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## PLUG: A FORTRAN Program for the Analysis of Plug Flow Reactors with Gas-Phase and Surface Chemistry

Version 2.0

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**PLUG:**

**A FORTRAN PROGRAM FOR THE ANALYSIS OF PLUG FLOW REACTORS  
WITH GAS-PHASE AND SURFACE CHEMISTRY\***

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**ABSTRACT**

This manual describes the structure and usage of the computer program PLUG, which simulates the behavior of plug flow chemical reactors. More specifically, the code is designed to model the non-dispersive one-dimensional flow of a chemically reacting ideal gas mixture in a conduit of essentially arbitrary geometry. The code makes use of the CHEMKIN and SURFACE CHEMKIN software packages to handle gas-phase and heterogeneous kinetics as well as thermodynamic properties. In addition, the standard implicit code DASSL is used to solve the set of differential/algebraic equations describing the reactor. These equations are briefly discussed here, after which the procedures for running PLUG are described in some detail. Input and output files for a sample problem involving chemical vapor deposition are given.

\*This manual describes version 2.0. This code is being incorporated into The CHEMKIN Collection of software, copyright 1995.

## INTRODUCTION

Tubular flow reactors have long been used throughout the chemical process industries. The tube flow configuration is a natural choice for processes that are carried out in a continuous fashion, and for this reason such reactors are usually operated at steady state. Traditional applications have included both homogeneous reactions (carried out in an empty tube) and fluid-solid heterogeneous reactions in packed beds. More recently, tubular reactors have been used extensively to deposit thin solid films via chemical vapor deposition (CVD). While this is technically a batch process with regard to the solid deposit, the reactor still operates essentially at steady state for extended periods of time. A general problem facing the analyst, then, is to develop a mathematical model for the steady-state tube flow reactor that can be used for process design, optimization, and control.

Because the general equations for chemically reacting flow involve transport phenomena in addition to kinetics and thermodynamics, rigorous reactor models are by necessity multidimensional. However, there are often practical as well as mathematical reasons for considering idealized models of reduced dimensionality. In the case of tube flow, the accepted ideal is the plug flow reactor, in which it is assumed that there is no mixing in the axial (flow) direction but perfect mixing in the direction(s) transverse to this. It can be shown<sup>1</sup> that the absence of axial mixing allows the achievable reactant conversion to be maximized. Likewise, the lack of transverse gradients implies that mass-transfer limitations are absent, once again enhancing the reactor performance. Along with these practical advantages, the plug flow reactor can be modeled using first-order ordinary differential equations (ODE's), and no transport properties are needed.

This manual describes a FORTRAN computer code that can be used to analyze plug flow reactors for arbitrary applications involving gases. Like other Sandia-developed codes such as SPIN, CRESLAF, and SURFACE PSR, it is designed to handle any user-specified gas-phase and surface reaction mechanisms by interfacing with the CHEMKIN<sup>2</sup> and SURFACE CHEMKIN<sup>3</sup> software. In addition, because the reactor equations can be formulated as a differential/algebraic system, the implicit solver DASSL<sup>4</sup> is a natural choice for the solution algorithm. Process parameters and solution control options are supplied to the code via keyword input, and a self-explanatory output file is provided.

In what follows, the governing equations for the plug flow reactor are first summarized for reference. The keyword input to be used in specifying the problem to be solved is then described in detail, and the mechanics of actually running the code are discussed. Finally, the input files for a sample problem are given, and the features of the output file are pointed out.

## REACTOR EQUATIONS

The equations governing the behavior of the plug flow reactor are drastically simplified versions of the general relations for conservation of mass, energy, and momentum.<sup>5</sup> They can be derived most easily by writing balances over a differential slice in the flow direction  $x$ , with the stipulations that (a) there are no variations in the transverse direction, and (b) axial diffusion of any quantity is negligible relative to the corresponding convective term. In this way the overall mass balance (continuity equation) for the gas is found to be

$$\rho u \frac{dA}{dx} + \rho A \frac{du}{dx} + u A \frac{d\rho}{dx} = a_i \sum_{\text{gas}}^{K_g} \dot{g}_k W_k \quad (1)$$

Here  $\rho$  is the (mass) density and  $u$  the axial velocity of the gas, which consists of  $K_g$  species;  $W_k$  is the molecular weight of species  $k$ , and  $\dot{g}_k$  is the molar production rate of this species by all *surface* reactions. The quantities  $A$  and  $a_i$  are the cross-sectional (flow) area and the internal surface area per unit length, respectively, of the reactor; each can be a function of  $x$ . Equation (1) simply states that the mass flow rate of the gas can change as a result of generation or consumption by surface reactions. A similar equation can be written for each species individually:

$$\rho u A \frac{dY_k}{dx} + Y_k a_i \sum_{\text{gas}}^{K_g} \dot{g}_k W_k = W_k (\dot{g}_k a_i + \dot{\omega}_k A) \quad (2)$$

Here  $Y_k$  is the mass fraction of species  $k$  and  $\dot{\omega}_k$  is its molar rate of production by homogeneous *gas* reactions. Such reactions cannot change the total mass of the gas, but they can alter its composition.

