produces a sequence  $\{\phi^{(n)}\}$  that converges to the solution of the nonlinear equations  $F(\phi)$ . The purest form of the algorithm,

$$\phi^{(n+1)} = \phi^{(n)} - \left(\frac{\partial F}{\partial \phi}\right)_{\phi^{(n)}}^{-1} F(\phi^{(n)})$$
(28)

is too expensive and delicate to be used in practice. On the one hand, evaluation of the Jacobian matrices  $\partial F/\partial \phi$  by numerical or other means is time consuming, and on the other hand, convergence usually requires a very good initial estimate  $\phi^{(0)}$ . TWOPNT employs the usual remedies. First, the Jacobian matrix is replaced by one,  $J^{(n)}$ , inherited from a previous step of the algorithm. Second, the full step from  $\phi^{(n)}$  to  $\phi^{(n+1)}$  may be cut short by a damping parameter  $\lambda^{(n)}$ . In this way the iteration becomes

$$\phi^{(n+1)} = \phi^{(n)} - \lambda^{(n)} (J^{(n)})^{-1} F(\phi^{(n)})$$
(29)

where,  $0 < \lambda^{(n)} \leq 1$ , and

$$J^{(n)} = J^{(n-1)}$$
 or  $J^{(n)} = \left(\frac{\partial F}{\partial \phi}\right)_{\phi^{(n)}}$ . (30)

Of course, the inverse Jacobian matrix in Eq. (28) is not computed; instead a system of linear equations  $J^{(n)}\Delta\phi^{(n)} = F(\phi^{(n)})$  is solved for the undamped correction vector  $\Delta\phi^{(n)}$  using the LINPACK software.<sup>18</sup> The TWOPNT documentation provides a full description of the damping strategy.

#### 3.5 Jacobian Matrix

TWOPNT requires that the SPIN Application form Jacobian matrices and factor them into upper and lower triangular parts. The Jacobian is a large banded (actually block tridiagonal) matrix. In principle, we could derive and evaluate analytic expressions for the Jacobian elements. However, because this is a difficult and error-prone task, and because the modified Newton method can work well with old (and hence inaccurate) Jacobians, the effort to develop analytic Jacobian expressions is not warranted. Instead, we form the elements of the Jacobian by finite difference perturbations in the manner suggested by Curtis et al.<sup>19</sup> Specifically, we evaluate a one-sided finite difference formula,

$$J_{i,j} \approx \frac{F_i(\phi_j + \delta) - F_i(\phi_j)}{\delta},\tag{31}$$

where

$$\delta = r \times \phi_i + a \,. \tag{32}$$

We choose the relative and absolute perturbations, *r* and *a*, to be the square root of the computer's unit roundoff. These parameters, therefore, may depend on the user's particular computer. The Jacobian factorization is accomplished with the LINPACK software.

#### 3.6 Adaptation

We have found that starting the solution search on a coarse mesh has several advantages. One is that the Newton iteration is more likely to converge from a bad guess on a coarse mesh than on a fine mesh. Since the iteration begins from a user-specified "guess" at the solution, it is likely that many iterations will be required. But since the number of variables is small on a coarse mesh, the cost per iteration is relatively small. Ultimately, of course, the solution must be obtained on a fine mesh to be accurate. However, as the solution is computed on each successively finer mesh, the starting estimates are better and, in general, the solution on one mesh lies within the domain of convergence of Newton's method on the next finer mesh.<sup>20</sup> Thus, even though the cost per iteration is increasing on refined meshes, the number of required iterations is decreasing.

The adaptive placement of the mesh points to form the finer meshes is done in such a way that the total number of mesh points needed to represent the solution accurately is minimized. Specifically, we place the mesh points in the following way. We exclude variables that are essentially zero, but due to rounding errors may show locally high derivatives. To resolve the gradients we bound the variation in the solution components between mesh points as

$$\left|\phi_{n,j} - \phi_{n,j-1}\right| \leq \operatorname{GRAD} \times \left(\max \phi_n - \min \phi_n\right),\tag{33}$$

and to resolve the curvature in the solution we bound the variation in the solution's derivatives between mesh points by

$$\left| \left( \frac{d\phi_n}{dx} \right)_j - \left( \frac{d\phi_n}{dx} \right)_{j-1} \right| \le \text{CURV} \times \left( \max \frac{d\phi_n}{dx} - \min \frac{d\phi_n}{dx} \right).$$
(34)

In the program, we evaluate the above expressions between each of the mesh points. In each of the subintervals where the inequality is not satisfied, a new mesh point is placed at the midpoint of the subinterval. The parameters GRAD and CURV are specified by the user through Keyword parameters (Chapter 5). The starting estimate for the dependent variable vector  $\phi$  is determined by a linear interpolation of the coarse mesh solution onto the new finer mesh. After determining a converged solution on this new fine mesh, the adaptation procedure is performed once again. A sequence of solutions on successively finer meshes is computed until the inequalities in Eqs. (33) and (34) are satisfied between all mesh points.

#### 3.7 Time Stepping

Even though the transient path is not of interest here, the steady state deposition solution that we seek is the result of a physically transient process. Determining the steady solution by solving the transient equations is a very reliable, but often slow, process. Therefore, we attempt to use a Newton method that converges very rapidly, when it converges. When it does not, then we condition the guess by evolving it in time.

SPIN (through TWOPNT) solves the transient parabolic system of partial differential equations with a firstorder backward Euler method. In this method, the time derivatives are approximated by finite differences as illustrated by

$$\rho c_p \frac{\partial T}{\partial t} \approx \rho_j^{n+1} c_{pj} \frac{T_j^{n+1} - T_j^n}{\Delta t}, \qquad (35)$$

where the subscript *n* indicates the time level and  $\Delta t$  represents the size of the time step. All other terms are approximated with finite differences as before, but at time level *n*+1. Since all variables are known at time level *n*, the discretized problem is just a system of nonlinear algebraic equations for the dependent variable vector  $\phi$  at the time level *n*+1.

To solve the system for each time step we use the same Newton method that we attempted to use to solve the steady state boundary value problem in the first place. However, the transient problem is much more likely to converge. It should always converge for a sufficiently small time step. From a physical point of view, as the time step approaches zero, the solution for  $t^{n+1}$  should approach the initial condition or the solution at  $t^n$ ; thus, convergence should be rapid and reliable. From a mathematical point of view, the Jacobian of the transient system has a factor  $1/\Delta t$  on the diagonal. Therefore, the condition number of the Jacobian will be reduced as the time step is reduced. The objective is to choose a time step that is large enough to make progress toward the steady solution, but not so large that the transient method also has convergence difficulties. We typically use time steps of around one to ten microseconds, although there are often cases where much smaller time steps are needed.

Through communication via keywords, SPIN users can control the course of the transient solution. The number of time steps and their size can be specified, and the time step size can be increased by a certain factor after a certain number of steps. If convergence difficulties are encountered in attempting to solve any time step, SPIN will reduce the size of the time step by a factor specified by the user. All these control keywords are described in Chapter 5.

#### 3.8 Sensitivity Analysis

Sensitivity analysis is a way to understand quantitatively how the solution to a model depends on parameters in the model. Once the Jacobian of the residual function has been computed for the purposes of solving the boundary value problem, then the sensitivity coefficients can be computed easily. These techniques have been developed and used in the chemical engineering literature for some time.<sup>21-23</sup> We find that sensitivity analysis is often an invaluable tool in helping to interpret the results of a deposition model. Coffee and Heimerl<sup>24, 25</sup> have also discussed the use of sensitivity analysis in flame modeling, although their computational method is quite different from the one we use here. Also, Rueven et al.,<sup>26</sup> using model problems, have explored various ways that sensitivity analysis can be applied to flames. Here we consider the first order sensitivity coefficients of the solution profiles with respect to the reaction rate coefficients. To specify the sensitivity coefficients, let us begin with the boundary value problem stated in the abstract notation that we introduced in Eq. (26),

$$F(\phi;\alpha) = 0 \quad . \tag{36}$$

Note, however, that now we have introduced the idea that the equation may be parameterized by some parameters  $\alpha$ . In our case, these  $\alpha$ 's will be the "A-factors" of the reaction rate coefficients. By differentiating Eq. (36) with respect to  $\alpha$  we obtain a matrix equation for the sensitivity coefficients.

$$\frac{\partial F}{\partial \phi} \frac{\partial \phi}{\partial \alpha} + \frac{\partial F}{\partial \alpha} = 0.$$
(37)

The matrix  $\partial F/\partial \phi$  is the Jacobian of the original system and  $\partial F/\partial \alpha$  is the matrix of partial derivatives of *F* with respect to the parameters. We will think of the  $\partial F/\partial \alpha$  matrix column by column, with each column indicating the dependence of the residual vector *F* on a parameter. There are as many columns as there are parameters, i.e., reactions. The sensitivity coefficients are defined by  $\partial \phi/\partial \alpha$ . This matrix contains quantitative information on how each reaction rate coefficient affects the temperature and species profiles

at each point in the reactor. The sensitivity matrix has a structure similar to that of the  $\partial F/\partial \alpha$  matrix. That is, each column shows the dependence of the solution vector on a particular reaction rate coefficient. The Jacobian and its LU factorization are already available from the solution of the original system by Newton's method, and the parameter derivatives are computed by finite differences in a manner similar to computation of the Jacobian. Therefore, the linear system of equations (37) is readily solved for each column of the sensitivity matrix, corresponding to the sensitivities of the solution vector to each of the *I* reaction rates (gas plus surface reactions). The LINPACK software<sup>18</sup> is used to perform these computations. It is set up so that the Jacobian is factored only once, and each column of the sensitivity matrix is computed by back substitution, a relatively inexpensive operation.

We find that some manipulation of the raw sensitivity coefficients makes them more useful. We compute normalized sensitivity coefficients in the form of logarithmic derivatives, i.e.,

$$\frac{\alpha_i}{Y_k} \frac{\partial Y_k}{\partial \alpha_i} \tag{38}$$

or

$$\frac{\alpha_i}{T} \frac{\partial T}{\partial \alpha_i}.$$
(39)

In interpreting chemical information, we are more often interested in molar quantities, rather than mass quantities, so we compute the sensitivity coefficients in terms of mole fractions, i.e.,

$$\frac{\alpha_i}{X_k} \frac{\partial X_k}{\partial \alpha_i} = \frac{\alpha_i}{Y_k} \frac{\partial Y_k}{\partial \alpha_i} - \alpha_i \overline{M} \sum_{j=1}^K \frac{1}{M_j} \frac{\partial Y_k}{\partial \alpha_i}$$
(40)

where  $X_k$  are the mole fractions and  $\overline{M}$  is the mean molecular weight.

It is sometimes easier to interpret sensitivity coefficients that are normalized by the maximum value of a dependent variable rather than the local value. For example, we might modify Eq. (38) as

$$\frac{\alpha_i}{Y_k^{\max}} \frac{\partial Y_k}{\partial \alpha_i},\tag{41}$$

where  $Y_k^{\text{max}}$  is the maximum value of the *k*th species anywhere on the mesh. This normalization avoids artificially high sensitivity coefficients in regions where the mass fractions are approaching zero, and thus

subject to numerical errors. SPIN reports the normalized sensitivity coefficients as represented by Eqs. (39) and (40). Any further normalization can be done by the user in their own post-processing software. SPIN considers as parameters  $\alpha$  the forward rate constant "A-factors" for both the gas-phase and surface reaction mechanisms. Sensitivity coefficients are computed for all dependent variables at all mesh points (including the surface composition). Thus, one can determine the effect of all reactions on all components of the solution.

## 4. PROGRAM STRUCTURE

The CHEMKIN Application User Interface runs the SPIN program automatically through a mouse-driven interface and then allows the user to directly launch visualization of solution results using the CHEMKIN Graphical Post-processor. The SPIN program has a modular structure with interfaces to the CHEMKIN Utility package for obtaining kinetic, thermodynamic, and transport parameters. In addition to input directly from the user, SPIN depends on data obtained from the CHEMKIN Gas-phase, SURFACE CHEMKIN and TRANSPORT packages. Therefore, to solve a SPIN problem the user must first execute the three preprocessor programs, "chem", "tran" and "surf", which have access to thermodynamic and transport-property databases. SPIN then reads input from the user (described in Chapter 5), defines the governing equations, solves the equations, and prints resulting solutions. The CHEMKIN Graphical Post-processor can then be launched from the Application User Interface to plot solution data. Figure 3 shows the relationships between these components. For more information about the CHEMKIN Application User Interface or Graphical Post-processor, please see the CHEMKIN Getting Started manual.

The first step is to execute the CHEMKIN Interpreter, "chem". The CHEMKIN Interpreter first reads usersupplied information about the species and chemical reactions for a particular reaction mechanism. It then extracts further information about the species' thermodynamic properties from a database, "therm.dat". The user may also optionally input thermodynamic property data directly in the input file to the CHEMKIN Interpreter to override or supplement the database information. The information from the user input and the thermodynamic properties is stored in the CHEMKIN Linking File, "chem.asc"; a file that is needed by the TRANSPORT property fitting program, "tran", by the SURFACE CHEMKIN Interpreter, and later by the CHEMKIN subroutine library, which will be accessed by the SPIN program. The CHEMKIN Interpreter also writes text output (e.g. "chem.out") that includes a formatted display of the user input and diagnostic messages from the Interpreter.

The next program to be executed is the TRANSPORT property-fitting program, "tran". It needs input from a transport property database, "tran.dat" and from the CHEMKIN subroutine library. The user may also optionally input transport property data directly in a separate input file (e.g. "tran.inp") to override or supplement the database information. The purpose of the TRANSPORT fitting program is to compute polynomial representations of the temperature-dependent parts of the individual species viscosities, thermal conductivities, and the binary diffusion coefficients. Like the CHEMKIN Interpreter, the TRANSPORT property-fitting program produces a Linking File, "tran.asc" that is later needed in the transport property library routines, which will evaluate mixture properties during the course of the SPIN computation.



Figure 3. Relationship of the SPIN program to the CHEMKIN, SURFACE CHEMKIN, and TRANSPORT preprocessors and the associated input and output files.

The SURFACE CHEMKIN Interpreter must also be executed after the CHEMKIN Interpreter has been run, because it relies on gas-phase species and element information in the CHEMKIN Linking file. The SURFACE CHEMKIN Interpreter reads user-supplied information (e.g., "surf.inp") about surface and bulk species names, surface site types, surface reactions, and optional thermochemical information. This information is written to a SURFACE CHEMKIN Linking File ("surf.asc"), and later accessed by the SURFACE CHEMKIN subroutine library when called by the SPIN program. The SURFACE CHEMKIN Interpreter also generates a text file (e.g., "surf.out") containing the input mechanism information and diagnostic messages.

Once the pre-processors have run successfully, the SPIN program can then be executed. Since the CHEMKIN, SURFACE CHEMKIN, and TRANSPORT subroutine libraries must be initialized before use, the SPIN program begins by making the appropriate initialization subroutine calls. The purpose of the initialization is to read the Linking Files and to set up the internal working and storage space required by all subroutines in the libraries.

SPIN then reads the user input that defines a particular reacting flow problem and the parameters needed to solve it. This input is read in Keyword format from the input file (e.g. "spin.inp"), described in Chapter 5. In addition to this input, there is a provision for the SPIN program to begin its solution from a previously computed solution. In this case the old solution is read from a binary Restart File, called "rest.bin". The program produces printed output (e.g. "spin.out") and it saves the solution in a binary Save File, "save.bin". The Save File can be used to restart SPIN, such that the user may modify flow conditions, and the previous solution provides the initial estimates for the new solution. The Restart File is the same format as the Save File; a Restart File can therefore be created simply by copying a Save File, e.g. "save.bin" to the Restart File name, "rest.bin".

