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SURFTHERM

A PROGRAM FOR ANALYZING THERMOCHEMICAL AND KINETIC DATA IN GAS-PHASE AND SURFACE CHEMICAL REACTION MECHANISMS

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Reaction Design cautions that some of the material in this manual may be out of date.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.

SURFTHERM: A PROGRAM FOR A PROGRAM FOR ANALYZING THERMOCHEMICAL AND KINETIC DATA IN GAS-PHASE AND SURFACE CHEMICAL REACTION MECHANISMS

ABSTRACT

The SURFTHERM program analyzes transport coefficients, thermochemical, and kinetic rate information in complex gas-phase and surface chemical reaction mechanisms. The program works with the CHEMKIN (gas-phase chemistry) and SURFACE CHEMKIN (heterogeneous chemistry) Utility packages. It was developed as a "chemist's companion" in using the CHEMKIN software with complex chemical reaction mechanisms. The program presents in tabular form detailed information about the temperature and pressure dependence of chemical reaction rate constants and their reverse rate constants, reaction equilibrium constants, reaction thermochemistry, chemical species thermochemistry and transport properties.

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1. INTRODUCTION

Complex chemically reacting flow simulations are commonly employed to develop a quantitative understanding and to optimize reaction conditions in systems such as combustion, catalysis, chemical vapor deposition and plasma processing. Although reaction conditions, geometries, and fluid flow can vary widely in the applications of chemically reacting flows, what they share in common is the need for accurate, detailed descriptions of the chemical kinetics occurring in the gas-phase or on reactive surfaces. Chemical reaction mechanisms containing hundreds of reactions and involving fifty or more chemical species are not uncommon in such models. The CHEMKIN and SURFACE CHEMKIN packages were developed to deal with complex chemical systems.

The CHEMKIN Gas-phase Utility software was specifically developed to aid in the incorporation of complex gas-phase chemical reaction mechanisms into numerical simulations. The CHEMKIN Gas-phase interface allows the user to specify the necessary input through a high-level symbolic interpreter, which parses the information and passes it to a CHEMKIN Application. To specify the needed information, the user forms a text input file declaring the chemical elements in the problem, the name of each chemical species, thermochemical information about each chemical species, a list of chemical reactions (written in the same fashion that a chemist would write them, i.e., a list of reactants converted to products), and rate constant information, in the form of modified Arrhenius coefficients. The thermochemical information is entered in a very compact form as a series of polynomial coefficients describing the species entropy (S), enthalpy (H), and heat capacity (C_p) as a function of temperature. The polynomial coefficients are in a form compatible with the NASA chemical equilibrium code.[2] Because all of the information about the reaction mechanism is parsed and summarized by the CHEMKIN Interpreter, if the user desires to modify the reaction mechanism by adding species or deleting a reaction, for instance, they only change the Interpreter input file and the CHEMKIN Application does not have to be altered. The modular approach of separating the description of the chemistry from the set-up and solution of the reacting flow problem allows the software designer great flexibility in writing chemical-mechanism-independent code. Moreover, the same mechanism can be used in different chemically reacting flow programs without alteration.

The SURFACE CHEMKIN Utility software was designed for the complementary task of specifying mechanistic and kinetic rate information for heterogeneous chemical reactions. SURFACE CHEMKIN was designed to run in conjunction with CHEMKIN Gas-phase Utilities and, indeed, execution of the CHEMKIN Gas-phase Interpreter is required before the SURFACE CHEMKIN Interpreter may be run. The user input for SURFACE CHEMKIN is very similar to that of CHEMKIN, but is expanded to account for the richer nomenclature and formalism required to specify heterogeneous reaction mechanisms.

The input that gives the complete specification of the chemical reaction mechanism to the CHEMKIN and SURFACE CHEMKIN Interpreters is necessarily very compact and efficient. The numerical values

provided consist of polynomial coefficients from fits to the temperature-dependent thermochemical data, and Arrhenius rate coefficients from fits to the temperature-dependence of the forward rate constant. Typically, reverse reaction rate constants are not specified, but are calculated by CHEMKIN via the equilibrium constant (which is derived from the thermochemistry).

Often, however, in developing or analyzing a chemical reaction mechanism, the information that might be most useful to the CHEMKIN user is not readily available because it is "hidden" in the efficient, but terse, Interpreter input file. A good example would be rate information about the reverse of some reaction in a mechanism. Often, one finds a published rate constant for a reaction which is identical to one in a CHEMKIN mechanism, but written in the reverse direction. The reverse rate information is not available simply by examining the CHEMKIN reaction input or output files. In practice, the user must write a small CHEMKIN application to evaluate the forward rate constants at a given temperature and pressure, evaluate the equilibrium constants, and take the ratio to obtain the reverse rate information. Getting Arrhenius coefficients would further require fitting the reverse rate constants at several temperatures to an Arrhenius form, for example. SURFTHERM, then, provides a means to obtain this type of information, without requiring the user to do any programming.