Turning now to the energy equation, one finds

$$\begin{aligned} \rho u A \left( \sum_{\text{gas}}^{K_g} h_k \frac{dY_k}{dx} + \bar{C}_p \frac{dT}{dx} + u \frac{du}{dx} \right) + \left( \sum_{\text{gas}}^{K_g} h_k Y_k + \frac{1}{2} u^2 \right) a_i \sum_{\text{gas}}^{K_g} \dot{g}_k W_k \\ = a_e Q_e - a_i \sum_{\text{bulk}}^{K_b} \dot{b}_k W_k h_k \quad (3) \end{aligned}$$

where  $h_k$  is the specific enthalpy of species  $k$ ,  $\bar{C}_p$  is the mean heat capacity per unit mass of the gas,  $T$  is the (absolute) gas temperature, and  $\dot{b}_k$  is the molar production rate of bulk solid species  $k$  by surface reactions. The distinction between bulk and surface species is discussed in the SURFACE CHEMKIN manual.<sup>3</sup> Equation (3) states that the total energy (enthalpy plus kinetic) of the flowing gas changes due to the heat flux  $Q_e$  from the surroundings to the outer tube wall (whose surface area per unit length is  $a_e$ ) and also due to accumulation of enthalpy in the bulk solid. Equivalently, the right-hand side of Eq. (3) can be written as

$$a_i Q_i + a_i \sum_{\text{gas}}^{K_g} \dot{g}_k W_k h_k$$

where  $Q_i$  is the heat flux to the gas from the inner tube wall. The methods for handling  $Q_e$  and  $Q_i$  will be discussed below. It is worth noting that Eq. (3) does not involve the enthalpies of the *surface* species.

The momentum equation for the gas expresses the balance between pressure forces, inertia, viscous drag, and momentum added to the flow by surface reactions. Thus

$$A \frac{dP}{dx} + \rho u A \frac{du}{dx} + \frac{dF}{dx} + u a_i \sum_{\text{gas}}^{K_g} \dot{g}_k W_k = 0 \quad (4)$$

where  $P$  is the absolute pressure and  $F$  is the drag force exerted on the gas by the tube wall, to be discussed below. The pressure is related to the density via the ideal-gas equation of state:

$$P \bar{W} = \rho R T \quad (5)$$

where  $R$  is the universal gas constant and  $\bar{W}$  is the mean molecular weight.

Since the heterogeneous production rates  $\dot{g}_k$  and  $\dot{b}_k$  will depend, in general, on the composition of the surface as well as that of the gas, equations determining the site fractions  $Z_k$  of the  $K_s$  surface species are now needed. Assuming that these species are immobile, the steady-state conservation equations are extremely simple:

$$\dot{s}_k = 0 \quad (6)$$

i.e., the net production rate of each surface species by heterogeneous reactions must be zero. There is, however, a complication. In PLUG it is assumed that the total site density for each surface phase is a constant. As a result, the algebraic equations represented by (6) are not all independent, and for each phase one of the equations must be replaced by the condition

$$\sum_{\text{phase}} Z_k = 1 \quad (7)$$

In order to minimize errors, Eq. (7) is used to replace Eq. (6) for the species having the largest site fraction. An analogous relation for the gas phase is not needed, since (2) is a differential (as opposed to algebraic) equation. In fact, by summing Eqs. (2) it can be shown that the  $Y_k$  will automatically add up to unity at each point.

The system of governing equations for the reactor is now mathematically closed. However, because the residence time  $\tau$  of the gas is often a quantity of interest, it is useful to include an equation that computes it automatically. This is simply

$$\frac{d\tau}{dx} = \frac{1}{u} \quad (8)$$

Equations (1)–(8) provide a total of  $5 + K_g + K_s$  differential/algebraic relations involving the dependent variables  $\rho$ ,  $u$ ,  $T$ ,  $P$ ,  $\tau$ ,  $Y_k$ , and  $Z_k$ . The functions  $\bar{W}$ ,  $h_k$ ,  $\bar{C}_p$ ,  $\dot{\omega}_k$ ,  $\dot{g}_k$ ,  $\dot{s}_k$ , and  $\dot{b}_k$  can all be expressed in terms of these and are obtained from calls to CHEMKIN and SURFACE CHEMKIN subroutines. The quantities  $A(x)$ ,  $a_i(x)$ , and  $a_e(x)$  are fixed by the reactor geometry. This then leaves only  $Q_e$ ,  $Q_i$ , and  $F$  to be addressed.

PLUG actually provides five different options for handling the reactor energy balance. First of all, the reactor can be declared to be isothermal, or the (axial) temperature profile can be specified via a subroutine; in either case Eq. (3) is not used. Alternatively, the reactor can be declared to be adiabatic ( $Q_e = 0$ ), or the axial heat flux profile  $Q_e(x)$  can be specified. The final option is to write  $Q_i$  in terms of the ambient temperature  $T_\infty$  and an *overall* heat-transfer coefficient  $U$ :

$$Q_i = U(T_\infty - T) \quad (9)$$

Both  $T_\infty$  and  $U$  must be supplied by the user.

The viscous drag force  $F$  is written in terms of a friction factor  $f$  as follows:

$$\frac{dF}{dx} = a_i \cdot \frac{1}{2} \rho u^2 f \quad (10)$$

The friction factor can in turn be expressed as a function of the local Reynolds number

$$\text{Re} = \frac{D u \rho}{\mu} \quad (11)$$

where  $D$  is the tube diameter (or the mean hydraulic diameter for a conduit with a noncircular cross section) and  $\mu$  is the gas viscosity. For laminar flow ( $Re < 2100$ ) the analytical result for round tubes is

$$f = \frac{16}{Re} \quad (12)$$

while for turbulent flow one can use the approximate Blasius formula<sup>5</sup>

$$f = 0.0791 Re^{-0.25} \quad (13)$$

This approach is rather crude, especially for noncircular conduits, but viscous drag is usually of very minor importance in gas-phase reactors. In keeping with this, and in order to avoid having to use the CHEMKIN Transport package, the gas viscosity is computed by scaling the inlet value (supplied by the user) by  $(T/T_{in})^{0.5}$  and ignoring the composition dependence.