### 4.1 Optional User Programming

In addition to using SPIN through the CHEMKIN Application User Interface, users have the flexibility to write their own interface to the reacting-flow model. To facilitate this, the SPIN program itself is written as a Fortran subroutine that may be called from a user-supplied driver routine. We provide examples of such driver routines as part of the SPIN software distribution, written in both C++ and Fortran. The driver routine performs the function of allocating total memory usage through definition of array sizes, as well as opening input and output files. SPIN checks internally to make sure that the allocated work arrays are sufficiently large to address the problem described by the input files. Programs can be linked to the SPIN subroutine by following the examples in the makefiles provided in the sample driver subdirectories ("drivers\_f77" or "drivers\_cpp") of the standard distribution. Users taking advantage of this flexibility should be experienced with compiling and linking program files on their operating system and must have either a C++ or Fortran compiler installed.

### 4.2 Save, Restart, and Recover Files

In addition to printed output the program produces a binary Save File ("save.bin") that contains the solution and the first order sensitivity coefficients, if they were requested. This file has several uses. The solution in the file can be an initial estimate for a different calculation, through the restart option. It often saves computer time to begin a computation for a given set of conditions by starting with the solution of another set of conditions that are in some way related. In the case of a restart, the SPIN reads the input keywords to specify some of the parameters, but the initial solution estimate will be read from the Restart file.

The binary solution Save File is written after the solution to a problem is complete. However, another file, the Recover File, is rewound and written after every successful return from a Newton iteration or a sequence of time steps. In the event that the program fails to complete a problem for some reason it may be possible to restart it from the Recover File. Starting from Recover File, but with different keyword inputs (for example a different time step) may be more efficient than restarting the problem from the beginning.

The binary solution file is also used to post-process the solution. Further information on this subject can be found in Chapter 6 of this document.

## 5. PROGRAM INPUT

## 5.1 Keyword Syntax and Rules

The SPIN program's input is in a keyword format. On each input line an identifying keyword must appear first. For some keywords, only the keyword itself is required, while for others, additional information is required. Some keywords have default values associated with them and in such cases the keyword line need not be included. In the case of restarts or continuation problems, some of the keywords can be changed. If not changed, they retain their former values. In each keyword description, we note whether or not it can be changed upon a restart or continuation. The order in which the keywords are input is unimportant, but some keywords that appear as lists must be ordered. (For example, when entering an initial temperature profile as pairs of heights and temperatures, the heights are required to be in ascending order.) For those keywords that affect control of the solution through interface with the TWOPNT software, the appropriate TWOPNT parameter is stated. An example keyword line is provided for all keywords. The rules governing the syntax of the keywords are listed below:

- 1. The first four columns of the line are reserved for the keyword itself, which must begin in the first column.
- 2. Any further input associated with the key word can appear anywhere in columns 5 through 80. The specific column in which the information begins is unimportant.
- 3. When the keyword requires more than one piece of data, the order in which the information appears is important. The data must be separated by one or more blank space.
- 4. When numbers are required as input, they must be stated in integer, floating point, or E format. The program converts the numbers to the proper type. The double precision specification is not required. If a double precision version of the program is being run, the double precision conversion is done internally.
- 5. When gas-phase species names are required as input, they must appear exactly as they were specified in the CHEMKIN input. When surface or bulk species names are required as input, they must appear exactly as they were specified in the SURFACE CHEMKIN input.
- 6. If keywords are repeated or conflict, then the last-read values are used. For example if the same keyword is encountered twice, the data with the last one read is accepted.
- 7. A "comment" line can be inserted by placing either a period (.), a slash (/), or an exclamation point (!) in the first column. The program ignores such a line, but it is echoed back in the printed output.
- 8. The keyword END must be the last input line.

### 5.2 Problem Type

- STAG Specify a stagnation point flow reactor. If the keyword STAG is given and the spin rate OMEG is nonzero, then this inconsistent input will generate a fatal error. Default – stagnation point reactor is *not* assumed. Example – STAG
- ENGR Inclusion of this keyword means that a solution will be obtained for the coupled energy-species equations. However, the user must still specify a temperature profile for the initial guess. Default – none, either TGIV or ENGR *must* be specified. Example – ENGR
- **TGIV** Inclusion of this keyword means that a solution will be obtained using a user-specified temperature profile. The profile is specified with a sequence of TEMP keywords. An energy equation is not solved.

Default – none, either TGIV or ENGR *must* be specified. Example – TGIV

- RADB This keyword indicates that the susceptor temperature is calculated from an energy balance. If RADB is specified, TDSK is used as the initial guess for the susceptor temperature. Default – susceptor temperature is fixed as TDSK. Example – RADB
- COMP This keyword indicates that the boundary condition used at the inlet for the gas species equations will be that of a fixed gas composition, as specified by the REAC keywords. Default – a flux balance is solved at the inlet (see keyword FLUX). Example – COMP
- FLUX This keyword indicates that a flux balance will determine the mass fractions of the species at the inlet (rather than a fixed composition). If FLUX is specified, the REAC keywords are used to determine the convective mass flux in, which is balanced against diffusive fluxes to determine the inlet gas composition. See Eq. (20).

Default – a flux balance is solved at the inlet. Example – FLUX

NSDN – Inclusion of this keyword prevents SPIN from solving for variable surface-phase site densities, regardless of whether or not reactions are included in the surface reaction mechanism that do not conserve sites. If non-conserving reactions are included in the mechanism and this keyword is omitted, the program will attempt to solve an equation to determine the surface site densities.

Default – site densities are calculated when there are non-conserving surface reactions Example – NSDN
### 5.3 Solution Method Options

**NOFT** – Inclusion of this keyword means that the solution will be obtained without first solving the species and momentum equations with a fixed temperature as an intermediate stage before coupling in the energy equation. This option is useful, for example, when starting from a previous solution, but with a new surface temperature. In this case there is no advantage to solving the species equations on the old temperature field.

Default – fixed-temperature problem solved first. Example – NOFT

**USTG** – Including this keyword on a restart means that the user-specified temperature profile, as given on the TEMP keywords, is to be used instead of the temperature profile that is on the restart file.

Default – use the temperature profile on the restart file. Example – USTG

# 5.4 Newton Iteration Controls

**ATOL** – Absolute tolerance for termination of the Newton iteration. The Newton iteration is considered to be converged when the maximum norm of the solution correction vector  $\Delta \phi$  is reduced to below the following criteria:  $|\Delta \phi| \leq \max(\text{ATOL}, \text{RTOL} \times |\phi|)$ . Typically ATOL should be smaller than the maximum mass fraction of any species of interest.

Default – 1.E-9 TWOPNT Parameter – SSABS Example – ATOL 1.E-8

**RTOL** – Relative tolerance for termination of the Newton iteration. The Newton iteration is considered to be converged when the maximum norm of the solution correction vector  $\Delta \phi$  is reduced to below the following criteria:  $|\Delta \phi| \leq \max(\text{ATOL}, \text{RTOL} \times |\phi|)$ . Typically RTOL should be in the range of 10<sup>-3</sup> to 10<sup>-6</sup> which would provide roughly three to six significant digits.

Default – 1.E-4 TWOPNT Parameter – SSREL Example – RTOL 1.E-3

**NJAC** – This keyword specifies the maximum number of Newton steps that can be taken in solving the steady state problem before a new Jacobian is evaluated. If NJAC=1, then a full Newton method will result.

Default – 20 TWOPNT Parameter – SSAGE Example – NJAC 10

#### 5.5 Time Step Controls

ATIM – Absolute tolerance for the termination of the Newton iteration as it is used in the time stepping procedure. For a precise definition see the above description of ATOL. Since we are not seeking accuracy in a transient solution, this convergence criteria typically does not need to be as stringent as for the Newton iteration on the boundary value problem itself.

> Default – 1.E-9 TWOPNT Parameter – TDABS Example – ATIM 1.E-8

RTIM – Relative tolerance for the termination of the Newton iteration as it is used in the time stepping procedure. For a precise definition see the above description of RTOL. Since we are not seeking accuracy in a transient solution, this convergence criterion typically does not need to be as stringent as for the Newton iteration on the boundary value problem itself.

> Default – 1.E-4 TWOPNT Parameter – TDREL Example – RTIM 1.E-3

TIME – If the Newton method fails to converge, then SPIN performs a time evolution to bring the current iterate within the domain of convergence of Newton's method. If the ISTP keyword is used, then SPIN will take initial time steps without first attempting a Newton iteration. The TIME keyword specifies the size of the initial time step and how many time steps are to be taken. For example, the input TIME 100 1.E-6, specifies that any time Newton's method fails 100 time steps with an initial step size of 1 microsecond.

Units – none, seconds Default – 100, 1.E-6 TWOPNT Parameter – STEPS1, STRID0 Example – TIME 100 1.E-5

**TIM2** – This keyword is the same as TIME except that TIME applies to the fixed temperature problem and TIM2 is used after the energy equation is included. Naturally, this input only has meaning in problems that solve the energy equation for a temperature profile.

Units – none, seconds Default – 100, 1.E-6 TWOPNT Parameter – STEPS1, STRID0 Example – TIM2 100 1.E-5

**UFAC** – This keyword is a multiplicative factor by which the time step will be increased when appropriate (see IRET).

Units – none Default – 2.0 TWOPNT Parameter – TINC Example – UFAC 2.0 DFAC - This keyword is a factor by which to divide the current time step if time integration procedure fails to converge. Units - none Default - 2.2

TWOPNT Parameter – TDEC Example – DFAC 2.5

**DTMN** – This keyword is the minimum time step allowed. That is, the time integration procedure will not decrease the time step below this value. If the solver attempts to decrease the time step below this value, then the time-stepping procedure fails.

Units – seconds Default – 1.E-10 TWOPNT Parameter – TMIN Example – DTMN 1.E-8

**DTMX** – This keyword is the maximum time step allowed. That is, the time integration procedure will not increase the time step above this value.

Units – seconds Default – 1.E-4 TWOPNT Parameter – TMAX Example – DTMX 1.E-2

**TJAC** – This keyword specifies the maximum number of Newton steps that can be taken in solving the transient problem before a new Jacobian is evaluated. If TJAC=1, then a full Newton method will result.

Default – 20 TWOPNT Parameter – TDAGE Example – TJAC 10

ISTP - A positive value of this keyword specifies the number of initial time steps that are taken prior to attempting a Newton iteration. Normally, the Newton iteration will be attempted first, with time steps invoked only if the Newton iteration fails. Nevertheless, there may be circumstances where initial time stepping is desirable. The time step size is specified with the TIME keyword. The ISTP keyword only applies to the first grid network, not the subsequently refined ones. If ISTP has a negative value (e.g., ISTP -1000), then no Newton steps will be attempted. Invoking this option would be unusual, but could be used to find a steady state solution via pure time integration.

> Default – 0 TWOPNT Parameter – STEPS0 and STEADY Example – ISTP 200

IRET – This keyword specifies the number of time steps to be taken before the time step value is increased by the factor UFAC. Default – 50 TWOPNT Parameter – STEPS2 Example – IRET 100

#### 5.6 Solution Bounds Controls

**SFLR** – Sometimes during the solution procedure some of the very small gas-phase mass fractions, surface site fractions, or bulk species fractions may be calculated as negative. No solution component will be allowed to drop below the floor value specified by SFLR.

Default – –1.E-4 TWOPNT Parameter – BELOW Example – SFLR –1.E-5

SPOS – This keyword provides a (small positive) number that will replace any negative species mass fractions. The replacement is made after every successful sequence of time steps, upon adding mesh points, and on restart or continuation. SPOS is often helpful in starting difficult problems when the initial guess is far from the solution. SPOS attempts to force the transient solution away from nonphysical regions that may otherwise be entered due to bad initial conditions and badly conditioned systems.

> Default – no replacement is applied. Example – SPOS 1.E-9

#### 5.7 Grid Control Parameters

NPTS – The number of initial mesh points. The inclusion of NPTS will generate an equispaced mesh of NPTS points between XSTR and XEND. The user can also specify an initial non-uniform mesh using the keyword GRID, in which case the NPTS input is not needed.

> Default – 6 TWOPNT Parameter – POINTS Example – NPTS 20

**NMAX** – The maximum number of mesh points allowed for this solution. The adaptive gridding will stop when this number of grid points has been reached.

Default – NTOT, a dimension supplied by the Driver program. TWOPNT Parameter – PMAX Example – NMAX 50 NADP – The maximum number of mesh points allowed to be added at each step in the grid adaptation process. Occasionally the program has trouble converging when adding too many points at once. This keyword will limit the number of new points added before a new solution will be found.

> Default – NMAX TWOPNT Parameter – PADD Example – NADP 2

JJRG – On continuations or restarts, the number of mesh points can be reduced. TWOPNT itself does not remove grid points. Therefore, on a sequence of continuation problems the number of grid points can grow because the region where they are needed may change. SPIN thus provides a capability to remove grid points. JJRG is the reduced number of grid points that will be used. The old solution is adaptively interpolated onto a new grid of JJRG points.

> Default – no grid reduction; old grid used Example – JJRG 40

PCAD - On continuations or restarts the number of mesh points can be reduced. PCAD is a parameter that influences the fraction of grid points that are dedicated to adaptation. PCAD of zero would result in a uniform grid. The old solution is adaptively interpolated onto a new grid of JJRG points.

Default – 0.75 Example – PCAD 0.5

- RGTC On continuations or restarts the number of mesh points can be reduced. RGTC is a parameter that influences the ratio of gradient regrid points to curvature regrid points. RGTC of zero would cause all regrid points dedicated to adaptation to be used to equidistribute curvature in the old solution. The old solution is adaptively interpolated onto a new grid of JJRG points.
   Default 1.0
   Example RGTC 1
- GRID This optional keyword allows the user to input an initial grid. Up to NMAX of these GRID inputs can be included. Each GRID input provides the coordinate of a mesh point. They must appear in ascending order. If this keyword is not included, the grid will be assumed to be equispaced and based on NPTS.

Units – cm Default – equally spaced grid Example – GRID 0.1

GRAD – Adaptive mesh parameter that controls the number of grid points inserted in regions of high gradient. Smaller values of GRAD cause more grid points to be used. See Eq. (33). Default – 0.1 TWOPNT Parameter – TOLER1 Example – GRAD .2 CURV - Adaptive mesh parameter that controls the number of grid points inserted in regions of high curvature. Smaller values of CURV cause more grid points to be used. See Eq. (34). Default – 0.5 TWOPNT Parameter – TOLER2 Example – CURV 0.5

#### 5.8 Initial Guess and Reactor Operating Conditions

**PRES** – The pressure. Units – atmospheres Default – required input Example – PRES 0.5

**REAC** – Mole fraction values of the reactants entering at the inlet. One of these REAC inputs must appear for each reactant species, for example "REAC SIH4 0.5". The sum of all the reactant mole fractions should equal one. However, if they do not, a cautionary message will be printed and the mole fractions will be normalized so the sum does equal one. Any given species can be specified simultaneously as a reactant, intermediate, or product.

Units – none (mole fractions) Default – at least one REAC keyword is required; 0.0 for any species not specified Example – REAC H2 0.3

INTM – The estimated peak mole fraction values for "intermediate" species. Providing one of these INTM inputs for each intermediate species often aids in the convergence. It is usually better to estimate values somewhat higher than those that are actually present in the gas. Any given species can be specified simultaneously as a reactant, intermediate, or product.

> Units – none (mole fractions) Default – 0.0 Example – INTM SIH2 1.E-5

PROD – Estimated values of the gas-phase mole fractions at the deposition surface. One of these PROD inputs should appear for each species in large concentration at the surface. The sum of the product mole fractions should equal one. However, if they do not, a cautionary message will be printed and the mole fractions will be normalized so the sum does equal one. Any given species can be specified simultaneously as a reactant, intermediate, or product. If no PROD is given, all species PROD value will be set to equilibrium values.

Units – none (mole fractions) Default – 0.0 for any species not specified Example – PROD SIH4 0.1

SURF – Surface site fraction values estimated for the surface species on each surface site type (surface phase) on the deposition surface. One of these SURF inputs should appear for each surface species that is expected to be in large concentration on the surface. The sum of the site fractions should equal one for each surface site type (surface phase). However, if they do not, a

cautionary message will be printed and the site fractions for each surface site type will be normalized so the sum does equal one.