Another example of information that would be useful to extract from a CHEMKIN mechanism are transport parameter and property values. The TRANSPORT package incorporated within CHEMKIN provides for a full Dixon-Lewis, multicomponent, dilute gas treatment of the gas-phase transport properties. It also includes the effects of such phenomena as thermal diffusion. Often the user is interested in simple measures of transport rates, usually expressed in terms of dimensionless numbers. SURFTHERM has the capability of reporting, as a function of temperature, the pure species viscosity, pure species thermal conductivity, and binary diffusion coefficient in a carrier gas for every gas-phase species in the mechanism. Many multicomponent gas mixtures are dominated by one gas-phase component, called the "carrier gas." A good approximation to the mixture viscosity and thermal conductivities in these cases are the pure species viscosity and thermal conductivities of the carrier gas. Also, the binary diffusivity of the species in the carrier gas can be a good approximation to the mixture diffusivity for that species. Combined with a film theory approach to mass transfer (i.e., an additional "film thickness" parameter must be supplied), SURFTHERM then allows for the calculation of a gas-phase Damköhler number for every reaction in the mechanism. The Damköhler number is a dimensionless number describing the relative rate of reaction versus transport. Surface Damköhler numbers are also calculated for every surface reaction in the mechanism.

Users of CHEMKIN Applications daily encounter questions about reaction rates, thermochemical and transport information derivable from CHEMKIN mechanisms. SURFTHERM presents in tabular form detailed information about the temperature and pressure dependence of chemical reaction rate constants and their reverse rate constants, reaction equilibrium constants, reaction thermochemistry, chemical species thermochemistry and transport properties. All of this information is determined once a CHEMKIN

reaction mechanism has been passed through the interpreters. SURFTHERM is useful in quickly obtaining kinetics and thermochemical information used in testing and analyzing complex reaction mechanisms.

2. INFORMATION REPORTED BY SURFTHERM

The printed output from SURFTHERM reports information about gas-phase CHEMKIN and SURFACE CHEMKIN input reaction mechanisms. Some of the information reported simply echoes information (species or reaction names, rate constant coefficients); other parts of the output include tables of quantities derived from the input files, such as rate constants or thermodynamic quantities as a function of temperature or pressure. The level of detail (and length) of output is controlled by Keyword input parameters, which are described in Chapter 4. The description of the SURFTHERM output here is in the order it appears if all printing options are turned on, as in the example output supplied in Chapter 5. It may be helpful to refer to the sample output in reading the descriptions here.

2.1 Banner Information

The program prints banners showing the current version numbers of SURFTHERM, the CHEMKIN subroutine library and the SURFACE CHEMKIN subroutine library that are being used, and the precision (single or double). The name of the input file used to control SURFTHERM is printed, as well. The keyword input to SURFTHERM is then echoed as a record of what information was used to create the current output.

2.2 General Mechanism Information

General information about the reaction mechanism is given, including the total number of elements, species, phases, gas-phase and surface reactions, the number of species in each phase and the phase names. For surface phases, it reports the number of surface reactions in which that site type is not conserved. (If this is non-zero, the NONCON option was used in the SURFACE CHEMKIN input file.) For bulk phases, it also reports the number of surface reactions in which the number of moles of a bulk species change. These correspond to deposition or etching reactions.

2.3 Summary of Species and Bath-Gas Composition

The concept of a “bath gas” is used throughout SURFTHERM . The specification of a bath gas consists of a characteristic temperature, pressure, and composition at which quantities are to be evaluated by default. Composition, here, refers to the default composition for all phases defined in the mechanism. Reaction rate information is evaluated at the bath gas conditions, unless it is tabulated as a function of a system parameter, such as temperature. In this case, all other parameters are fixed at the bath gas conditions in the table. The default temperature for the bath gas is 298.15 K. The default pressure is 1 atmosphere, and the default composition is an equimolar composition in each phase. All defaults can be overridden by keyword entries in the SURFTHERM input file.

The concept of a "carrier gas" is also used in the program. Unless overridden by a keyword, the carrier gas is assumed to be the gas component having the largest mole fraction. SURFTHERM calculates a single number for the characteristic time scale of diffusion (to be compared with the characteristic time scale of reaction). To make this comparison, the diffusion coefficient is calculated for a specified "major" species in the carrier gas. For example, the diffusion of the major species CH_4 in the carrier gas H_2 is used to calculate the characteristic diffusion time scale. Unless overridden by a keyword, the major species in the gas phase is assumed to be the gas component having the second largest mole fraction.

2.4 Summary of Species Thermochemical Information at Bath-Gas Conditions

The program reports a table of thermochemical information on each species. It gives the enthalpy evaluated at 298 K and at the bath-gas temperature, and the heat capacity, entropy and free energy all evaluated at the bath-gas temperature.