It remains to specify the initial (inlet) conditions for the reactor. Clearly, values for  $\rho$ ,  $u$ ,  $T$ ,  $P$ , and  $Y_k$  at  $x = 0$  should be known or easily obtainable from the problem statement, the ideal gas law, and the reactor geometry, and of course  $\tau = 0$  at this point. Since there are no derivatives of the  $Z_k$  in the governing equations, it might appear that no initial conditions are needed for them. However, DASSL requires that all algebraic equations be satisfied at the initial point, so Eqs. (6) and (7) must be solved for the  $Z_k$  using the known values of the other variables. In PLUG this is accomplished in a separate preliminary calculation, in which DASSL is used to integrate the fictitious transient equations

$$\frac{dZ_k}{dt} = \frac{\dot{s}_k \sigma_k}{\Gamma} \quad (14)$$

in conjunction with Eq. (7) until steady state is reached. Here  $\sigma_k$  is the site occupancy number for species  $k$  and  $\Gamma$  is the total site density of the phase in question. The initial values of  $Z_k$  for Eqs. (14) are essentially arbitrary (unless there are multiple steady states), although better guesses will naturally lead to faster convergence.

## KEYWORD INPUT

Before running PLUG, the user must prepare three separate input files: one for CHEMKIN, one for SURFACE CHEMKIN, and one for PLUG itself. The first two are described in the respective user's manuals,<sup>2,3</sup> so attention will be focused here on the third, which enables the user to specify the process parameters for a particular simulation. The file also contains some solution control options which should ideally have little effect on the final results, but which may allow the solution to be obtained more easily and/or accurately.

Each line in the input file begins with a keyword, which may be followed by a chemical species name and/or a numerical value. The specific rules governing keyword input are as follows:

1. The first four columns in the line are reserved for the keyword, which must begin in column 1.
2. Any other items on the line (species name and/or numerical value) can appear anywhere in columns 5–80.
3. A species name, if required, must appear before the corresponding numerical value and be separated from it by at least one space.
4. A species name must match exactly one of the names declared in the CHEMKIN or SURFACE CHEMKIN input file.

5. A numerical value can be stated in any format (integer, fixed point, or floating point). The precision (single vs. double) is determined by the code rather than the input format.
6. If a keyword is repeated or conflicts with another, then the one last read takes precedence.
7. The last line must contain the keyword END alone. Aside from this, the order of the lines is unimportant.

A summary of the available keywords and their usage is given below. It should be emphasized that many of the keywords will not appear in a given input file, either because there are default values or because there are other (perhaps conflicting) options available. For each keyword, the short description clearly indicates the circumstances, if any, under which it must be used.

### Reactor Dimensions

**XSTR** Inlet axial position.

Units: cm

Default value: 0.

Example: XSTR 1.5

**XEND** Outlet axial position, equal to the overall reactor length if XSTR is zero.

Units: cm

Default value: None; this is required input.

**DIAM** Tube diameter. This is to be input only if the reactor is a round, empty tube of constant cross section (and with a negligible wall thickness if keyword QFIX or HEAT is used). Otherwise, subroutine GEOM must be used to specify the reactor geometry.

Units: cm

Default value: None; if omitted, subroutine GEOM will be used.

### Reactor Type

**ADIA** Flag indicating that the reactor is adiabatic. This is the default.

**ISO** Flag indicating that the reactor is isothermal, i.e., the temperature is constant at the value specified by TEMP.

**TFIX** Flag indicating that the reactor has a specified axial temperature profile. This must be provided in the function TSPEC(X), and any value specified with keyword TEMP will be ignored.

**QFIX** Flag indicating that the reactor has a specified external heat flux profile. This must be provided in the function QE(X).

**HEAT** Flag indicating that the heat flux to the reactor will be calculated using a specified ambient temperature (TINF) and overall heat-transfer coefficient (BIGU).

### Process Parameters

**TEMP** Inlet gas temperature.

Units: Kelvins

Default value: None; this is required input unless keyword TFIX is used, in which case the axial temperature profile is specified via function TSPEC(X).

PRES Inlet pressure.

Units: atm

Default value: None; this is required input.

VEL Inlet velocity.

Units: cm/s

Default value: None; this is required input if and only if the inlet volumetric flow rate is not specified (via keyword VDOT).

VDOT Inlet volumetric flow rate.

Units:  $\text{cm}^3/\text{s}$

Default value: None; this is required input if and only if the inlet velocity is not specified (via keyword VEL).

MOLE Flag indicating that the input gas composition (keyword GAS) is in mole fractions. This is the default.

MASS Flag indicating that the input gas composition (keyword GAS) is in mass fractions.

GAS Inlet gas-phase mole or mass fraction (see keywords MOLE and MASS) for the given species. The input values will be normalized, but their sum must still be within 0.01 of unity.

Units: None

Default value: 0.

Example: GAS NH3 0.75

VIS Viscosity of the inlet gas mixture.

Units: Poise ( $\text{g}/\text{cm}\cdot\text{s}$ )

Default value: 0., i.e., viscous drag is neglected.

SURF Estimate (initial guess) for the inlet surface site fraction of the given species. The input values for each phase will be normalized, but their sum must still be within 0.01 of unity.

Units: None

Default value: 0.