Units – none (surface site fractions) Default – 0.0 for any species not specified Example – SURF SI(S) 1.E-2

ACT – Estimated activities for the bulk species in each bulk phase. One of these ACT inputs should appear for each species in a bulk phase. For an ideal bulk-phase mixture the sum of the bulk species activities should equal one. However, if they do not, a cautionary message will be printed and the bulk species fractions for each bulk phase will be normalized so the sum does equal one.

> Units – none (bulk species fractions) Default – required input Example – ACT SI(B) 1.0

**ETCH** – Inclusion of this keyword and a valid bulk phase name tells the program that the user expects the surface chemistry to result in this phase being etched, rather than deposited. In this case, the activities of the bulk species will be used as the initial mole fraction values. Note that, when bulk phases are not explicitly named in the SURFACE CHEMKIN input file, the names assigned are "BULK1", "BULK2", etc., in order of appearance in the file.

Units – none (bulk species fractions) Default – required input Example – ETCH BULK1 1.0

**SDEN** – Site density for a surface phase. Inclusion of this keyword will override the values given for surface-phase site densities in the SURFACE CHEMKIN input file.

Units – moles/cm<sup>2</sup> Default – values from SURFACE CHEMKIN input file are used. Example – SDEN PLANE 1.0E-9

**TEMP** – This input allows specification of the initial guess or given temperature profile. Each input provides an (x, T) pair and the *x* coordinates must be in ascending order. Up to NMAX (x, T) pairs may be input.

Units – cm, K Default – required input, except on restart Restart – can be changed, provided USTG is included Example – TEMP 0.1 1540

- TINF Inlet gas temperature, i.e., temperature at XEND. Units – K Default – required input Example – TINF 1000
- **TDSK** Temperature of the deposition surface. This is a constant value taken as a boundary condition, unless the keyword RADB is given, indicating that the susceptor temperature is calculated

from an energy balance. If RADB is specified, TDSK is taken as the initial guess for the susceptor temperature. Units – K Default – required input Example – TDSK 1200

- OMEG The disk rotation rate. A stagnation-point flow can be specified either by using "OMEG 0", or by using the keyword STAG. Units – rpm Default – required input, unless the STAG option is used Example – OMEG 1000
- **AINL** The radial velocity spreading rate. At the inlet x = L, v/r = AINL. Units – 1/seconds Default – 0.0 Example – AINL 2.3
- **OINL** The inlet-gas spin rate. At the inlet x = L, w/r = OINL. Units – rpm Default – 0.0 Example – OINL 100
- UINF The axial inlet velocity at position XEND to be specified as a boundary condition. In the usual rotating-disk solution, the velocity at the outer domain is calculated as a part of the solution. However, using the keyword UINF, one may impose this velocity upon the solution. If the rotations rate OMEG is zero, or if the STAG option is used, then UINF is no longer optional, but must be given to specify the problem.

Units – cm/sec Default – none; required input for stagnation-point flow Example – UINF 23.6

- XSTR The beginning of the computational interval. Units – cm Default – 0.0 Restart – can be changed to a smaller value Example – XSTR 0.0
- XCEN An estimated value for center of the reaction boundary layer. Units – cm Default – 0.35\*(XEND-XSTR) Example – XCEN 1.8

 XEND – The end of the computational interval. That is, the inlet position above the disk. Units – cm
 Default – required input
 Restart – can be changed to a larger value
 Example – XEND 5.0

WMIX – Estimated width of the reaction boundary layer. Units – cm Default – 0.5\*(XEND-XSTR) Example – WMIX 1.0

# 5.9 Substrate Energy Balance Options

**TWAL** – Temperature of a neighboring "wall" used in calculating a surface radiation balance. This value is used only if the disk temperature is being calculated by including keyword RADB. See Eq. (17).

Units – K Default – 500 K Example – TWAL 850.0

- EMIS The emissivity of the disk. This value is used only if the disk temperature is being calculated from an energy balance by including keyword RADB. See Eq. (17). Units – none Default – 0.85 Example – EMIS 0.9
- POWR The power being supplied to heat the disk. This value is used only if the disk temperature is being calculated from an energy balance by including keyword RADB. See Eq. (17). Units – ergs/cm<sup>2</sup>/sec

Default – 0.0 Example – POWR 15.E7

CDCT – Include conduction through the substrate in the energy balance. Inclusion of this keyword requires specification of a substrate thickness (CNDX). This value is used only if the disk temperature is being calculated from an energy balance by including keyword RADB. See Eq. (17).

Default – conduction through the substrate is not included Example – CDCT

**CNDX** – The thickness of the substrate for calculation of conduction losses. This value is used only if the disk temperature is being calculated from an energy balance by including keywords RADB and CDCT. See Eq. (17).

Units – cm Default – 0.0 Example – CNDX 0.03

**COND** – The thermal conductivity of the substrate in SI units, for use in calculation of conduction losses. This value is used only if the disk temperature is being calculated from an energy balance by including keywords RADB and CDCT. See Eq. (17).

> Units – W/cm-K Default – 1.38 Example – COND 2.1

**CNDT** – The back-side temperature of the substrate for use in calculation of conduction losses. This value is used only if the disk temperature is being calculated from an energy balance by including keywords RADB and CDCT. See Eq. (17).

Units – K Default – 300. Example – CNDT 350.

TRAD – Temperature of a radiating disk located above and parallel to the substrate, used in calculating a surface radiation balance. A hot radiating disk may be included in addition to a cool "wall" (TWAL), to represent, for example, a burner inlet. The geometry and location of the radiating disk are controlled by keywords RDSK and RRAD. TRAD is used only if the disk temperature is being calculated by including keyword RADB. See Eq. (17).

Units – K Default – 1000 K Example – TRAD 2500.

**RRAD** – Ratio of the upper radiating-disk radius to the separation distance between it and the lower substrate. This is used in calculating a surface radiation balance. RRAD is used only if the disk temperature is being calculated by including keyword RADB. See Eq. (17).

Units – none Default – none; required input when RDSK is included Example – RRAD 3.0

RDSK – Ratio of the substrate radius to the separation distance between it and the upper radiating disk. This is used in calculating a surface radiation balance. RRAD is used only if the disk temperature is being calculated by including keyword RADB. See Eq. (17). Units – none Default – none; required input when RRAD is included Example – RDSK 3.0

### 5.10 Heat Source Options

- QDOT The power being supplied to heat the gas as a spatially distributed Gaussian heat source.
   QDOT is the total power, i.e., the spatial integral of the heat source function. See Eq. (13).
   Units ergs/cm<sup>2</sup>/sec
   Default 0.0
   Example QDOT 1.0E7
- XSRC Height above the disk which is the center of a Gaussian-shaped power source. See Eq. (12). Units – cm Default – 0.0, required input if QDOT is nonzero Example – XSRC 0.6
- WSRC Half-width of the Gaussian source term if the gas is being heated by an optional heat source. See Eq. (12). Units – cm

Default – 0.0, required input if QDOT is nonzero Example – WSRC 0.07

# 5.11 Gas Radiation Loss Options

EMSG - Approximation of the temperature-dependent emissivity of the gas-mixture, used to calculate a radiation loss term in the gas energy equation. The radiation is calculated between the gas and the disk (using the gas temperature) and between the gas and the inlet (using the inlet temperature). The EMSG keyword provides temperature, emissivity pairs for the gas mixture. Units – K, none Default – no gas radiation loss is included in the energy equation. Example – EMSG 2000 0.03

# 5.12 Strained Flame Options

FLAM – Position and fixed-temperature value for calculating strained, lifted flames. In this case, the inlet gas velocity is calculated (rather than fixed) based on a fixed location of the flame front. The flame front location is specified by giving a location and value of a temperature (above the inlet temperature value) to fix at this position.

Units – cm, K Default – none; no temperature is fixed in the calculation. Example – FLAM 0.5 700. **TOFF** – This keyword is used to tell the TWOPNT solver to ignore the temperature when adapting the grid. This can be useful for strained flames, since the temperature gradients can be very steep and, without this option, too many points will be placed in the same place without improving the solution. The flame can be well resolved by basing adaptation only on the species and velocity profiles.

Default – the temperature is considered during adaptation. Example – TOFF

## 5.13 Multicomponent TRANSPORT Options

**MULT** – Including this keyword causes the calculation to be run with a full multicomponent model for the transport coefficients and diffusion fluxes.

Default – mixture-average, not multicomponent, transport is used Example – MULT

MIX – Including this keyword causes the calculation to be run using a mixture-average model for calculating the transport coefficients and diffusion fluxes.

Default – mixture averaged transport is used Example – MIX

- VCOR Including this keyword causes the calculation to be run using a correction velocity to ensure mass conservation, i.e., the sum of the diffusion fluxes is zero. See Eq. (11). If VCOR is not used, then TRCE is in effect.

Default – a correction velocity is not used Example – VCOR

**TRCE** – Including this keyword causes the calculation to be run by setting the mass fraction of the lastnamed CHEMKIN gas-phase species to be one minus the sum of the mass fractions of the other species. A conservation equation is not solved for the last species.

Default – TRCE is used Example – TRCE REOR – The option may be used when the TRCE option is in effect. Using TRCE, the conservation equation for the last species in the gas-phase and each surface and bulk phase is not solved: the last species concentration (mass fraction or site fraction) is chosen so that the fractions sum to one. The REOR option causes TRCE to choose dynamically and locally (at each mesh point and in each phase) the species of largest concentration and not solve its conservation equation. Default – the last species in each phase is chosen Example – REOR

## 5.14 Gas Injection Options

INJS – Injection of gas species at a location along the axis of symmetry can be included using one or more INJS keywords. The injection is specified as a spatially distributed Gaussian source. INJM is the total mass flow, i.e., the spatial integral of the mass flow function given. This source term will be added to Eq. (5). INJS specifies the species composition of the injected flow, in mole fractions.

> Units – none (mole fractions). Default – no injection Example – INJS H2 0.5

- INJX Height above the disk which is the center of the Gaussian-shaped injection source. See Eq. (5). Units – cm Default – 0.0, required input if INJS keywords are included. Example – INJX 0.6
- INJW Half-width of the Gaussian gas-injection source. See Eq. (5). Units – cm Default – 0.0, required input if INJS keywords are included. Example – INJW 0.07
- INJM Total mass flow rate of the injected gas. See Eq. (5). Units – g/cm<sup>2</sup>-sec Default – 0.0, required input if INJS keywords are included. Example – INJM 0.15
- INJT Temperature of the injected gas. Units – K Default – no enthalpy is added to the energy equation with the injected gas. Example – INJT 300.

#### 5.15 Sensitivity Options

- ASEN Including this keyword causes all the first-order sensitivity coefficients with respect to the reaction rate constants to be determined. Default – no sensitivities computed Example – ASEN
- HSEN Including this keyword causes all the first-order sensitivity coefficients with respect to the species heats of formation to be determined.
   Default no sensitivities computed
   Example HSEN

# 5.16 Chemistry Control Options

**NONR** – This keyword specifies that the non-reacting problem will not be solved as the first stage in the solution of the full problem.

Default – the non-reacting problem is solved first Example – NONR

- NOCH This keyword specifies that the rates of all gas-phase reactions will be set to zero, no matter what the values specified in the CHEMKIN input. Default – actual values for chemistry rates are used Example – NOCH
- **CHEM** This keyword specifies that the rates of all gas-phase reactions will be calculated. This option is used to reactivate the chemical kinetics if the NOCH option was in effect for the previous calculation.

Default – actual values for chemistry rates are used Example – CHEM

GFAC – This keyword specifies that the rates of all gas-phase reactions will be multiplied (scaled) by the factor GFAC. This option is sometimes useful if convergence difficulties are encountered due to unusually large reaction rates. The problem would be first solved with artificially reduced reaction rates, which then can be increased in subsequent continuations or restarts until GFAC is one.

> Default – 1.0 Example – GFAC 0.3

SFAC – This keyword specifies that the rates of all surface reactions will be multiplied (scaled) by the factor SFAC. This option is sometimes useful if convergence difficulties are encountered due to unusually large reaction rates. The problem would be first solved with artificially reduced reaction rates, which then can be increased in subsequent continuations or restarts until SFAC is one. SFAC can be a very small number, but it cannot be exactly zero.

Default – 1.0 Example – SFAC 0.3

**GDOT** – This keyword may be used to specify explicitly the net surface production rates of gas-phase species at the substrate, instead of using SURFACE CHEMKIN. In order to use this option, the SURFACE CHEMKIN input file must be empty, which means that the number of surface reactions, surface site species and bulk species must all be zero in the SURFACE CHEMKIN linking file.

> Units – moles/cm<sup>2</sup>-s Default – 0.0 Example – GDOT H -1.3E-7

# 5.17 Printing Options

- PRNT Printing control. "PRNT 1" provides less printed output of intermediate solutions than does "PRNT 2". More printing is often helpful when there are convergence difficulties. Default – 1 TWOPNT Parameter – LEVELD and LEVELM Example – PRNT 1
- LPRT Printing control. LPRT turns on extensive printing that provides information on rates of progress of individual surface reactions. This can be very informative in understanding the surface reaction behavior.

Default – LPRT not invoked Example – LPRT

# 5.18 Miscellaneous Keywords

**RSTR** – Inclusion of this keyword causes the program to begin with a previously computed solution as the starting estimate. This previously computed solution will be read from the Restart File (e.g. "rest.bin".

Default –solution started from input, not from a restart file. Example – RSTR

- FILE A restart file may contain more than one solution. Specifying the keyword FILE causes the program to select the specified solution number from a restart file. For example, "FILE 3" means that the first two solutions on the restart file should be skipped and the next one used. If solutions have already been read from a restart file, the number of the solution to use starts from its current position. The FILE keyword is valid only if the RSTR keyword is also used. Default if RSTR was specified, the first solution will be used Example FILE 3
- CNTN Including this keyword causes the program to expect keywords for another problem following the END keyword. The following problem will use the solution of the previous problem as its initial guess. This capability is very similar to that provided by RSTR. However, in the case of CNTN, several related problems can be solved by one job submission without having to manipulate the restart files. Any keyword that can be changed for a RSTR problem can be changed on continuation.

Default – no continuation is expected Example – CNTN

**END** – This line signifies the end of a given set of input data. It must appear after each set of input when continuation jobs are indicated using the CNTN keyword.

Default – required input Example – END

# 6. POST PROCESSING

# 6.1 CHEMKIN Graphical Post-processor

The CHEMKIN Graphical Post-processor provides a means for quick visualization of results from SPIN. Launched from the CHEMKIN Application User Interface, the Graphical Post-processor will automatically read in the solution date from the "save.bin" file in the working directory. Alternatively, the post-processor may be launched independently and a solution file may be opened from within the Post-processor. The user may open one or more solution files in the Post-processor and may also import external data for comparisons with the simulation results. In addition, the Graphical Post-processor can be used to export all of the solution data into comma-, tab-, or space-delimited text for further analysis with other software packages. For more information on the Graphical Post-processor, please see the CHEMKIN Getting Started manual.

# 6.2 Configurable Command-line Post-processor

In addition to the CHEMKIN Graphical Post-processor representation of solution data, we provide the user with a FORTRAN post-processor called SPIN\_POST. This program reads the binary solution file and prints selected data to text files, which can then be imported by many other graphics programs. The full source-code, spin\_post.f, is provided in the CHEMKIN "post\_processors" subdirectory. Also in this directory is a makefile script for re-building the SPIN\_POST program, in case the user makes changes to the source code. In this way, users may easily configure SPIN\_POST for their own analysis needs.

To run SPIN\_POST from the command-line, you will need to do the following:

- 1. Open a MS-DOS Prompt (PC) or shell (UNIX).
- 2. Change directories to your working directory, where your "save.bin" solution file resides.
- 3. Run SPIN\_POST from the command-line, specifying the full path to the CHEMKIN "bin" directory where the "spin\_post" executable resides, unless this is already in your environment "path" variable:

spin\_post < spin\_post.inp > spin\_post.out

Here, "spin\_post.inp" is an input file that contains keywords described below. The output "spin\_post.out" will contain diagnostics and error messages for the SPIN\_POST run. SPIN\_POST will also create text files containing comma-separated values. The names for these files use a suffix (extension) of ".csv".

SPIN\_POST uses keyword input. The available keywords are printed as a banner when the program is invoked; they are also described briefly here:

- **PREF** A character-string prefix used to name output files. Default — "spin".
- NSOL Index of the solution to be selected from the binary solution file. Default — The final solution in the solution file. Example: NSOL 2
- **SPEC** List of the names of species for which fractions are output. Default — No species fractions will be printed. Example: SPEC H2 O2 H2O H O OH
- MASS— Print species fractions as mass fractions Default — Mole fractions are printed.
- **MOLE** Print species fractions as mole fractions Default — Mole fractions are printed.
- **SMIN** Minimum species fraction quantity of interest. Default —0.0, all species fractions listed. Example: SMIN 1.0E-3
- **RATE** List of the names of species for which production rates are listed. Default — No species production rates will be printed. Example: PROD H2 O2 H2O H O OH
- SENS List of the names of species for which reaction rate sensitivity coefficients are listed. Default — No species reaction rate sensitivity coefficients will be printed. Example: SENS H2 O2 H2O H O OH
- **TSEN** List temperature reaction rate sensitivity coefficients.

Default — No temperature reaction rate sensitivity coefficients will be printed.

- HSEN List of the names of species for which formation enthalpy sensitivity coefficients are listed.
   Default No species formation enthalpy sensitivity coefficients will be printed.
   Example: HSEN H2 O2 H2O H O OH
- **TSNH** List temperature formation enthalpy sensitivity coefficients.

Default — No temperature formation enthalpy sensitivity coefficients will be printed.

- DROP Filter out lowest reaction rates and sensitivity coefficients, by percent. Default — 10., lowest 10% of reaction rates and sensitivity coefficients are not printed. Example: DROP 15
- **HELP** List descriptions of the keywords available.
- END Must be the last keyword in the input

# 7. SAMPLE PROBLEM

This section shows an example using the SPIN Application. All sample input and output files are included. We have chosen as a sample the deposition of  $Si_3N_4$  from  $SiF_4$  and  $NH_3$ . The gas-phase reaction mechanism contains a detailed description of  $NH_3$  decomposition (about which there is much published information), two reactions describing  $SiF_4$  decomposition, and three cross reactions. At the low pressures we consider, the gas-phase decomposition of reactants is slow. The surface reaction mechanism contains six steps describing the overall conversion of 3 SiF\_4 and 4 NH\_3 molecules to 3 Si(d) and 4 N(d) and 12 HF. (Note that the surface reaction mechanism is from a preliminary analysis at one temperature, and thus we have not supplied any activation energies. As such, this mechanism should only be considered as illustrative and not as a source of kinetic data on the  $Si_3N_4$  system.)

The first file is the input file for the CHEMKIN Interpreter, which defines the gas-phase reaction mechanism. The output from the CHEMKIN Interpreter follows. The input to and output from the SURFACE CHEMKIN Interpreter show the surface species and surface reactions in the problem. More details on the CHEMKIN and SURFACE CHEMKIN Interpreters can be found in the CHEMKIN Collection user's manuals.

The file containing the keyword input to SPIN specifies the specific run conditions for the problem: the energy equation (ENRG), rotation rate of 1000 rpm (OMEG), disk temperature 1713 K (TDSK), inlet temperature 300 K (TINF), 11 mesh points in the initial grid (NPTS), the computational domain ends at 10 cm (XEND), and pressure of  $2.3684 \times 10^{-3}$  atm (PRES). The reactant mole fractions at the inlet are given (REAC), along with estimates of the major product considerations at the surface (PROD), site fractions of the surface species (SURF), and activities of the bulk phase species (ACT). A crude temperature profile to begin the iteration is specified (TEMP). The remaining keywords specify numerical error tolerances, etc.

The last file is the output from SPIN. A series of banners chows the version numbers of SPIN and the CHEMKIN, SURFACE CHEMKIN, and TRANSPORT libraries. After giving statistics on the working space requirements, SPIN echoes back the keyword inputs. The program first solves the non-reacting problem, calculating the temperature and velocity fields. The first thing printed is the initial guess at the solution, which is based on the keyword inputs.

The numerical two-point boundary-value solver TWOPNT actually solves the problem. TWOPNT reports the progress of its solution as part of the printed output. Since the PRNT keyword was set to one, only brief statistics for the progress of the iteration are provided. There are three major functions in the TWOPNT program, and each reports what it has done at each stage of the solution. The functions are NEWTON (which attempts to solve the boundary value problem on the given mesh by Newton's method), TIMSTP (which takes the user-specified time steps if Newton's method fails), and REFINE (which performs the mesh adaptation). The first column reports the logarithm of the maximum residual

norm  $|F(\phi)|$ . The second column reports the logarithm of the largest Jacobian condition number encountered during the current iteration. These condition numbers are obtained from the LINPACK condition number estimates. The next column reports the number of mesh points, the number of Newton or time steps, and the number of Jacobian evaluations. The last column provides a remark about the given operation. For example, the "FAILURE" remarks would indicate that the Newton method failed to converge and thus time steps would be attempted next. Since the non-reacting problem is quite easy to solve there is little diagnostics coming from TWOPNT. When TWOPNT has solved the problem it reports the solution and gives statistics on the amount of time required for various parts of the computation.

Next, SPIN includes the gas-phase species continuity and surface species equations, although the energy equation is omitted. The temperature and velocity fields in the initial guess are from the non-reacting solution just obtained. The initial species fractions are set from the user's keyword input. TWOPNT reports that the log of the solution's residuals was reduced by 5.2 during the Newton iteration. Again, the Newton iteration had no trouble solving the problem, and no time stepping was required. The final solution to the fixed temperature problem is then printed.

The solution from this calculation is used as input to the final one, which now turns on the energy equation to solve the fully coupled problem. Note that now the initial guess should be very close to the solution and the Newton procedure converges rapidly. At this stage in the calculation, TWOPNT begins to add mesh points adaptively to resolve the solution to the accuracy specified on input. The final solution is calculated on a mesh of 34 grid points.

#### 7.1 Input to CHEMKIN Interpreter for the Example

```
ELEMENTS H N SI F
END
SPECIES
H2 H N2 N NH NH2 NNH N2H2 N2H3 N2H4
HF F SIF4 SIF3 SIHF3 SIF3NH2
NH3
END
THERMO
                 J 3/67SI 100 0000 0000 00G 300.000 5000.000
ST
                                                                             1
0.26506014E 01-0.35763852E-03 0.29592293E-06-0.72804829E-10 0.57963329E-14
                                                                             2
0.53437054E 05 0.52204057E 01 0.31793537E 01-0.27646992E-02 0.44784038E-05
                                                                             3
-0.32833177E-08 0.91213631E-12 0.53339032E 05 0.27273204E 01
                                                                             4
                  41889SI 1F 2 0 0G 300.000 3000.000 1000.00
SIF2
                                                                           0 1
0.61424704E+01 0.78079745E-03-0.13393120E-06-0.62648393E-10 0.17251383E-13
                                                                             2
-0.77440422E+05-0.47123275E+01 0.38453453E+01 0.60384651E-02-0.11677322E-05
                                                                             3
-0.45795536E-08 0.26074143E-11-0.76816336E+05 0.72729836E+01
                                                                             4
SIF
                  41889SI 1F 1 0 0G 300.000 3000.000 1000.00
                                                                           0 1
0.41200666E+01 0.35488207E-03-0.72002223E-07-0.21904345E-10 0.67645906E-14
                                                                             2
-0.75613784E+04 0.27842460E+01 0.31449478E+01 0.25885573E-02-0.57959124E-06
                                                                             3
-0.18072788E-08 0.10411718E-11-0.72944390E+04 0.78767738E+01
                                                                             4
SIF3NH2
                  41889SI 1N 1F 3H 2G 300.000 3000.000 1000.00
                                                                           0 1
0.12109636E+02 0.43832823E-02-0.41422453E-06-0.39890902E-09 0.89589543E-13
                                                                             2
-0.16417678E+06-0.30469284E+02 0.62294030E+01 0.17780151E-01-0.26123043E-05
                                                                             3
-0.12672435E-07 0.70445559E-11-0.16258489E+06 0.20454407E+00
                                                                             4
                  41889SI 1H 1F 3
SIHF3
                                        0G 300.000 3000.000 1000.00
                                                                           0 1
0.93635674E+01 0.29475559E-02-0.35776330E-06-0.28582245E-09 0.69157286E-13
                                                                             2
-0.14860736E+06-0.21694529E+02 0.39180529E+01 0.14639172E-01-0.18560698E-05
                                                                             3
-0.10582003E-07 0.56175433E-11-0.14704386E+06 0.70242615E+01
                                                                             4
STF3
                  41889SI 1F 3 0
                                        OG 300.000 3000.000 1000.00
                                                                           0 1
0.85247898E+01 0.13237924E-02-0.21042787E-06-0.11495040E-09 0.30553014E-13
                                                                             2
-0.12235223E+06-0.15502343E+02 0.46628685E+01 0.10087878E-01-0.18055442E-05
                                                                             3
-0.77692990E-08 0.43778518E-11-0.12129652E+06 0.46729660E+01
                                                                             4
                 J 6/76SI 1F 4 0 0G 300.000 5000.000
STF4
                                                                             1
0.10478473E 02 0.28586756E-02-0.12646314E-05 0.24746863E-09-0.17824296E-13
                                                                             2
-0.19790550E 06-0.27520641E 02 0.21893068E 01 0.33702007E-01-0.46723179E-04
                                                                             3
0.31584638E-07-0.84506114E-11-0.19603289E 06 0.13287308E 02
                                                                             4
HF
                 J 6/77H 1F 1 0 0G 300.000 5000.000
                                                                             1
0.29919110E 01 0.71489475E-03-0.68630973E-07-0.11617130E-10 0.19412375E-14
                                                                             2
-0.33621364E 05 0.38123288E 01 0.34379986E 01 0.53571598E-03-0.15229655E-05
                                                                             3
0.17564491E-08-0.57869940E-12-0.33818972E 05 0.11930153E 01
                                                                             4
F
                J 9/65F 1 0 0 0G 300.000 5000.000
                                                                             1
0.27004353E 01-0.22293182E-03 0.97941385E-07-0.19123038E-10 0.13768154E-14
                                                                             2
0.87163617E 04 0.38067182E 01 0.28128740E 01-0.33023098E-05-0.12897310E-05
                                                                             3
0.16837365E-08-0.64587833E-12 0.86604019E 04 0.30984198E 01
                                                                             4
END
```

REACTIONS					
H+H+M=H2+M	0.100E+19	-1.000	0.000	!	D-L
H2/0.0/					
H+H+H2=H2+H2	0.920E+17	-0.600	0.000		
NH+N=N2+H	0.300E+14	0.000	0.000	!	JAM
NH+H=N+H2	0.100E+15	0.000	0.000	!	NH3 CST
NH2+H=NH+H2	0.692E+14	0.000	3650.000		
NH3+H=NH2+H2	0.636E+06	2.390	10171.000	!	MICHAEL
NNH=N2+H	0.100E+05	0.000	0.000	!	JAM
NNH+H=N2+H2	0.100E+15	0.000	0.000	!	JAM
NNH+NH2=N2+NH3	0.500E+14	0.000	0.000	!	JAM
NNH+NH=N2+NH2	0.500E+14	0.000	0.000	!	JAM
NH2+NH=N2H2+H	0.500E+14	0.000	0.000	!	NH3CST
NH+NH=N2+H+H	0.254E+14	0.000	0.000	!	NH3 CST
NH2+N=N2+H+H	0.720E+14	0.000	0.000	!	PG
N2H2+M=NNH+H+M	0.500E+17	0.000	50000.000	!	NH3 CST
N2/2/ H2/2/					
N2H2+H=NNH+H2	0.500E+14	0.000	1000.000	!	NH3 CST
N2H2+NH=NNH+NH2	0.100E+14	0.000	1000.000	!	NH3 CST
N2H2+NH2=NH3+NNH	0.100E+14	0.000	1000.000	!	NH3 CST
NH2+NH2=N2H2+H2	0.500E+12	0.000	0.000	!	NH3 CST
NH3+M=NH2+H+M	0.140E+17	0.000	90600.000	!	MSGK
N2H3+H=NH2+NH2	1.60E+12	0.0	0.0	!	MSGK
N2H3+M=N2H2+H+M	3.50E+16	0.0	46000.0	!	MSGK
N2H3+NH=NH2+N2H2	2.00E+13	0.0	0.0	!	MSGK
NH2+NH2+M=N2H4+M	3.00E+20	-1.0	0.0	!	MSGK
H+N2H4=H2+N2H3	1.30E+13	0.0	2500.0	!	MSGK
NH2+N2H4=NH3+N2H3	3.90E+12	0.0	1500.0	!	MSGK
NH+H+M=NH2+M	2.00E+16	-0.5	0.0	!	MSGK
NH2+NH2=NH3+NH	5.00E+12	0.0	10000.0	!	MSGK
F+NH3=NH2+HF	4.27E+11	0.5	800.0	!	KONDRATIEV
SIF4=SIF3+F	3.00E+12	0.0	147170.0	!	PHO&MEC
H+SIF4=HF+SIF3	1.00E+13	0.0	50000.0	!	PHO&MEC
NH2+SIF4=SIF3NH2+F	1.00E+11	0.0	40950.0	!	GUESS
NH3+SIF3=SIF3NH2+H	1.00E+11	0.0	5000.0	!	GUESS
NH3+SIF3=SIHF3+NH2	1.00E+11	0.0	10000.0	!	PHO&MEC
END					

# 7.2 Output from CHEMKIN Interpreter for the Example

CHEMKIN-III GAS-PHASE MECHANISM INTERPRETER: DOUBLE PRECISION Vers. 6.24 2000/06/18 Copyright 1995, Sandia Corporation. The U.S. Government retains a limited license in this software.