BULK Bulk phase activity for the given species (assumed constant). The input values for each phase will be normalized, but their sum must still be within 0.01 of unity.

Units: None

Default value: 1.

TINF Ambient temperature. This will be used only if keyword HEAT is specified.

Units: Kelvins

Default value: 298.

**BIGU** Overall heat-transfer coefficient based on the internal surface area.

Units: erg/cm<sup>2</sup>·s·K

Default value: None; this is required input if keyword HEAT is specified, but it will be ignored otherwise.

## Solution Control Parameters

**ATOL** Absolute error tolerance used by DASSL.

Units: None

Default value: 10<sup>-8</sup>

**RTOL** Relative error tolerance used by DASSL.

Units: None

Default value: 10<sup>-6</sup>

**DX** Output distance interval. This governs the frequency of printing and has no effect on the accuracy of the solution.

Units: cm

Default value: 0.01

**NNEG** Flag instructing DASSL to try to constrain all components of the solution vector to be non-negative. This is usually unnecessary, but it may help to use this keyword if negative solution components appear to be causing problems.

**TSTP** Initial time step for integration of the fictitious transient equations by DASSL. Steady state is assumed to be reached when there is no significant change in the surface site fractions over the course of one time step (see RCHG below). Clearly, this will be erroneous if the time step is simply too short to allow any significant reaction to take place. In this case the main reactor simulation should fail, with DASSL returning an error flag of IDID = -12. This signifies that DASSL is unable to adjust the initial derivatives so as to satisfy all of the equations at the reactor inlet, and this is a foregone conclusion if any purely algebraic equations are not already satisfied. Should this occur, the simulation should be repeated with a larger value for TSTP (or, perhaps, a smaller value for RCHG).

Units: sec

Default value: 1.

**RCHG** Maximum relative change in the surface site fractions (over one time step) for which the fictitious transient equations can be considered to have converged to steady state. Caution: If this parameter is set too large relative to RTOL, then the main reactor simulation may fail with IDID = -12, as discussed above, because the algebraic equations will not appear to be satisfied at the inlet.

Units: None

Default value: 10<sup>-6</sup>

**END** Flag indicating the end of the input file. This line is required, and all subsequent lines will be ignored.

## RUNNING THE CODE

The first step in preparing to run PLUG is to generate a standard CHEMKIN input file, which should be named chem.inp. When this is processed by the CHEMKIN interpreter, one obtains both a text file chem.out, which contains summary and diagnostic information, and a binary linking file chem.bin. Next a surface input file surf.inp must be created, and the SURFACE CHEMKIN interpreter uses both this and chem.bin to produce its own output files, surf.out and surf.bin. (If one is solving a purely gas-phase problem, then surf.inp should consist of a single blank line.) The two binary linking files are now available to provide PLUG with information on the gas-phase and surface kinetics and thermodynamics. The last piece of input is the keyword file described above, which should be named plug.inp.

The next step is to compile the PLUG code itself, if this has not already been done. Recompilation will be necessary if any of the problem-specific subroutines or functions (i.e., GEOM, TSPEC, or QE) has been altered or if any of the parameters limiting the problem size has been reset. (The code generates an error message and halts execution if one of more of these parameters is too small.) Of course, the code must also be re-compiled if it has been switched from double to single precision (or vice versa), which is easily accomplished using the CHANGE utility.<sup>6</sup> In any case, once PLUG has been compiled, it must be linked with the object codes for DASSL and the CHEMKIN and SURFACE CHEMKIN subroutine libraries. If the version of DASSL being used is not completely self-contained, it will also be necessary to link some additional math routines; this will be evident from the diagnostic messages.

Assuming that the linking is successful, an executable version of PLUG is produced, and this can be run (in conjunction with chem.bin, surf.bin, and plug.inp) to yield the output file plug.out. If the execution terminates normally, then results are printed at intervals along the entire reactor, as specified in the keyword input. A sample output file for a successful run is shown in the following section. If a fatal error is encountered during execution, then the results obtained to that point are still printed, but these are followed by a self-explanatory error message and the program halts.

For reference, a sample set of UNIX commands for running PLUG is as follows:

```
chem.exe
surf.exe
f77 -c -static plug.f
f77 -o plug.exe plug.o sklib.o cklib.o cdassl.o \
      math.o xerror.o pcmach.o
plug.exe
```

## SAMPLE PROBLEM

This section contains the input and output files for a sample problem involving the chemical vapor deposition of silicon nitride ( $Si_3N_4$ ) from  $SiF_4$  and  $NH_3$ . This is the same system that has been used to demonstrate most of the other CHEMKIN-based reactor codes developed at Sandia. Since the CHEMKIN and SURFACE CHEMKIN input and output files have been described previously,<sup>3</sup> the following discussion will focus on the files specific to PLUG.

The input file plug.inp specifies a process in which a gas mixture with an  $NH_3/SiF_4$  mole ratio of 6:1 is fed into a tubular reactor at a rate of 588 sccm. The inlet pressure is 2 Torr, and, because

the surface kinetic data is valid only at 1713 K, the entire reactor is maintained at this temperature. The length and diameter of the reactor are 60 cm and 5.08 cm, respectively. From this information it can be shown that the axial Peclet number based on inlet conditions is about 70, while the radial Damkohler number is roughly 0.2. It follows that the plug flow assumptions are reasonably well satisfied by this process.

The input file also contains guesses for the surface site fractions at the reactor inlet. In order to test the code as fairly as possible, these are all assigned the same value of 1/6.