			EL CC	EMENTS	ATOMIC WEIGHT	-				
			1 2 3 4	. H 1 . N 1 . SI 2 . F 1	L.00797 L4.0067 28.0860 L8.9984	-				
SPECI CONSI	IES IDERED	 P H A S E	C H A G E	MOLECULAR WEIGHT	TEMPEF LOW	RATURE HIGH	ELE H	IMEN N	NT ( SI	COUNT F
1. 2. 3. 4. 5.	H2 H N2 N NH	9 9 9 9 5 9 9 9 9 9	0 0 0 0	2.01594 1.00797 28.01340 14.00670 15.01467	300 300 300 300 300	5000 5000 5000 5000 5000	2 1 0 0	0 0 2 1	0 0 0 0	0 0 0 0
6. 7. 8. 9. 10.	NH2 NNH N2H2 N2H3 N2H4	5 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	0 0 0 0 0	16.02264 29.02137 30.02934 31.03731 32.04528	300 250 300 300 300	5000 4000 5000 5000 5000	2 1 2 3 4	1 2 2 2 2	0 0 0 0 0	0 0 0 0 0
11. 12. 13. 14. 15. 16.	HF F SIF4 SIF3 SIHF3 SIF3NH2	9 9 9 9 9 9 9 9 9	0 0 0 0 0	20.00637 18.99840 104.07960 85.08120 86.08917 101.10384	300 300 300 300 300 300	5000 5000 5000 3000 3000 3000	1 0 0 1 2	0 0 0 0 1	0 0 1 1 1	1 1 3 3 3
17.	NH3	G	0	17.03061	300	5000	3	1	0	0

				(k = A	T**b exp	(-E/RT))
	REACTIONS CONSI	DERED		A	b	Е
1.	H+H+M=H2+M			1.00E+18	-1.0	0.0
	Н2	Enhanced by	0.000E+00			
2.	H+H+H2=H2+H2			9.20E+16	-0.6	0.0
3.	NH+N=N2+H			3.00E+13	0.0	0.0
4.	NH+H=N+H2			1.00E+14	0.0	0.0
5.	NH2+H=NH+H2			6.92E+13	0.0	3650.0
б.	NH3+H=NH2+H2			6.36E+05	2.4	10171.0
7.	NNH=N2+H			1.00E+04	0.0	0.0
8.	NNH+H=N2+H2			1.00E+14	0.0	0.0
9.	NNH+NH2=N2+NH3			5.00E+13	0.0	0.0
10.	NNH+NH=N2+NH2			5.00E+13	0.0	0.0
11.	NH2+NH=N2H2+H			5.00E+13	0.0	0.0
12.	NH+NH=N2+H+H			2.54E+13	0.0	0.0

13.	NH2+N=N2+H+H			7.20E+13	0.0	0.0
14.	N2H2+M=NNH+H+M			5.00E+16	0.0	50000.0
	N2	Enhanced by	2.000E+00			
	Н2	Enhanced by	2.000E+00			
15.	N2H2+H=NNH+H2			5.00E+13	0.0	1000.0
16.	N2H2+NH=NNH+NH2			1.00E+13	0.0	1000.0
17.	N2H2+NH2=NH3+NN	H		1.00E+13	0.0	1000.0
18.	NH2+NH2=N2H2+H2			5.00E+11	0.0	0.0
19.	NH3+M=NH2+H+M			1.40E+16	0.0	90600.0
20.	N2H3+H=NH2+NH2			1.60E+12	0.0	0.0
21.	N2H3+M=N2H2+H+M			3.50E+16	0.0	46000.0
22.	N2H3+NH=NH2+N2H	2		2.00E+13	0.0	0.0
23.	NH2+NH2+M=N2H4+	М		3.00E+20	-1.0	0.0
24.	H+N2H4=H2+N2H3			1.30E+13	0.0	2500.0
25.	NH2+N2H4=NH3+N2	Н3		3.90E+12	0.0	1500.0
26.	NH+H+M=NH2+M			2.00E+16	-0.5	0.0
27.	NH2+NH2=NH3+NH			5.00E+12	0.0	10000.0
28.	F+NH3=NH2+HF			4.27E+11	0.5	800.0
29.	SIF4=SIF3+F			3.00E+12	0.0	147170.0
30.	H+SIF4=HF+SIF3			1.00E+13	0.0	50000.0
31.	NH2+SIF4=SIF3NH	2+F		1.00E+11	0.0	40950.0
32.	NH3+SIF3=SIF3NH	2+H		1.00E+11	0.0	5000.0
33.	NH3+SIF3=SIHF3+	NH2		1.00E+11	0.0	10000.0

NOTE: A units mole-cm-sec-K, E units cal/mole

NO ERRORS FOUND ON INPUT: ASCII Vers. 1.1 CHEMKIN linkfile chem.asc written.

WORKING SPACE REQUIREMENTS ARE

INTEGER: 1086 REAL: 723 CHARACTER: 21 Total CPUtime (sec): 0.171875

#### 7.3 Input to SURFACE CHEMKIN Interpreter for the Example

```
MATERIAL/TEST1/
SITE/SI3N4/
             SDEN/4.1683E-9/
  HN_SIF(S)/2/ F3SI_NH2(S)/2/ F2SINH(S)/2/
  H2NFSINH(S)/2/ HN(FSINH)2(S)/4/
  HN NH2(S)/2/
END
BULK SI(D)/2.066/
BULK N(D) /1.374/
END
THERMO ALL
 300.
           600.
                    1685.
                          1H 1SI 1F 1S 300.000 1685.000
HN_SIF(S)
                 J 3/67N
                                                                             1
0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
                J 3/67N 2H 3SI OF OS 300.000 1685.000
HN NH2(S)
                                                                             1
0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
F3SI_NH2(S)
                J 3/67N 1H 2SI 1F 3S 300.000 1685.000
                                                                             1
0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
F2SINH(S)
               J 3/67N 1H 1SI 1F 2S 300.000 1685.000
                                                                             1
0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
               J 3/67N 2H 3SI 1F 1S 300.000 1685.000
H2NFSINH(S)
                                                                             1
0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
HN(FSINH)2(S) J 3/67N 3H 3SI 2F 2S 300.000 1685.000
                                                                             1
0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
ST(D)
                J 3/67SI 100 000 000 0S 300.000 1685.000
                                                                             1
 0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
 0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
                 J 3/67N 100 000 000 0S 300.000 1685.000
N(D)
                                                                             1
0.24753989E 01 0.88112187E-03-0.20939481E-06 0.42757187E-11 0.16006564E-13
                                                                             2
-0.81255620E 03-0.12188747E 02 0.84197538E 00 0.83710416E-02-0.13077030E-04
                                                                             3
0.97593603E-08-0.27279380E-11-0.52486288E 03-0.45272678E 01
                                                                             4
END
REACTIONS
                                                          7.562E08 0.5 0.0
NH3
                + HN_SIF(S) => HN_NH2(S) + SI(D) + HF
 STF4
                + HN_NH2(S) => F3SI_NH2(S) + N(D) + HF
                                                          3.0967E8 0.5 0.0
                            => F2SINH(S)
                                                  + HF
                                                          1.0E05 0.0 0.0
 F3SI_NH2(S)
                + F2SINH(S) => H2NFSINH(S)
                                                  + HF
                                                          7.562E08 0.5 0.0
NH3
               + F2SINH(S) => HN(FSINH)2(S) + HF
                                                          1.0E15 0.0 0.0
H2NFSINH(S)
```

 $HN(FSINH)2(S) + F2SINH(S) => 3HN_SIF(S) + N(D) + HF$ 

END

1.0E15 0.0 0.0

# 7.4 Output from SURFACE CHEMKIN Interpreter for the Example

CHEMKIN-III SURFACE MECHANISM INTERPRETER: DOUBLE PRECISION Vers. 7.20 2000/06/18 Copyright 1995, Sandia Corporation. The U.S. Government retains a limited license in this software.

CKLIB: CHEMKIN-III GAS-PHASE CHEMICAL KINETICS LIBRARY, DOUBLE PRECISION Vers. 5.28 2000/08/05 Copyright 1995, Sandia Corporation. The U.S. Government retains a limited license in this software.

SPECIES	MOLECULAR			ELE	MEN	т С	OUNT
CONSIDERED	WEIGHT	Density	Nsites	Η	Ν	SI	F
Gas phase species:							
1. H2	2.01594			2	0	0	0
2. Н	1.00797			1	0	0	0
3. N2	28.01340			0	2	0	0
4. N	14.00670			0	1	0	0
5. NH	15.01467			1	1	0	0
6. NH2	16.02264			2	1	0	0
7. NNH	29.02137			1	2	0	0
8. N2H2	30.02934			2	2	0	0
9. N2H3	31.03731			3	2	0	0
10. N2H4	32.04528			4	2	0	0
11. HF	20.00637			1	0	0	1
12. F	18,99840			0	0	0	1
13. STF4	104.07960			0	0	1	4
14 STF3	85 08120			0	0	1	3
15 STHE3	86 08917			1	0	1	3
16 STE2NH2	101 10384			2	1	1	3
17 NH2	17 02061			2	1		0
17. NH3	17.03001			3	T	0	0
SPECIES	MOLECIILAR			जनज	MEN	тC	TINT
CONSIDERED	WEIGHT	Density	Nsites	Н	N	SI	F
SITE: SI3N4		0.417E-08 mc	les/cm**2				
18. HN SIF(S)	62.09907		2	1	1	1	1
19. F3ST NH2(S)	101.10384		2	2	1	1	3
20, F2SINH(S)	81.09747		2	1	1	1	2
21 + 2NESINH(S)	78 12171		2	3	2	1	1
22. $HZ(FSINH(S))$	130 21281		2 A	3	2	2	2
22  IN NU2(C)	21 02721			2	2	0	0
23. HN_NH2(3)	51.05751		2	3	2	0	0
BULK: BULK1							
24. SI(D)	28.08600	0.207E+01 g/	cm**3	0	0	1	0
BULK: BULK2							
25. N(D)	14.00670	0.137E+01 g/	cm**3	0	1	0	0

		(k = A 1	**b exp(	-E/RT))
	SURFACE REACTIONS CONSIDERED	А	b	Е
1.	NH3+HN_SIF(S)=>HN_NH2(S)+SI(D)+HF	7.56E+08	0.5	0.0
2.	$SIF4+HN_NH2(S) = >F3SI_NH2(S)+N(D)+HF$	3.10E+08	0.5	0.0
3.	F3SI_NH2(S)=>F2SINH(S)+HF	1.00E+05	0.0	0.0
4.	NH3+F2SINH(S)=>H2NFSINH(S)+HF	7.56E+08	0.5	0.0
5.	H2NFSINH(S)+F2SINH(S)	1.00E+15	0.0	0.0
	=>HN(FSINH)2(S)+HF			
б.	HN(FSINH)2(S)+F2SINH(S)	1.00E+15	0.0	0.0
	$=>3HN_SIF(S)+N(D)+HF$			

NOTE: A units mole-cm-sec-K, E units cal/mole

NO ERRORS FOUND ON INPUT: ASCII Version 1.1 surface linkfile surf.asc written.

WORKING SPACE REQUIREMENTS ARE INTEGER: 481 REAL: 642 CHARACTER: 34 Total CPUtime (sec): 0.046875

## 7.5 Output from the TRANSPORT Preprocessor for the Example

TRANFIT: CHEMKIN-III Transport property fitting code, DOUBLE PRECISION Vers. 3.18 00/08/11 Copyright 1995, Sandia Corporation. The U.S. Government retains a limited license in this software.

	WORKING SPA	CE REQUIREMENTS
	PROVIDED	REQUIRED
INTEGER	1137	1137
REAL	3618	3618
CHARACTER	38	38

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DATA HAS BEEN FIT OVER THE RANGE: TLOW= 300.00, THIGH= 3000.00

TRANSPORT PARAMETERS FROM DATA BASE:

F	0	80.000	2.750	0.000	0.000	0.000	
Н	0	145.000	2.050	0.000	0.000	0.000	
Н2	1	38.000	2.920	0.000	0.790	280.000	
HF	1	330.000	3.148	1.920	2.460	1.000	! sv/mec
N	0	71.400	3.298	0.000	0.000	0.000	!(*)
N2	1	97.530	3.621	0.000	1.760	4.000	
N2H2	2	71.400	3.798	0.000	0.000	1.000	!(*)
N2H3	2	200.000	3.900	0.000	0.000	1.000	!(*)
N2H4	2	205.000	4.230	0.000	4.260	1.500	
NH	1	80.000	2.650	0.000	0.000	4.000	
NH2	2	80.000	2.650	0.000	2.260	4.000	
NH3	2	481.000	2.920	1.470	0.000	10.000	
NNH	2	71.400	3.798	0.000	0.000	1.000	!(*)
SIF3	2	309.6	4.359	0.000	0.000	1.000	!(mec)
SIF3NH2	2	231.0	4.975	0.000	0.000	1.000	!(mec)
SIF4	2	171.9	4.880	0.000	0.000	1.000	!(sve)
SIHF3	2	180.8	4.681	0.000	0.000	1.000	!(mec)

COEFFICIENTS FOR SPECIES CONDUCTIVITIES MAXIMUM FITTING ERROR = 4.777E-03

Н2	0.913E+01	-0.435E+00	0.113E+00	-0.253E-02
Н	-0.855E+00	0.365E+01	-0.398E+00	0.176E-01
N2	0.129E+02	-0.353E+01	0.646E+00	-0.319E-01
N	0.196E+01	0.171E+01	-0.144E+00	0.654E-02
NH	0.132E+02	-0.291E+01	0.507E+00	-0.230E-01
NH2	0.167E+02	-0.469E+01	0.800E+00	-0.377E-01
NNH	0.731E+01	-0.150E+01	0.416E+00	-0.233E-01
N2H2	0.642E+01	-0.157E+01	0.487E+00	-0.288E-01
N2H3	-0.722E+01	0.391E+01	-0.249E+00	0.423E-02
N2H4	-0.142E+02	0.687E+01	-0.663E+00	0.235E-01
HF	0.474E+01	-0.560E+00	0.273E+00	-0.154E-01
F	0.160E+01	0.193E+01	-0.174E+00	0.784E-02
SIF4	-0.205E+02	0.101E+02	-0.120E+01	0.516E-01
SIF3	-0.211E+02	0.101E+02	-0.118E+01	0.496E-01
SIHF3	-0.195E+02	0.944E+01	-0.109E+01	0.451E-01
SIF3NH2	-0.157E+02	0.786E+01	-0.869E+00	0.353E-01
NH3	0.159E+02	-0.619E+01	0.121E+01	-0.648E-01

COEFFICIENTS FOR SPECIES VISCOSITIES MAXIMUM FITTING ERROR = 2.318E-03

Н2	-0.138E+02	0.100E+01	-0.502E-01	0.233E-02
Н	-0.204E+02	0.365E+01	-0.398E+00	0.176E-01
N2	-0.166E+02	0.239E+01	-0.234E+00	0.105E-01
N	-0.150E+02	0.171E+01	-0.144E+00	0.654E-02
NH	-0.151E+02	0.193E+01	-0.174E+00	0.784E-02
NH2	-0.150E+02	0.193E+01	-0.174E+00	0.784E-02
NNH	-0.149E+02	0.171E+01	-0.144E+00	0.654E-02
N2H2	-0.149E+02	0.171E+01	-0.144E+00	0.654E-02
N2H3	-0.228E+02	0.467E+01	-0.522E+00	0.226E-01
N2H4	-0.231E+02	0.474E+01	-0.531E+00	0.230E-01
HF	-0.188E+02	0.224E+01	-0.994E-01	0.956E-04
F	-0.150E+02	0.193E+01	-0.174E+00	0.784E-02
SIF4	-0.213E+02	0.421E+01	-0.467E+00	0.204E-01
SIF3	-0.247E+02	0.526E+01	-0.570E+00	0.235E-01
SIHF3	-0.218E+02	0.436E+01	-0.485E+00	0.212E-01
SIF3NH2	-0.238E+02	0.506E+01	-0.567E+00	0.243E-01
NH3	-0.162E+02	0.120E+01	0.438E-01	-0.647E-02

#### COEFFICIENTS FOR SPECIES DIFFUSION COEFFICIENTS MAXIMUM FITTING ERROR = 3.926E-03

Н2	Н2	-0.103E+02	0.219E+01	-0.754E-01	0.351E-02
н	н2	-0 120E+02	0 303E+01	-0 186E+00	0 836E-02
ч	н2	-0 152F+02	0.438F+01	-0.356F+00	0.050E 02
11	11	0.1521.02	0.1501/01	0.5501100	0.1555 01
N2	Н2	-0.127E+02	0.290E+01	-0.170E+00	0.774E-02
N2	Н	-0.171E+02	0.483E+01	-0.421E+00	0.186E-01
N2	N2	-0.155E+02	0.346E+01	-0.240E+00	0.106E-01
N	Н2	-0.108E+02	0.219E+01	-0.710E-01	0.313E-02
N	Н	-0.157E+02	0.436E+01	-0.363E+00	0.162E-01
Ν	N2	-0.145E+02	0.321E+01	-0.208E+00	0.931E-02
N	N	-0.134E+02	0.287E+01	-0.164E+00	0.737E-02
NH	Н2	-0.109E+02	0.231E+01	-0.874E-01	0.390E-02
NH	Н	-0.152E+02	0.423E+01	-0.343E+00	0.152E-01
NH	N2	-0.148E+02	0.339E+01	-0.232E+00	0.104E-01
NH	Ν	-0.134E+02	0.296E+01	-0.175E+00	0.784E-02
NH	NH	-0.135E+02	0.306E+01	-0.189E+00	0.845E-02
NH2	H2	-0.109E+02	0.231E+01	-0.874E-01	0.390E-02
NH2	Н	-0.152E+02	0.424E+01	-0.344E+00	0.153E-01
NH2	N2	-0.147E+02	0.337E+01	-0.230E+00	0.103E-01
NH2	N	-0.134E+02	0.295E+01	-0.175E+00	0.784E-02
NH2	NH	-0.135E+02	0.306E+01	-0.189E+00	0.846E-02
NH2	NH2	-0.135E+02	0.306E+01	-0.189E+00	0.845E-02
NNH	Н2	-0.110E+02	0.219E+01	-0.709E-01	0.313E-02
NNH	Н	-0.167E+02	0.470E+01	-0.409E+00	0.183E-01
NNH	N2	-0.147E+02	0.314E+01	-0.198E+00	0.884E-02
NNH	Ν	-0.138E+02	0.295E+01	-0.175E+00	0.786E-02
NNH	NH	-0.140E+02	0.306E+01	-0.190E+00	0.854E-02
NNH	NH2	-0.140E+02	0.305E+01	-0.188E+00	0.846E-02
NNH	NNH	-0.140E+02	0.287E+01	-0.164E+00	0.737E-02
N2H2	Н2	-0.110E+02	0.219E+01	-0.709E-01	0.313E-02
N2H2	Н	-0.167E+02	0.470E+01	-0.410E+00	0.184E-01
N2H2	N2	-0.147E+02	0.314E+01	-0.198E+00	0.884E-02
N2H2	N	-0.139E+02	0.295E+01	-0.175E+00	0.790E-02
N2H2	NH	-0.140E+02	0.307E+01	-0.191E+00	0.859E-02
N2H2	NH2	-0.140E+02	0.306E+01	-0.189E+00	0.850E-02
N2H2	NNH	-0.140E+02	0.287E+01	-0.164E+00	0.737E-02
N2H2	N2H2	-0.140E+02	0.287E+01	-0.164E+00	0.737E-02
N2H3	Н2	-0.150E+02	0.376E+01	-0.285E+00	0.128E-01
N2H3	Н	-0.176E+02	0.475E+01	-0.384E+00	0.159E-01
N2H3	N2	-0.178E+02	0.429E+01	-0.345E+00	0.150E-01
N2H3	Ν	-0.168E+02	0.404E+01	-0.314E+00	0.138E-01
N2H3	NH	-0.172E+02	0.423E+01	-0.338E+00	0.148E-01
N2H3	NH2	-0.171E+02	0.421E+01	-0.336E+00	0.147E-01
N2H3	NNH	-0.168E+02	0.389E+01	-0.294E+00	0.129E-01
N2H3	N2H2	-0.168E+02	0.389E+01	-0.294E+00	0.129E-01
N2H3	N2H3	-0.199E+02	0.492E+01	-0.414E+00	0.176E-01
N2H4	Н2	-0.154E+02	0.388E+01	-0.301E+00	0.135E-01
N2H4	Н	-0.178E+02	0.478E+01	-0.386E+00	0.158E-01
N2H4	N2	-0.180E+02	0.433E+01	-0.349E+00	0.152E-01
N2H4	N	-0.171E+02	0.413E+01	-0.325E+00	0.143E-01
N2H4	NH	-0.175E+02	0.433E+01	-0.351E+00	0.154E-01

N2H4	NH2	-0.175E+02	0.431E+01	-0.348E+00	0.152E-01
N2H4	NNH	-0.170E+02	0.394E+01	-0.301E+00	0.132E-01
N2H4	N2H2	-0.170E+02	0.394E+01	-0.301E+00	0.132E-01
N2H4	N2H3	-0.200E+02	0.495E+01	-0.417E+00	0.176E-01
N2H4	N2H4	-0.202E+02	0.495E+01	-0.417E+00	0.176E-01
HF	Н2	-0.169E+02	0.457E+01	-0.386E+00	0.171E-01
HF	Н	-0.166E+02	0.434E+01	-0.314E+00	0.121E-01
HF	N2	-0.195E+02	0.496E+01	-0.421E+00	0.179E-01
HF	N	-0.178E+02	0.448E+01	-0.367E+00	0.159E-01
HF	NH	-0.179E+02	0.458E+01	-0.377E+00	0.162E-01
HF	NH2	-0.199E+02	0.528E+01	-0.460E+00	0.195E-01
HF	NNH	-0.181E+02	0.448E+01	-0.366E+00	0.158E-01
HF	N2H2	-0.181E+02	0.448E+01	-0.366E+00	0.158E-01
HF	N2H3	-0.203E+02	0.507E+01	-0.418E+00	0.171E-01
HF	N2H4	-0.208E+02	0.516E+01	-0.423E+00	0.170E-01
HF	HF	-0.184E+02	0.379E+01	-0.179E+00	0.395E-02
-		0.1000.00	0 021 . 01	0 0745 01	0 2005 00
r T	п∠ 11	-U.LUYE+UZ	0.420T+U1		0.3908-02
F.	H	-0.154E+02	0.429E+01	-0.351E+00	0.1568-01
F.	NZ	-0.14/E+02	0.333E+U1	-0.224E+00	0.998E-02
F.	N	-0.135E+02	0.2968+01	-0.1/5E+00	0.785E-02
F.	NH	-0.136E+02	0.307E+01	-0.190E+00	0.851E-02
F	NH2	-0.136E+02	0.307E+01	-0.190E+00	0.849E-02
F'	NNH	-0.140E+02	0.301E+01	-0.183E+00	0.822E-02
F,	N2H2	-0.140E+02	0.302E+01	-0.184E+00	0.825E-02
F'	N2H3	-0.171E+02	0.416E+01	-0.329E+00	0.144E-01
F.	N2H4	-0.174E+02	0.424E+01	-0.340E+00	0.149E-01
F'	HF'	-0.180E+02	0.456E+01	-0.375E+00	0.162E-01
F,	F	-0.137E+02	0.306E+01	-0.189E+00	0.845E-02
STF4	н2	-0.154E+02	0.384E+01	-0.298E+00	0.135E-01
STF4	н	-0.197E+02	0.553E+01	-0.491E+00	0.207E-01
SIF4	N2	-0 186E+02	0.444E+01	-0.365E+00	0.160E-01
SIF4	N	-0 180E+02	0 439E+01	-0.365E+00	0 162E-01
SIF1 SIF4	NH	-0 184F+02	0.461F+01	-0.391F+00	0.172E-01
SIF4	NH2	-0 184E+02	0.459E+01	-0.388E+00	0.171E-01
SIF4	NNH	-0.177E+02	0 410E+01	-0.325E+00	0 144E-01
SIF4	N2H2	-0.177E+02	0 409E+01	-0.324E+00	0 143E-01
SIF4	N2H3	-0.198E+02	0.473E+01	-0.388E+00	0.163E-01
SIF4	N2H4	-0 200E+02	0.475E+01	-0.391E+00	0.165E-01
SIF4	HF	-0 194E+02	0 450E+01	-0.336E+00	0 132E-01
SIF4	F	-0 183E+02	0.450E+01	-0.376E+00	0.152E 01
SIF4	SIF4	-0.201E+02	0.467E+01	-0.388E+00	0.166E-01
SIF3	Н2	-0.173E+02	0.460E+01	-0.393E+00	0.175E-01
SIF3	Н	-0.161E+02	0.388E+01	-0.238E+00	0.814E-02
SIF3	N2	-0.194E+02	0.472E+01	-0.391E+00	0.166E-01
SIF3	N	-0.187E+02	0.464E+01	-0.386E+00	0.167E-01
SIF3	NH	-0.193E+02	0.488E+01	-0.415E+00	0.178E-01
SIF3	NH2	-0.193E+02	0.487E+01	-0.414E+00	0.178E-01
SIF3	NNH	-0.188E+02	0.451E+01	-0.370E+00	0.160E-01
SIF3	N2H2	-0.188E+02	0.450E+01	-0.369E+00	0.160E-01
SIF3	N2H3	-0.205E+02	0.490E+01	-0.394E+00	0.160E-01
SIF3	N2H4	-0.207E+02	0.494E+01	-0.400E+00	0.162E-01
SIF3	HF	-0.197E+02	0.452E+01	-0.322E+00	0.119E-01
SIF3	F	-0.192E+02	0.483E+01	-0.408E+00	0.175E-01
SIF3	SIF4	-0.214E+02	0.510E+01	-0.430E+00	0.179E-01
SIF3	SIF3	-0.220E+02	0.521E+01	-0.425E+00	0.170E-01
стиро	ц)	-0 1540.00	0 204		0 12250 01
OTUES	112 U	-0.107E-02	0.304E+UL 0 510E+01	-0.2935+00 -0.4305+00	0.1335-01
OTUES	11 N2	-0.10/E+UZ	0.0105+01	-0.4295+00	0.1610.01
STHES STHES	N	-0.1005+02 -0 1005+02	0.440E+01 0 441F±01	-0.300E+00 -0 367E±00	0.1632-01
5 7111 5	T4	0.1006402	0.1410+01	0.30/6+00	0.1038-01

SIHF3	NH	-0.184E+02	0.461E+01	-0.390E+00	0.172E-01
SIHF3	NH2	-0.183E+02	0.459E+01	-0.388E+00	0.171E-01
SIHF3	NNH	-0.177E+02	0.411E+01	-0.326E+00	0.144E-01
SIHF3	N2H2	-0.176E+02	0.410E+01	-0.324E+00	0.144E-01
SIHF3	N2H3	-0.199E+02	0.479E+01	-0.395E+00	0.166E-01
SIHF3	N2H4	-0.200E+02	0.478E+01	-0.395E+00	0.166E-01
SIHF3	HF	-0.195E+02	0.456E+01	-0.344E+00	0.135E-01
SIHF3	F	-0.182E+02	0.449E+01	-0.375E+00	0.165E-01
SIHF3	SIF4	-0.202E+02	0.472E+01	-0.393E+00	0.168E-01
SIHF3	SIF3	-0.214E+02	0.512E+01	-0.432E+00	0.180E-01
SIHF3	SIHF3	-0.202E+02	0.477E+01	-0.399E+00	0.170E-01
SIF3NH2	Н2	-0.166E+02	0.429E+01	-0.354E+00	0.159E-01
SIF3NH2	Н	-0.176E+02	0.448E+01	-0.329E+00	0.126E-01
SIF3NH2	N2	-0.192E+02	0.460E+01	-0.380E+00	0.164E-01
SIF3NH2	N	-0.187E+02	0.463E+01	-0.391E+00	0.171E-01
SIF3NH2	NH	-0.197E+02	0.506E+01	-0.448E+00	0.196E-01
SIF3NH2	NH2	-0.197E+02	0.505E+01	-0.445E+00	0.195E-01
SIF3NH2	NNH	-0.185E+02	0.438E+01	-0.358E+00	0.157E-01
SIF3NH2	N2H2	-0.185E+02	0.438E+01	-0.357E+00	0.156E-01
SIF3NH2	N2H3	-0.202E+02	0.477E+01	-0.384E+00	0.158E-01
SIF3NH2	N2H4	-0.204E+02	0.482E+01	-0.391E+00	0.161E-01
SIF3NH2	HF	-0.194E+02	0.439E+01	-0.310E+00	0.116E-01
SIF3NH2	F	-0.195E+02	0.495E+01	-0.432E+00	0.189E-01
SIF3NH2	SIF4	-0.209E+02	0.492E+01	-0.414E+00	0.175E-01
SIF3NH2	SIF3	-0.219E+02	0.520E+01	-0.434E+00	0.178E-01
SIF3NH2	SIHF3	-0.209E+02	0.494E+01	-0.416E+00	0.176E-01
SIF3NH2	SIF3NH2	-0.216E+02	0.512E+01	-0.432E+00	0.180E-01
NH3	Н2	-0.175E+02	0.478E+01	-0.409E+00	0.179E-01
NH3	Н	-0.164E+02	0.417E+01	-0.279E+00	0.101E-01
NH3	N2	-0.199E+02	0.508E+01	-0.426E+00	0.178E-01
NH3	N	-0.186E+02	0.478E+01	-0.399E+00	0.170E-01
NH3	NH	-0.187E+02	0.488E+01	-0.409E+00	0.174E-01
NH3	NH2	-0.199E+02	0.527E+01	-0.453E+00	0.190E-01
NH3	NNH	-0.189E+02	0.474E+01	-0.392E+00	0.166E-01
NH3	N2H2	-0.189E+02	0.474E+01	-0.391E+00	0.166E-01
NH3	N2H3	-0.203E+02	0.499E+01	-0.393E+00	0.154E-01
NH3	N2H4	-0.203E+02	0.489E+01	-0.374E+00	0.143E-01
NH3	HF	-0.177E+02	0.361E+01	-0.161E+00	0.338E-02
NH3	F	-0.188E+02	0.488E+01	-0.409E+00	0.174E-01
NH3	SIF4	-0.188E+02	0.419E+01	-0.279E+00	0.100E-01
NH3	SIF3	-0.193E+02	0.426E+01	-0.275E+00	0.940E-02
NH3	SIHF3	-0.191E+02	0.434E+01	-0.299E+00	0.110E-01
NH3	SIF3NH2	-0.187E+02	0.402E+01	-0.246E+00	0.825E-02
NH3	NH3	-0.166E+02	0.316E+01	-0.986E-01	0.549E-03

#### COEFFICIENTS FOR THERMAL DIFFUSION RATIOS MAXIMUM FITTING ERROR = 1.306E-02

Н2	Н2	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Н2	Н	0.144E+00	0.800E-04	-0.490E-07	0.914E-11
Н2	N2	-0.431E+00	-0.921E-04	0.595E-07	-0.121E-10
Н2	N	-0.401E+00	-0.155E-04	0.103E-07	-0.297E-11
Н2	NH	-0.400E+00	-0.378E-04	0.251E-07	-0.577E-11
Н2	NH2	-0.407E+00	-0.385E-04	0.255E-07	-0.587E-11
Н2	NNH	-0.467E+00	-0.180E-04	0.119E-07	-0.346E-11
Н2	N2H2	-0.469E+00	-0.181E-04	0.120E-07	-0.347E-11
Н2	N2H3	-0.322E+00	-0.318E-03	0.187E-06	-0.335E-10
Н2	N2H4	-0.318E+00	-0.327E-03	0.192E-06	-0.343E-10
Н2	HF	-0.152E+00	-0.529E-03	0.287E-06	-0.481E-10
Н2	F	-0.423E+00	-0.401E-04	0.265E-07	-0.610E-11
Н2	SIF4	-0.384E+00	-0.292E-03	0.175E-06	-0.319E-10
Н2	SIF3	-0.251E+00	-0.509E-03	0.285E-06	-0.490E-10
Н2	SIHF3	-0.371E+00	-0.308E-03	0.183E-06	-0.332E-10
Н2	SIF3NH2	-0.321E+00	-0.402E-03	0.232E-06	-0.410E-10
Н2	NH3	-0.877E-01	-0.590E-03	0.309E-06	-0.509E-10
Н	Н2	-0.144E+00	-0.800E-04	0.490E-07	-0.914E-11
Н	Н	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Н	N2	-0.202E+00	-0.563E-03	0.309E-06	-0.523E-10
Н	N	-0.255E+00	-0.419E-03	0.238E-06	-0.413E-10
Н	NH	-0.233E+00	-0.462E-03	0.259E-06	-0.446E-10
Н	NH2	-0.235E+00	-0.466E-03	0.261E-06	-0.449E-10
Н	NNH	-0.275E+00	-0.451E-03	0.256E-06	-0.445E-10
Н	N2H2	-0.276E+00	-0.452E-03	0.257E-06	-0.446E-10
Н	N2H3	-0.270E-01	-0.789E-03	0.400E-06	-0.643E-10
Н	N2H4	-0.212E-01	-0.797E-03	0.403E-06	-0.647E-10
Н	HF	0.827E-01	-0.852E-03	0.407E-06	-0.631E-10
Н	F	-0.240E+00	-0.475E-03	0.266E-06	-0.458E-10
Н	SIF4	-0.666E-01	-0.784E-03	0.404E-06	-0.657E-10
Н	SIF3	0.754E-01	-0.912E-03	0.439E-06	-0.684E-10
Н	SIHF3	-0.536E-01	-0.796E-03	0.408E-06	-0.661E-10
Н	SIF3NH2	0.733E-02	-0.861E-03	0.429E-06	-0.683E-10
Н	NH3	0.148E+00	-0.861E-03	0.390E-06	-0.585E-10