PLUG is able to solve this problem with no apparent difficulty, and the file plug.out shown below contains the results. First, the version numbers for PLUG, CHEMKIN, and SURFACE CHEMKIN are printed. These are followed by an echo of the keyword input. If any errors had been detected in plug.inp, appropriate messages would have been printed here. Next is a statement that PLUG was successful in integrating the fictitious transient equations to steady state, despite the crudeness of the initial estimates. This yields the true surface site fractions at the inlet and allows the main reactor simulation to begin.

The results of the computation are printed at intervals of 10 cm, a specified by the keyword DX. At each point there is information about the states of the gas and surface phases, the gas flow velocity, the residence time, and the bulk phase deposition rates. Several interesting features can be noted. First, it is clear that there is very little gas-phase reaction occurring: at the reactor exit, 99.99% of the gas is comprised of SiF<sub>4</sub>, NH<sub>3</sub>, and HF. On the other hand, the surface processes are fairly rapid, causing SiF<sub>4</sub> to be severely depleted and HF to build up. The resultant net increase in the number of gas-phase molecules causes the flow velocity to rise by 17% between the inlet and the exit. Still, the overall pressure drop is a barely perceptible 0.04 Torr.

Turning to the solid phases, one sees that the surface is dominated by the species HN\_NH2(S); not surprisingly, the same result has been observed in other reactor simulations.<sup>3</sup> Of more practical interest is the Si<sub>3</sub>N<sub>4</sub> deposition rate, which falls by a factor of 3 along the reactor. This is a direct result of the SiF<sub>4</sub> depletion noted above. At all points, however, the Si:N molar deposition ratio is maintained precisely at 0.75, a good indication that the equations are being solved correctly.

### CHEMKIN Input File for Sample Problem

```

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
SI           J 3/67SI  100 0000 0000 00G  300.000  5000.000      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      0.00000000  4
SIF2         41889SI  1F   2   0   0G  300.000  3000.000 1000.00  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 OG 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  
 SIHF3 41889SI 1H 1F 3 OG 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  
 SIF3 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  
 SIF4 J 6/76SI 1F 4 0 OG 300.000 5000.000 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 0.00000000 4  
 HF J 6/77H 1F 1 0 OG 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 0.00000000 4  
 F J 9/65F 1 0 0 OG 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 0.00000000 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						

### CHEMKIN Output File for Sample Problem

CHEMKIN INTERPRETER OUTPUT: CHEMKIN-II Version 4.0 Feb. 1995  
 DOUBLE PRECISION

ELEMENTS CONSIDERED	ATOMIC WEIGHT
1. H	1.00797
2. N	14.0067
3. SI	28.0860
4. F	18.9984

SPECIES CONSIDERED	ELEMENT COUNT								
	S	G	MOLECULAR WEIGHT	TEMPERATURE LOW	TEMPERATURE HIGH	H	N	SI	F
1. H2	G	0	2.01594	300	5000	2	0	0	0
2. H	G	0	1.00797	300	5000	1	0	0	0
3. N2	G	0	28.01340	300	5000	0	2	0	0
4. N	G	0	14.00670	300	5000	0	1	0	0

5. NH	G 0	15.01467	300	5000	1	1	0	0
6. NH2	G 0	16.02264	300	5000	2	1	0	0
7. NNH	G 0	29.02137	250	4000	1	2	0	0
8. N2H2	G 0	30.02934	300	5000	2	2	0	0
9. N2H3	G 0	31.03731	300	5000	3	2	0	0
10. N2H4	G 0	32.04528	300	5000	4	2	0	0
11. HF	G 0	20.00637	300	5000	1	0	0	1
12. F	G 0	18.99840	300	5000	0	0	0	1
13. SIF4	G 0	104.07960	300	5000	0	0	1	4
14. SIF3	G 0	85.08120	300	3000	0	0	1	3
15. SIHF3	G 0	86.08917	300	3000	1	0	1	3
16. SIF3NH2	G 0	101.10384	300	3000	2	1	1	3
17. NH3	G 0	17.03061	300	5000	3	1	0	0

---

REACTIONS CONSIDERED	$(k = A T^{**b} \exp(-E/RT))$		
	A	b	E
1. H+H+M=H2+M	1.00E+18	-1.0	0.0
H2	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
6. 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	
H2	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+NNH	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+N2H2	2.00E+13	0.0	0.0
23. NH2+NH2+M=N2H4+M	3.00E+20	-1.0	0.0

24. H+N2H4=H2+N2H3	1.30E+13	0.0	2500.0
25. NH2+N2H4=NH3+N2H3	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=SIF3NH2+F	1.00E+11	0.0	40950.0
32. NH3+SIF3=SIF3NH2+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...CHEMKIN LINKING FILE WRITTEN.

WORKING SPACE REQUIREMENTS ARE

INTEGER: 1101  
 REAL: 771  
 CHARACTER: 21

### SURFACE CHEMKIN Input File for Sample Problem

```

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.
HN_SIF(S)      J 3/67N  1H   1SI  1F   1S   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
HN_NH2(S)      J 3/67N  2H   3SI  OF   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
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
H2NFSINH(S)	J 3/67N	2H 3SI 1F 1S	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
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
SI(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
N(D)	J 3/67N	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