WORKING SPACE REQUIREMENTS ARE

INTEGER: 70 REAL: 6086

Total CPUtime (sec): 0.125

# 7.6 Input to SPIN for the Example

COMP		
ENRG		
OMEG	1000	
TDSK	1713	
TINF	300	
NPTS	11	
XEND	10.0	
PRES	2.3684E-3	
GRAD	.9	
CURV	.9	
REAC	SIF4	0.14286
REAC	NH3	0.85714
PROD	SIF4	0.123
PROD	NH3	0.8547
PROD	HF	0.02231
SURF	HN_SIF(S)	6.2511E-02
SURF	HN_NH2(S)	0.915873
SURF	F3SI_NH2(S)	2.3540E-04
SURF	F2SINH(S)	2.0837E-02
SURF	H2NFSINH(S)	1.8063E-04
SURF	HN(FSINH)2(S)	3.6127E-04
ACT	SI(D)	1.0
ACT	N(D)	1.0
ATOL	1.E-8	
RTOL	1.E-5	
ATIM	1.E-8	
RTIM	1.E-3	
PRNT	1	
NADP	4	
XCEN	.4	
WMIX	.35	
TIME	100 1.0E-8	
TIM2	100 1.0E-8	
SFLR	-1.0E-3	
TEMP	0. 1713.	
TEMP	1. 1713.	
TEMP	10. 300.	
ASEN		
HSEN		
END		

# 7.7 Output from SPIN for the Example

SPIN: 1-D steady rotating disk/stagnation-point reactor solving dimensional equations CHEMKIN-III Version 5.43 August 9, 2000 DOUBLE PRECISION

	WORKING	SPACE	REQUIREMENTS
	PROVID	ED	REQUIRED
LOGICAL	223	3	223
INTEGER	8524	1	8524
REAL	807353	3	807353
CHARACTER	139	9	139

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KEYW	ORD INPUT	
COMP		
ENRG		
OMEG	1000	
TDSK	1713	
TINF	300	
NPTS	11	
XEND	10.0	
PRES	2.3684E-3	
GRAD	.9	
CURV	.9	
REAC	SIF4	0.14286
REAC	NH3	0.85714
PROD	SIF4	0.123
PROD	NH3	0.8547
PROD	HF	0.02231
SURF	HN_SIF(S)	6.2511E-02
SURF	HN_NH2(S)	0.915873
SURF	F3SI_NH2(S)	2.3540E-04
SURF	F2SINH(S)	2.0837E-02
SURF	H2NFSINH(S)	1.8063E-04
SURF	HN(FSINH)2(S)	3.6127E-04
ACT	SI(D)	1.0
ACT	N(D)	1.0
ATOT.	1.E-8	

RTOL 1.E-5 ATIM 1.E-8 RTIM 1.E-3 PRNT 1 4 NADP XCEN .4 WMIX .35 TIME 100 1.0E-8 TIM2 100 1.0E-8 -1.0E-3 SFLR TEMP 0. 1713. TEMP 1. 1713. TEMP 10. 300. ASEN HSEN END CAUTION... PRODUCT FRACTIONS SUM TO 1.0000100000000 CAUTION...SITE FRACTIONS SUM TO 0.99999830 FOR PHASE SI3N4  $\,$ 

TWOPNT: DOUBLE PRECISION (TWO POINT BOUNDARY VALUE PROBLEM) SOLVER, VERSION 3.30 OF APRIL 1998 BY DR. JOSEPH F. GRCAR.

TWOPNT: INITIAL GUESS:

	X(CM)	T(K)	U(C/S)	V/R(1/S)	W/R(1/S)
11	10.0000	3.000E+02	-1.023E+01	0.000E+00	0.000E+00
10	9.0000	4.413E+02	-9.210E+00	6.545E+00	1.047E+01
9	8.0000	5.826E+02	-8.187E+00	1.309E+01	2.094E+01
8	7.0000	7.239E+02	-7.163E+00	1.963E+01	3.142E+01
7	6.0000	8.652E+02	-6.140E+00	2.618E+01	4.189E+01
б	5.0000	1.007E+03	-5.117E+00	3.272E+01	5.236E+01
5	4.0000	1.148E+03	-4.093E+00	3.927E+01	6.283E+01
4	3.0000	1.289E+03	-3.070E+00	4.581E+01	7.330E+01
3	2.0000	1.430E+03	-2.047E+00	5.236E+01	8.378E+01
2	1.0000	1.572E+03	-1.023E+00	2.618E+01	9.425E+01
1	0.0000	1.713E+03	0.000E+00	0.000E+00	1.047E+02

TWOPNT: SOLVE THE PROBLEM.

			LOG10	LOG10	
	EMARK	RI	COND J	NORM F	TASK
				F 47	
				5.4/	SIARI
STEPS	SEARCH	8	6.59	-0.64	SEARCH

TWOPNT: FINAL SOLUTION:

11 10 9 8	X(CM) 10.0000 9.0000 8.0000 7.0000	T(K) 3.000E+02 4.258E+02 5.620E+02 7.063E+02	U(C/S) -5.369E+01 -6.495E+01 -8.509E+01 -1.014E+02	V/R(1/S) 0.000E+00 1.427E+00 3.489E+00 6.215E+00	W/R(1/S) 0.000E+00 2.088E+00 5.197E+00 9.643E+00	
7	6.0000	8.564E+02	-1.112E+02	9.502E+00	1.581E+01	
6	5.0000	1.010E+03	-1.120E+02	1.304E+01	2.414E+01	
5	4.0000	1.163E+03	-1.023E+02	1.623E+01	3.503E+01	
4	3.0000	1.312E+03	-8.206E+01	1.810E+01	4.878E+01	
3	2.0000	1.455E+03	-5.358E+01	1.726E+01	6.543E+01	
2	1.0000	1.589E+03	-2.283E+01	1.191E+01	8.450E+01	
1	0.0000	1.713E+03	0.000E+00	0.000E+00	1.047E+02	
TWOPNT: SUCCESS. PROBLEM SOLVED.						
## 

SPINDR: FINISHED SOLVING THE NONREACTING PROBLEM

TWOPNT: DOUBLE PRECISION (TWO POINT BOUNDARY VALUE PROBLEM) SOLVER, VERSION 3.30 OF APRIL 1998 BY DR. JOSEPH F. GRCAR.

TWOPNT: INITIAL GUESS:

	X(CM)	Т(К)	U(C/S)	V/R(1/S)	W/R(1/S)	RHO(G/CC)	LAMBDA	Sum_Yk
11	10.00	3.000E+02	-5.369E+01	0.000E+00	0.000E+00	2.835E-06	0.000E+00	1.000E+00
10	9.000	4.258E+02	-7.502E+01	1.427E+00	2.088E+00	1.997E-06	1.165E-27	1.000E+00
9	8.000	5.620E+02	-9.323E+01	3.489E+00	5.197E+00	1.513E-06	1.679E-22	1.000E+00
8	7.000	7.063E+02	-1.063E+02	6.215E+00	9.643E+00	1.204E-06	-3.701E-22	1.000E+00
7	6.000	8.564E+02	-1.116E+02	9.502E+00	1.581E+01	9.931E-07	-1.046E-21	1.000E+00
б	5.000	1.010E+03	-1.072E+02	1.304E+01	2.414E+01	8.424E-07	8.366E-22	1.000E+00
5	4.000	1.163E+03	-9.220E+01	1.623E+01	3.503E+01	7.315E-07	1.567E-21	1.000E+00
4	3.000	1.312E+03	-6.782E+01	1.810E+01	4.878E+01	6.481E-07	-3.123E-21	1.000E+00
3	2.000	1.455E+03	-3.820E+01	1.726E+01	6.543E+01	5.844E-07	4.925E-22	1.000E+00
2	1.000	1.589E+03	-1.141E+01	1.191E+01	8.450E+01	5.351E-07	5.279E-21	1.000E+00
1	0.0000E+00	1.713E+03	-5.110E+00	0.000E+00	1.047E+02	4.685E-07	5.279E-21	1.000E+00
	X(CM)	Н2	Н	N2	N	NH	NH2	
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
10	9.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
9	8.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
8	7.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
7	6.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
6	5.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
5	4,000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
4	3,000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
3	2 000	0 0005+00	0 000E+00	0.000E+00	0.000E+00	0 000F+00	0 0005+00	
2	1 000	0.000±+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
1	0 0000000000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
- FT.X((	2/CM2 S)	0.000±+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
1 111( (	3, 6112 6,	0.0001.00	0.0001.00	0.0001.00	0.0001.00	0.0001.00	0.0001.00	
	X(CM)	NNH	N2H2	N2H3	N2H4	HF	F	
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
10	9.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
9	8.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
8	7.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
7	6.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
б	5.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
5	4.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
4	3.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
3	2.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
2	1.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
1	0.0000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	2.231E-02	0.000E+00	
FLX(	G/CM2 S)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	4.216E-06	0.000E+00	
	-, - ,							
	X(CM)	SIF4	SIF3	SIHF3	SIF3NH2	NH3		
11	10.00	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
10	9.000	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
9	8.000	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
8	7.000	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
7	6.000	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
6	5.000	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
5	4.000	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
4	3,000	1.4298-01	0.000±+00	0.000±+00	0.000E+00	8.571E-01		
3	2 000	1 429E-01	0 000E+00	0 000E+00	0.000E+00	8 571E-01		
2	1,000	1.4298-01	0.000±+00	0.000±+00	0.000±+00	8.571E-01		
1	0.0000±+00	1.230E-01	0.000±+00	0.000±+00	0.000E+00	8.547E-01		
- FT.X/(	3/CM2 S)	-5 277E-06	0 000E+00	0 000E+00	0 000E+00	-1 333E-06		
~ ~ ~ ( \	, /	5.2,72 00	0.000000000	3.0000100	3.0000100	T.2222 00		

<pre>SITE 1: SI3N4     HN_SIF(S)     F3SI_NH2(S)     F2SINH(S)     H2NFSINH(S)     HN(FSINH)2(S     HN_NH2(S)</pre>	, SIT 6.251E-02 2.354E-04 2.084E-02 1.806E-04 3.613E-04 9.159E-01	FE DENSITY	4.168300E-0	09	
DEPOSITION RATE	(CM/SEC)	(MICRON/MIN)	MOLE H	FRACTION	
SI(D) BULK 2: BULK2	7.983E-07	4.790E-01	1.000	DE+00	
N(D)	6.835E-07	4.101E-01	1.000	)E+00	
HEAT FROM SURFACT HEAT FLUX TO INL HEAT FLUX TO SUB	E REACTIONS: ET: STRATE:	2.856E+05 ER 0.000E+00 ER 0.000E+00 ER	G/CM2-S ( G/CM2-S ( G/CM2-S (	2.856E-02 0.000E+00 0.000E+00	W/CM2) W/CM2) W/CM2)

TWOPNT: SOLVE THE PROBLEM.

	LOG10	LOG10	
TASK	NORM F	COND J	REMARK

START	0.67				
SEARCH	-4.58	10.64	10	SEARCH	STEPS

# TWOPNT: FINAL SOLUTION:

	X(CM)	Т(К)	U(C/S)	V/R(1/S)	W/R(1/S)	RHO(G/CC)	LAMBDA	Sum_Yk
11	10.00	3.000E+02	-5.364E+01	0.000E+00	0.000E+00	2.835E-06	0.000E+00	1.000E+00
10	9.000	4.258E+02	-7.478E+01	1.404E+00	2.065E+00	2.003E-06	0.000E+00	1.000E+00
9	8.000	5.620E+02	-9.285E+01	3.478E+00	5.207E+00	1.520E-06	3.991E-25	1.000E+00
8	7.000	7.063E+02	-1.059E+02	6.235E+00	9.735E+00	1.208E-06	-2.179E-24	1.000E+00
7	6.000	8.564E+02	-1.114E+02	9.543E+00	1.601E+01	9.936E-07	-2.803E-24	1.000E+00
6	5.000	1.010E+03	-1.075E+02	1.306E+01	2.443E+01	8.385E-07	-4.218E-24	1.000E+00
5	4.000	1.163E+03	-9.329E+01	1.618E+01	3.536E+01	7.229E-07	3.502E-24	1.000E+00
4	3.000	1.312E+03	-6.999E+01	1.795E+01	4.908E+01	6.349E-07	3.631E-23	1.000E+00
3	2.000	1.455E+03	-4.157E+01	1.703E+01	6.561E+01	5.670E-07	2.151E-23	1.000E+00
2	1.000	1.589E+03	-1.585E+01	1.171E+01	8.453E+01	5.141E-07	2.151E-23	1.000E+00
1	0.0000E+00	1.713E+03	-5.104E+00	0.000E+00	1.047E+02	4.723E-07	2.151E-23	1.000E+00
	X(CM)	Н2	Н	N2	N	NH	NH2	
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
10	9.000	1.006E-07	5.150E-11	6.701E-11	2.379E-15	2.059E-11	2.623E-07	
9	8.000	1.912E-07	1.332E-10	1.473E-10	4.939E-15	4.193E-11	5.343E-07	
8	7.000	2.748E-07	2.049E-10	2.399E-10	7.622E-15	6.391E-11	8.143E-07	
7	6.000	3.530E-07	2.766E-10	3.436E-10	1.038E-14	8.625E-11	1.100E-06	
6	5.000	4.266E-07	3.780E-10	4.562E-10	1.316E-14	1.082E-10	1.388E-06	
5	4.000	4.959E-07	5.886E-10	5.748E-10	1.591E-14	1.288E-10	1.674E-06	
4	3.000	5.611E-07	1.124E-09	6.959E-10	1.855E-14	1.466E-10	1.954E-06	
3	2.000	6.212E-07	2.629E-09	8.128E-10	2.095E-14	1.604E-10	2.223E-06	
2	1.000	6.724E-07	6.814E-09	9.106E-10	2.289E-14	1.696E-10	2.467E-06	
1	0.0000E+00	7.014E-07	1.508E-08	9.587E-10	2.383E-14	1.732E-10	2.628E-06	

	X(CM)	NNH	N2H2	N2H3	N2H4	HF	F
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
10	9.000	6.095E-16	1.069E-10	1.976E-11	3.499E-12	4.415E-03	3.880E-23
9	8.000	2.687E-15	2.369E-10	2.583E-11	6.474E-12	9.672E-03	2.778E-20
8	7.000	5.951E-15	3.629E-10	3.038E-11	8.323E-12	1.563E-02	6.541E-18
7	6.000	1.000E-14	4.725E-10	3.320E-11	9.046E-12	2.215E-02	3.561E-16
6	5.000	1.860E-14	5.567E-10	3.408E-11	8.781E-12	2.905E-02	6.765E-15
5	4.000	8.082E-14	6.092E-10	3.286E-11	7.692E-12	3.615E-02	6.261E-14
4	3.000	5.066E-13	6.268E-10	2.954E-11	5.957E-12	4.330E-02	3.484E-13
3	2.000	2.351E-12	6.104E-10	2.454E-11	3.840E-12	5.032E-02	1.336E-12
2	1.000	7.486E-12	5.707E-10	1.923E-11	1.921E-12	5.711E-02	3.872E-12
1	0.0000E+00	1.603E-11	5.375E-10	1.611E-11	9.964E-13	6.357E-02	8.977E-12
FLX(C	G/CM2 S)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	4.125E-06	0.000E+00
	X(CM)	SIF4	SIF3	SIHF3	SIF3NH2	NH3	
11	10.00	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01	
10	9.000	1.437E-01	6.584E-14	1.132E-12	5.886E-12	8.519E-01	
9	8.000	1.439E-01	1.775E-13	2.863E-12	1.552E-11	8.464E-01	
8	7.000	1.435E-01	3.903E-13	5.303E-12	2.981E-11	8.409E-01	
7	6.000	1.423E-01	8.325E-13	8.511E-12	4.931E-11	8.356E-01	
6	5.000	1.403E-01	1.766E-12	1.246E-11	7.391E-11	8.307E-01	
5	4.000	1.376E-01	3.688E-12	1.701E-11	1.026E-10	8.262E-01	
4	3.000	1.345E-01	7.495E-12	2.187E-11	1.332E-10	8.222E-01	
3	2.000	1.311E-01	1.472E-11	2.656E-11	1.625E-10	8.186E-01	
2	1.000	1.276E-01	2.785E-11	3.036E-11	1.858E-10	8.153E-01	
1	0.0000E+00	1.242E-01	4.872E-11	3.223E-11	1.970E-10	8.122E-01	
FLX(C	G/CM2 S)	-5.365E-06	0.000E+00	0.000E+00	0.000E+00	-1.171E-06	

SITE 1: SI3N4	, SITE DENSITY	4.168300E-09
HN_SIF(S)	5.775E-02	
F3SI_NH2(S)	2.473E-04	
F2SINH(S)	1.925E-02	
H2NFSINH(S)	2.055E-04	
HN(FSINH)2(S	4.110E-04	
HN_NH2(S)	9.221E-01	
DEPOSITION RATE BULK 1: BULK1	(CM/SEC) (MICRON/MIN)	MOLE FRACTION
SI(D) BULK 2: BULK2	7.008E-07 4.205E-01	1.000E+00

N(D) 7.007E-07 4.204E-01 1.000E+00

HEAT	FROM	SUE	RFACE	REACTIONS:	3.096E+05	ERG/CM2-S	(	3.096E-02	W/CM2)
HEAT	FLUX	то	INLET	г:	0.000E+00	ERG/CM2-S	(	0.000E+00	W/CM2)
HEAT	FLUX	то	SUBSI	FRATE:	0.000E+00	ERG/CM2-S	(	0.000E+00	W/CM2)

TWOPNT: SUCCESS. PROBLEM SOLVED.