END

REACTIONS

NH3	+ HN_SIF(S)	=> HN_NH2(S)	+ SI(D)	+ HF	7.562E08	0.5	0.0
SIF4	+ HN_NH2(S)	=> F3SI_NH2(S)	+ N(D)	+ HF	3.0967E8	0.5	0.0
F3SI_NH2(S)	=>	F2SINH(S)		+ HF	1.0E05	0.0	0.0
NH3	+ F2SINH(S)	=> H2NFSINH(S)		+ HF	7.562E08	0.5	0.0
H2NFSINH(S)	+ F2SINH(S)	=> HN(FSINH)2(S)		+ HF	1.0E15	0.0	0.0
HN(FSINH)2(S)	+ F2SINH(S)	=> 3HN_SIF(S)	+ N(D)	+ HF	1.0E15	0.0	0.0

END

**SURFACE CHEMKIN Output File for Sample Problem**

SURFACE INTERPRETER OUTPUT:

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CHEMKIN-II Version 4.7 June, 1995

DOUBLE PRECISION

CKLIB: Chemical Kinetics Library  
 CHEMKIN-II Version 4.6, February 1995  
 DOUBLE PRECISION

SPECIES CONSIDERED	MOLECULAR WEIGHT	Density	Nsites	ELEMENT COUNT			
				H	N	SI	F

Gas phase species:

1. H2	2.01594	2	0	0	0
-------	---------	---	---	---	---

2. H	1.00797	1	0	0
3. N2	28.01340	0	2	0
4. N	14.00670	0	1	0
5. NH	15.01467	1	1	0
6. NH2	16.02264	2	1	0
7. NNH	29.02137	1	2	0
8. N2H2	30.02934	2	2	0
9. N2H3	31.03731	3	2	0
10. N2H4	32.04528	4	2	0
11. HF	20.00637	1	0	0
12. F	18.99840	0	0	0
13. SIF4	104.07960	0	0	1
14. SIF3	85.08120	0	0	1
15. SIHF3	86.08917	1	0	1
16. SIF3NH2	101.10384	2	1	1
17. NH3	17.03061	3	1	0

SITE: Si3N4 0.417E-08 moles/cm\*\*2

18. HN_SIF(S)	62.09907	2	1	1	1	1
19. F3SI_NH2(S)	101.10384	2	2	1	1	3
20. F2SINH(S)	81.09747	2	1	1	1	2
21. H2NFSINH(S)	78.12171	2	3	2	1	1
22. HN(FSINH)2(S)	139.21281	4	3	3	2	2
23. HN_NH2(S)	31.03731	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

SURFACE REACTIONS CONSIDERED  $(k = A T^{b-1} \exp(-E/RT))$

1. $\text{NH}_3 + \text{HN\_SIF(S)} \rightarrow \text{HN\_NH}_2(\text{S}) + \text{SI(D)} + \text{HF}$	7.56E+08	0.5	0.0
2. $\text{SIF}_4 + \text{HN\_NH}_2(\text{S}) \rightarrow \text{F3SI\_NH}_2(\text{S}) + \text{N(D)} + \text{HF}$	3.10E+08	0.5	0.0
3. $\text{F3SI\_NH}_2(\text{S}) \rightarrow \text{F2SINH(S)} + \text{HF}$	1.00E+05	0.0	0.0
4. $\text{NH}_3 + \text{F2SINH(S)} \rightarrow \text{H2NFSINH(S)} + \text{HF}$	7.56E+08	0.5	0.0
5. $\text{H2NFSINH(S)} + \text{F2SINH(S)} \rightarrow \text{HN(FSINH)2(S)} + \text{HF}$	1.00E+15	0.0	0.0
6. $\text{HN(FSINH)2(S)} + \text{F2SINH(S)}$ $\Rightarrow 3\text{HN\_SIF(S)} + \text{N(D)} + \text{HF}$	1.00E+15	0.0	0.0

NOTE: A units mole, E units cal/mole

NO ERRORS FOUND ON INPUT...SURFACE LINKING FILE WRITTEN.

WORKING SPACE REQUIREMENTS ARE

INTEGER: 473  
REAL: 625  
CHARACTER: 34

**PLUG Input File for Sample Problem**

```
XEND          60.  
DIAM          5.08  
ISO  
TEMP          1713.  
PRES          2.632E-3  
VDOT          23370.  
GAS  SIF4      0.1427  
GAS  NH3       0.8573  
VIS           5.7E-4  
SURF  HN_SIF(S) 0.1667  
SURF  F3SI_NH2(S) 0.1667  
SURF  F2SINH(S)  0.1666  
SURF  H2NFSINH(S) 0.1666  
SURF  HN(FSINH)2(S) 0.1667  
SURF  HN_NH2(S)   0.1667  
DX             10.  
END
```

**PLUG Output File for Sample Problem**

PLUG: Plug Flow Reactor Code  
Version 2.0 of January 9, 1996  
DOUBLE PRECISION

CKLIB: Chemical Kinetics Library  
CHEMKIN-II Version 4.6, February 1995  
DOUBLE PRECISION

SKLIB: Surface kinetics library  
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CHEMKIN-II Version 5.4, June 1995  
DOUBLE PRECISION

```
XEND          60.  
DIAM          5.08  
ISO  
TEMP          1713.  
PRES          2.632E-3  
VDOT          23370.
```

GAS	SIF4	0.1427
GAS	NH3	0.8573
VIS		5.7E-4
SURF	HN_SIF(S)	0.1667
SURF	F3SI_NH2(S)	0.1667
SURF	F2SINH(S)	0.1666
SURF	H2NFSINH(S)	0.1666
SURF	HN(FSINH)2(S)	0.1667
SURF	HN_NH2(S)	0.1667
DX		10.
END		

#### SITE FRACTIONS AT REACTOR INLET FOUND SUCCESSFULLY

X = 0.000E+00 CM  
 RESIDENCE TIME = 0.000E+00 S  
 TEMPERATURE = 1713.0 K  
 GAS DENSITY = 5.515E-07 G/CM\*\*3  
 PRESSURE = 2.000E+00 TORR  
 VELOCITY = 1.153E+03 CM/S  
 TOTAL DEPOSITION RATE = 3.056E-06 G/CM\*\*2/S  
 GAS-PHASE MOLE FRACTIONS  

H2	= 0.000E+00	H	= 0.000E+00	N2	= 0.000E+00
N	= 0.000E+00	NH	= 0.000E+00	NH2	= 0.000E+00
NNH	= 0.000E+00	N2H2	= 0.000E+00	N2H3	= 0.000E+00
N2H4	= 0.000E+00	HF	= 0.000E+00	F	= 0.000E+00
SIF4	= 1.427E-01	SIF3	= 0.000E+00	SIHF3	= 0.000E+00
SIF3NH2	= 0.000E+00	NH3	= 8.573E-01		

 SURFACE SITE FRACTIONS  

HN_SIF(S)	= 6.242E-02	F3SI_NH2(S)	= 3.136E-04	F2SINH(S)	= 2.081E-02
H2NFSINH(S)	= 2.411E-04	HN(FSINH)2(S)	= 4.821E-04	HN_NH2(S)	= 9.157E-01

 BULK SPECIES DEPOSITION RATES (MOL/CM\*\*2/S)  

SI(D)	= 6.536E-08	N(D)	= 8.715E-08		
-------	-------------	------	-------------	--	--

X = 1.000E+01 CM  
 RESIDENCE TIME = 8.502E-03 S  
 TEMPERATURE = 1713.0 K  
 GAS DENSITY = 5.124E-07 G/CM\*\*3  
 PRESSURE = 1.994E+00 TORR  
 VELOCITY = 1.198E+03 CM/S  
 TOTAL DEPOSITION RATE = 2.520E-06 G/CM\*\*2/S  
 GAS-PHASE MOLE FRACTIONS  

H2	= 4.982E-06	H	= 2.260E-08	N2	= 1.305E-09
N	= 1.304E-13	NH	= 1.270E-09	NH2	= 9.969E-06
NNH	= 5.472E-11	N2H2	= 1.441E-09	N2H3	= 4.683E-11
N2H4	= 1.786E-12	HF	= 8.362E-02	F	= 4.476E-11

SIF4	= 1.168E-01	SIF3	= 1.376E-10	SIHF3	= 7.613E-11
SIF3NH2	= 3.900E-10	NH3	= 7.995E-01		
SURFACE SITE FRACTIONS					
HN_SIF(S)	= 5.536E-02	F3SI_NH2(S)	= 2.586E-04	F2SINH(S)	= 1.845E-02
H2NFSINH(S)	= 2.241E-04	HN(FSINH)2(S=	4.482E-04	HN_NH2(S)	= 9.253E-01
BULK SPECIES DEPOSITION RATES (MOL/CM**2/S)					
SI(D)	= 5.390E-08	N(D)	= 7.186E-08		

X = 2.000E+01 CM  
 RESIDENCE TIME = 1.671E-02 S  
 TEMPERATURE = 1713.0 K  
 GAS DENSITY = 4.817E-07 G/CM\*\*3  
 PRESSURE = 1.988E+00 TORR  
 VELOCITY = 1.237E+03 CM/S  
 TOTAL DEPOSITION RATE = 2.099E-06 G/CM\*\*2/S

GAS-PHASE MOLE FRACTIONS					
H2	= 9.413E-06	H	= 2.285E-08	N2	= 1.308E-08
N	= 1.191E-12	NH	= 6.086E-09	NH2	= 1.873E-05
NNH	= 2.604E-10	N2H2	= 6.753E-09	N2H3	= 1.879E-10
N2H4	= 6.517E-12	HF	= 1.486E-01	F	= 1.576E-10
SIF4	= 9.671E-02	SIF3	= 1.263E-10	SIHF3	= 1.566E-10
SIF3NH2	= 8.750E-10	NH3	= 7.546E-01		
SURFACE SITE FRACTIONS					
HN_SIF(S)	= 4.900E-02	F3SI_NH2(S)	= 2.153E-04	F2SINH(S)	= 1.633E-02
H2NFSINH(S)	= 2.108E-04	HN(FSINH)2(S=	4.217E-04	HN_NH2(S)	= 9.338E-01
BULK SPECIES DEPOSITION RATES (MOL/CM**2/S)					
SI(D)	= 4.488E-08	N(D)	= 5.984E-08		

X = 3.000E+01 CM  
 RESIDENCE TIME = 2.469E-02 S  
 TEMPERATURE = 1713.0 K  
 GAS DENSITY = 4.572E-07 G/CM\*\*3  
 PRESSURE = 1.981E+00 TORR  
 VELOCITY = 1.270E+03 CM/S  
 TOTAL DEPOSITION RATE = 1.761E-06 G/CM\*\*2/S

GAS-PHASE MOLE FRACTIONS					
H2	= 1.348E-05	H	= 2.328E-08	N2	= 4.567E-08
N	= 3.906E-12	NH	= 1.414E-08	NH2	= 2.661E-05
NNH	= 5.903E-10	N2H2	= 1.526E-08	N2H3	= 3.958E-10
N2H4	= 1.326E-11	HF	= 2.002E-01	F	= 3.163E-10
SIF4	= 8.074E-02	SIF3	= 1.117E-10	SIHF3	= 2.210E-10
SIF3NH2	= 1.325E-09	NH3	= 7.190E-01		
SURFACE SITE FRACTIONS					
HN_SIF(S)	= 4.329E-02	F3SI_NH2(S)	= 1.807E-04	F2SINH(S)	= 1.443E-02
H2NFSINH(S)	= 2.002E-04	HN(FSINH)2(S=	4.004E-04	HN_NH2(S)	= 9.415E-01
BULK SPECIES DEPOSITION RATES (MOL/CM**2/S)					