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TWOPNT: DOUBLE PRECISION (TWO POINT BOUNDARY VALUE PROBLEM) SOLVER, VERSION 3.30 OF APRIL 1998 BY DR. JOSEPH F. GRCAR.

TWOPNT:	INITIAL	GUESS:
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	X(CM)	Т(К)	U(C/S)	V/R(1/S)	W/R(1/S)	RHO(G/CC)	LAMBDA	Sum_Yk
11	10.00	3.000E+02	-5.364E+01	0.000E+00	0.000E+00	2.835E-06	0.000E+00	1.000E+00
10	9.000	4.258E+02	-7.478E+01	1.404E+00	2.065E+00	2.003E-06	0.000E+00	1.000E+00
9	8.000	5.620E+02	-9.285E+01	3.478E+00	5.207E+00	1.520E-06	3.991E-25	1.000E+00
8	7.000	7.063E+02	-1.059E+02	6.235E+00	9.735E+00	1.208E-06	-2.179E-24	1.000E+00
7	6.000	8.564E+02	-1.114E+02	9.543E+00	1.601E+01	9.936E-07	-2.803E-24	1.000E+00
6	5.000	1.010E+03	-1.075E+02	1.306E+01	2.443E+01	8.385E-07	-4.218E-24	1.000E+00
5	4,000	1.163E+03	-9.329E+01	1.618E+01	3.536E+01	7.229E-07	3.502E-24	1.000E+00
4	3.000	1.312E+03	-6.999E+01	1.795E+01	4.908E+01	6.349E-07	3.631E-23	1.000E+00
3	2,000	1.455E+03	-4.157E+01	1.703E+01	6.561E+01	5.670E-07	2.151E-23	1.000E+00
2	1.000	1.589E+03	-1.585E+01	1.171E+01	8.453E+01	5.141E-07	2.151E-23	1.000E+00
1	0 0000E+00	1 713E+03	-5 104E+00	0 000E+00	1 047E+02	4 723E-07	2 151E-23	1 000E+00
-	0.0000100	1,102.00	5.1012.00	0.0002.00	1.01/2.02	11,202 0,	2.1012 20	1.0001.00
	X(CM)	Н2	Н	N2	Ν	NH	NH2	
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
10	9.000	1.006E-07	5.150E-11	6.701E-11	2.379E-15	2.059E-11	2.623E-07	
9	8.000	1.912E-07	1.332E-10	1.473E-10	4.939E-15	4.193E-11	5.343E-07	
8	7.000	2.748E-07	2.049E-10	2.399E-10	7.622E-15	6.391E-11	8.143E-07	
7	6.000	3.530E-07	2.766E-10	3.436E-10	1.038E-14	8.625E-11	1.100E-06	
6	5.000	4.266E-07	3.780E-10	4.562E-10	1.316E-14	1.082E-10	1.388E-06	
5	4.000	4.959E-07	5.886E-10	5.748E - 10	1.591E-14	1.288E-10	1.674E-06	
4	3 000	5.611E = 07	1 124E-09	6 959E-10	1 855E-14	1 466E-10	1 954E-06	
3	2 000	6 212E-07	2 629E-09	8 128E-10	2 095E-14	1 604E-10	2 223E-06	
2	1 000	6 724E-07	6 814E-09	9 106E-10	2.099E 11 2.289E-14	1 696E-10	2.223E 00 2.467E-06	
1	0 0000 - 00	7 014F-07	1 508F-08	9 587F-10	2.2005 11 2.383F-14	1 732F-10	2.107E 00	
FLX((	3/CM2 S)	0 000E+00	0 000E+00	0 000E+00	0 000E+00	0 000E+00	0 000E+00	
	5, 0H2 5,	0.0001.00	0.0001.00	0.0002.00	0.0002.00	0.0001.00	0.0001.00	
	X(CM)	NNH	N2H2	N2H3	N2H4	HF	F	
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
10	9.000	6.095E-16	1.069E-10	1.976E-11	3.499E-12	4.415E-03	3.880E-23	
9	8.000	2.687E-15	2.369E-10	2.583E-11	6.474E-12	9.672E-03	2.778E-20	
8	7.000	5.951E-15	3.629E-10	3.038E-11	8.323E-12	1.563E-02	6.541E-18	
7	6.000	1.000E-14	4.725E-10	3.320E-11	9.046E-12	2.215E-02	3.561E-16	
б	5.000	1.860E-14	5.567E-10	3.408E-11	8.781E-12	2.905E-02	6.765E-15	
5	4.000	8.082E-14	6.092E-10	3.286E-11	7.692E-12	3.615E-02	6.261E-14	
4	3.000	5.066E-13	6.268E-10	2.954E-11	5.957E-12	4.330E-02	3.484E-13	
3	2.000	2.351E-12	6.104E-10	2.454E-11	3.840E-12	5.032E-02	1.336E-12	
2	1.000	7.486E-12	5.707E-10	1.923E-11	1.921E-12	5.711E-02	3.872E-12	
1	0.0000E+00	1.603E-11	5.375E-10	1.611E-11	9.964E-13	6.357E-02	8.977E-12	
FLX(C	G/CM2 S)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	4.125E-06	0.000E+00	
	X(CM)	SIF4	SIF3	SIHF3	SIF3NH2	NH3		
11	10.00	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01		
10	9.000	1.437E-01	6.584E-14	1.132E-12	5.886E-12	8.519E-01		
9	8.000	1.439E-01	1.775E-13	2.863E-12	1.552E-11	8.464E-01		
8	7.000	1.435E-01	3.903E-13	5.303E-12	2.981E-11	8.409E-01		
7	6.000	1.423E-01	8.325E-13	8.511E-12	4.931E-11	8.356E-01		
6	5.000	1.403E-01	1.766E-12	1.246E-11	7.391E-11	8.307E-01		
5	4.000	1.376E-01	3.688E-12	1.701E-11	1.026E-10	8.262E-01		
4	3.000	1.345E-01	7.495E-12	2.187E-11	1.332E-10	8.222E-01		
3	2.000	1.311E-01	1.472E-11	2.656E-11	1.625E-10	8.186E-01		
2	1 000	1 276〒-01	2 785〒-11	3 036〒-11	1 8588-10	8 153〒-01		
	1.000	1.2/05-01	2.7036-11	J.020E-II	T.020E-T0	0.1330 01		
1	0.0000E+00	1.242E-01	4.872E-11	3.223E-11	1.970E-10	8.122E-01		

SITE 1: SI3N4 HN_SIF(S) F3SI_NH2(S) F2SINH(S) H2NFSINH(S) HN(FSINH)2(S) HN_NH2(S)	, SIT 5.775E-02 2.473E-04 1.925E-02 2.055E-04 4.110E-04 9.221E-01	E DENSITY	4.168300E-09
DEPOSITION RATE	(CM/SEC)	(MICRON/MIN)	MOLE FRACTION
SI(D)	7.008E-07	4.205E-01	1.000E+00
N(D)	7.007E-07	4.204E-01	1.000E+00

 HEAT FROM SURFACE REACTIONS:
 3.096E+05 ERG/CM2-S
 ( 3.096E-02 W/CM2)

 HEAT FLUX TO INLET:
 -4.407E+05 ERG/CM2-S
 ( -4.407E-02 W/CM2)

 HEAT FLUX TO SUBSTRATE:
 -2.739E+06 ERG/CM2-S
 ( -2.739E-01 W/CM2)

TWOPNT: SOLVE THE PROBLEM.

	LOG10	LOG10	
TASK	NORM F	COND J	REMARK
START	4.86		11 GRID POINTS
SEARCH	0.52	11.70	8 SEARCH STEPS

REFINE

TWOPNT: FINAL SOLUTION:

	X(CM)	Т(К)	U(C/S)	V/R(1/S)	W/R(1/S)	RHO(G/CC)	LAMBDA	Sum_Yk
11	10.00	3.000E+02	-5.244E+01	0.000E+00	0.000E+00	2.835E-06	0.000E+00	1.000E+00
10	9.000	4.572E+02	-7.769E+01	1.555E+00	2.330E+00	1.865E-06	0.000E+00	1.000E+00
9	8.000	6.087E+02	-9.773E+01	3.716E+00	5.670E+00	1.401E-06	2.085E-24	1.000E+00
8	7.000	7.580E+02	-1.107E+02	6.489E+00	1.032E+01	1.124E-06	-1.897E-24	1.000E+00
7	6.000	9.057E+02	-1.152E+02	9.751E+00	1.663E+01	9.370E-07	9.991E-26	1.000E+00
6	5.000	1.051E+03	-1.100E+02	1.319E+01	2.500E+01	8.025E-07	-3.458E-23	1.000E+00
5	4.000	1.194E+03	-9.457E+01	1.622E+01	3.582E+01	7.012E-07	-9.648E-24	1.000E+00
4	3.000	1.332E+03	-7.045E+01	1.793E+01	4.940E+01	6.227E-07	3.423E-23	1.000E+00
3	2.000	1.465E+03	-4.165E+01	1.699E+01	6.580E+01	5.604E-07	3.884E-23	1.000E+00
2	1.000	1.593E+03	-1.582E+01	1.168E+01	8.461E+01	5.105E-07	3.884E-23	1.000E+00
1	0.0000E+00	1.713E+03	-5.073E+00	0.000E+00	1.047E+02	4.701E-07	3.884E-23	1.000E+00
	X(CM)	Н2	H	N2	N	NH	NH2	
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	
10	9.000	1.022E-07	6.438E-11	6.954E-11	2.417E-15	2.164E-11	2.749E-07	
9	8.000	1.916E-07	1.250E-10	1.491E-10	4.912E-15	4.321E-11	5.488E-07	
8	7.000	2.737E-07	1.789E-10	2.392E-10	7.501E-15	6.514E-11	8.272E-07	
7	6.000	3.507E-07	2.385E-10	3.393E-10	1.017E-14	8.730E-11	1.111E-06	
6	5.000	4.237E-07	3.361E-10	4.477E-10	1.288E-14	1.091E-10	1.397E-06	
5	4.000	4.930E-07	5.534E-10	5.624E-10	1.559E-14	1.294E-10	1.684E-06	
4	3.000	5.587E-07	1.114E-09	6.798E-10	1.822E-14	1.471E-10	1.966E-06	
3	2.000	6.195E-07	2.680E-09	7.931E-10	2.064E-14	1.610E-10	2.238E-06	
2	1.000	6.714E-07	6.937E-09	8.872E-10	2.258E-14	1.703E-10	2.485E-06	
1	0.0000E+00	7.005E-07	1.515E-08	9.333E-10	2.353E-14	1.740E-10	2.646E-06	
FLX(G	/CM2 S)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	

0.65 AND 0.80 RATIOS

	X(CM)	NNH	N2H2	N2H3	N2H4	HF	F
11	10.00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
10	9.000	6.681E-16	1.113E-10	8.891E-12	2.862E-12	4.640E-03	2.455E-22
9	8.000	2.659E-15	2.313E-10	1.462E-11	5.172E-12	9.870E-03	1.555E-19
8	7.000	5.654E-15	3.466E-10	1.938E-11	6.637E-12	1.566E-02	2.402E-17
7	6.000	9.605E-15	4.477E-10	2.289E-11	7.266E-12	2.194E-02	8.453E-16
6	5.000	2.106E-14	5.266E-10	2.487E-11	7.126E-12	2.859E-02	1.152E-14
5	4.000	1.034E-13	5.771E-10	2.504E-11	6.303E-12	3.547E-02	8.429E-14
4	3.000	5.826E-13	5.951E-10	2.330E-11	4.912E-12	4.243E-02	4.006E-13
3	2.000	2.441E-12	5.807E-10	1.993E-11	3.178E-12	4.932E-02	1.405E-12
2	1.000	7.336E-12	5.439E-10	1.600E-11	1.605E-12	5.600E-02	3.890E-12
1	0.0000E+00	1.534E-11	5.129E-10	1.357E-11	8.445E-13	6.238E-02	8.845E-12
FLX(C	G/CM2 S)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	4.081E-06	0.000E+00
	X(CM)	SIF4	SIF3	SIHF3	SIF3NH2	NH3	
11	10.00	1.429E-01	0.000E+00	0.000E+00	0.000E+00	8.571E-01	
10	9.000	1.435E-01	6.610E-14	1.259E-12	6.606E-12	8.519E-01	
9	8.000	1.435E-01	1.747E-13	3.079E-12	1.678E-11	8.466E-01	
8	7.000	1.428E-01	3.843E-13	5.562E-12	3.134E-11	8.415E-01	
7	6.000	1.414E-01	8.243E-13	8.767E-12	5.079E-11	8.366E-01	
6	5.000	1.392E-01	1.754E-12	1.268E-11	7.507E-11	8.322E-01	
5	4.000	1.364E-01	3.666E-12	1.717E-11	1.033E-10	8.282E-01	
4	3.000	1.330E-01	7.447E-12	2.197E-11	1.335E-10	8.246E-01	
3	2.000	1.295E-01	1.462E-11	2.661E-11	1.624E-10	8.212E-01	
2	1.000	1.261E-01	2.766E-11	3.038E-11	1.855E-10	8.179E-01	
1	0.0000E+00	1.227E-01	4.819E-11	3.223E-11	1.966E-10	8.149E-01	
FLX(C	G/CM2 S)	-5.308E-06	0.000E+00	0.000E+00	0.000E+00	-1.158E-06	

SITE 1: SI3N4	, SIT	TE DENSITY	4.168300E-09
HN_SIF(S)	5.695E-02		
F3SI_NH2(S)	2.447E-04		
F2SINH(S)	1.898E-02		
H2NFSINH(S)	2.062E-04		
HN(FSINH)2(S	4.124E-04		
HN_NH2(S)	9.232E-01		
DEPOSITION RATE BULK 1: BULK1	(CM/SEC)	(MICRON/MIN)	MOLE FRACTION
SI(D)	6.933E-07	4.160E-01	1.000E+00

BULK 2: BULK2 N(D) 6.932E-07 4.159E-01 1.000E+00

 HEAT FROM SURFACE REACTIONS:
 3.063E+05 ERG/CM2-S
 ( 3.063E-02 W/CM2)

 HEAT FLUX TO INLET:
 -5.826E+05 ERG/CM2-S
 ( -5.826E-02 W/CM2)

 HEAT FLUX TO SUBSTRATE:
 -2.671E+06 ERG/CM2-S
 ( -2.671E-01 W/CM2)

TWOPNT: SUCCESS. PROBLEM SOLVED.

RATE SENSITIVITY CALCULATION COMPLETE

H SENSITIVITY CALCULATION COMPLETE

Total CPUtime (sec): 0.859375

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