SI(D) = 3.765E-08 N(D) = 5.020E-08

X = 4.000E+01 CM  
RESIDENCE TIME = 3.247E-02 S  
TEMPERATURE = 1713.0 K  
GAS DENSITY = 4.372E-07 G/CM\*\*3  
PRESSURE = 1.974E+00 TORR  
VELOCITY = 1.299E+03 CM/S  
TOTAL DEPOSITION RATE = 1.485E-06 G/CM\*\*2/S

GAS-PHASE MOLE FRACTIONS

H2	= 1.731E-05	H	= 2.387E-08	N2	= 1.064E-07
N	= 8.404E-12	NH	= 2.470E-08	NH2	= 3.384E-05
NNH	= 1.019E-09	N2H2	= 2.631E-08	N2H3	= 6.540E-10
N2H4	= 2.150E-11	HF	= 2.418E-01	F	= 5.058E-10
SIF4	= 6.786E-02	SIF3	= 9.850E-11	SIHF3	= 2.727E-10
SIF3NH2	= 1.733E-09	NH3	= 6.903E-01		

SURFACE SITE FRACTIONS

HN_SIF(S)	= 3.818E-02	F3SI_NH2(S)	= 1.524E-04	F2SINH(S)	= 1.273E-02
H2NFSINH(S)	= 1.916E-04	HN(FSINH)2(S=	3.831E-04	HN_NH2(S)	= 9.484E-01

BULK SPECIES DEPOSITION RATES (MOL/CM\*\*2/S)

SI(D) = 3.177E-08 N(D) = 4.236E-08

X = 5.000E+01 CM  
RESIDENCE TIME = 4.009E-02 S  
TEMPERATURE = 1713.0 K  
GAS DENSITY = 4.206E-07 G/CM\*\*3  
PRESSURE = 1.967E+00 TORR  
VELOCITY = 1.325E+03 CM/S  
TOTAL DEPOSITION RATE = 1.259E-06 G/CM\*\*2/S

GAS-PHASE MOLE FRACTIONS

H2	= 2.100E-05	H	= 2.460E-08	N2	= 2.009E-07
N	= 1.441E-11	NH	= 3.716E-08	NH2	= 4.057E-05
NNH	= 1.529E-09	N2H2	= 3.951E-08	N2H3	= 9.524E-10
N2H4	= 3.090E-11	HF	= 2.758E-01	F	= 7.160E-10
SIF4	= 5.734E-02	SIF3	= 8.680E-11	SIHF3	= 3.148E-10
SIF3NH2	= 2.100E-09	NH3	= 6.668E-01		

SURFACE SITE FRACTIONS

HN_SIF(S)	= 3.362E-02	F3SI_NH2(S)	= 1.292E-04	F2SINH(S)	= 1.121E-02
H2NFSINH(S)	= 1.844E-04	HN(FSINH)2(S=	3.688E-04	HN_NH2(S)	= 9.545E-01

BULK SPECIES DEPOSITION RATES (MOL/CM\*\*2/S)

SI(D) = 2.692E-08 N(D) = 3.590E-08

X = 6.000E+01 CM  
RESIDENCE TIME = 4.757E-02 S  
TEMPERATURE = 1713.0 K  
GAS DENSITY = 4.068E-07 G/CM\*\*3

PRESSURE = 1.960E+00 TORR

VELOCITY = 1.347E+03 CM/S

TOTAL DEPOSITION RATE = 1.071E-06 G/CM\*\*2/S

GAS-PHASE MOLE FRACTIONS

H2	= 2.462E-05	H	= 2.549E-08	N2	= 3.337E-07
N	= 2.153E-11	NH	= 5.108E-08	NH2	= 4.693E-05
NNH	= 2.110E-09	N2H2	= 5.460E-08	N2H3	= 1.285E-09
N2H4	= 4.127E-11	HF	= 3.038E-01	F	= 9.395E-10
SIF4	= 4.867E-02	SIF3	= 7.644E-11	SIHF3	= 3.494E-10
SIF3NH2	= 2.429E-09	NH3	= 6.474E-01		

SURFACE SITE FRACTIONS

HN_SIF(S)	= 2.955E-02	F3SI_NH2(S)	= 1.099E-04	F2SINH(S)	= 9.851E-03
H2NFSINH(S)	= 1.784E-04	HN(FSINH)2(S=	3.568E-04	HN_NH2(S)	= 9.600E-01

BULK SPECIES DEPOSITION RATES (MOL/CM\*\*2/S)

SI(D)	= 2.290E-08	N(D)	= 3.053E-08
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## REFERENCES

1. J. M. Smith, *Chemical Engineering Kinetics*, 3rd edition. McGraw-Hill, New York, 1981.
2. R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia National Laboratories Report SAND89-8009 (1989).
3. M. E. Coltrin, R. J. Kee, and F. M. Rupley, Sandia National Laboratories Report SAND90-8003B (1991).
4. L. R. Petzold, Sandia National Laboratories Report SAND82-8637 (1982).
5. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*. Wiley, New York, 1960.
6. J. F. Grcar, Sandia National Laboratories Report SAND92-8225 (1992).

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