2.5 Stoichiometry Information for Reaction Phase Changes

The program lists each gas-phase and surface reaction and the number of moles of each phase that are created or destroyed by that reaction. For example, in the sample in Chapter 5, the first gas-phase reaction converts two gas-phase species into one gas-phase species. Similarly, in the second surface reaction there is one gas-phase reactant, but no gas-phase products. In both cases, the gas mole change is reported as -1.

2.6 Uniform-Dimensional and Non-Dimensional Reaction Rate Information

It is often useful to know, in some sense, which reactions in a mechanism are "fast" and which are "slow." It is difficult or misleading to simply compare rate constants, which can have different units depending on the molecularity of the reaction. In order to compare the rates of reactions in the mechanism, we define a quantity

$$k_f^* = k_f [G]^g \prod_i [Si]^{si} \tag{1}$$

which we call the "uniform-dimensional" rate constant. Regardless of the order of reaction, it will have units of mole cm^{-3} sec^{-1} for a gas-phase reaction or mole cm^{-2} sec^{-1} for a surface reaction. In this expression, k_f is the rate constant for the forward reaction, $[G]$ is the total concentration of gas-phase species determined at the bath gas conditions (in moles cm^{-3}), g is the sum of the stoichiometric coefficients of all gas-phase species appearing as reactants in the reaction, $[Si]$ is the total site density of surface phase i

determined at the bath gas conditions, *si* is the sum of the stoichiometric coefficients of all surface species in phase *i* participating as reactants in this reaction.

Using the usual rate constant, one calculates the forward reaction rate as k_f times the product of the concentrations of the reactant species (in moles cm^{-3} for gas species, or moles cm^{-2} for surface species) raised to the power of their stoichiometric coefficients. With the uniform-dimensional rate constant, one calculates the same reaction rate as k_f^* multiplied by the (dimensionless) species mole fractions (gas-phase reactants) or site fractions (surface species) raised to the power of their stoichiometric coefficients. Thus, independent of the molecularity of the reaction, the reaction rate is k_f^* times quantities that have maximum values on the order of unity (the mole and site fractions), and it is easier to compare one reaction to another.

The quantity k_f^* just discussed can point out which reactions are fast relative to one another. It can also be of interest to know if a reaction is "fast" relative to a competing process like molecular transport. The Damköhler number for gas-phase reactions, *Da,* allows for such a comparison.

$$Da = \frac{k_f^*}{D[G]/L^2} \tag{2}$$

In equation (2), *D* is a diffusion coefficient and *L* is a characteristic length scale for diffusion; for example, a boundary-layer thickness or a characteristic reactor dimension. The Damköhler number is a dimensionless number that is a measure of the relative importance of gas-phase kinetics versus mass transport. If *Da* is much greater than 1, then a reaction is fast relative to transport; if it is much less than 1, then transport processes occur on a shorter time scale than kinetic processes.

One must supply a diffusion coefficient in equation (2) to evaluate *Da.* To do this, SURFTHERM requires the user to name a "major species" and a "carrier gas species." Through internal calls to the TRANSPORT Subroutine Library, the program evaluates the binary diffusion coefficient between these two species at the specified bath temperature and pressure. SURFTHERM also lets the user specify the length scale *L*. The default value for *L* is 1 cm.

For each gas-phase reaction, SURFTHERM generates a report of k^* and *Da* for the forward and reverse directions. In some cases, the input CHEMKIN reaction mechanism specifies the reaction to be irreversible. In these cases, SURFTHERM still calculates the quantities k^* and *Da* for the reverse direction, but encloses the numbers in square brackets [ ] to flag these reactions as not being part of the mechanism.

A uniform-dimensional rate constant of equation (1) is also calculated for surface reactions. In this case, k_f^* has units of mole cm^{-2} s^{-1}. Thus, one can make a comparison between reaction rates for surface reactions. The surface Damköhler number is defined to be

$$Da = \frac{k_f^*}{D[G]/L} \tag{3}$$

The equation for the surface Damköhler number differs from the equation for the gas-phase Damköhler number by a factor of the length scale *L*. As before, it provides a measure of the relative speed of the surface reaction rate versus the mass transport rate.

2.7 Thermodynamic Function and Transport Parameter Table for Each Species

The next major portion of output from SURFTHERM gives more detailed thermochemical and physical information for the gas-phase species. For each species in the mechanism, SURFTHERM reports the species index, the index number and name of the phase to which the species belongs, and the elemental composition. The program reports all of the information used in calculating the species transport properties, which includes the Lennard-Jones well depth and collision diameter, the dipole moment, the molecular polarizability, the rotational collision number, and the molecular structure (atom, linear, or non-linear molecule). The values for the standard-state heat of formation and the molecular weight are also given.

A table then follows, which reports the species' enthalpy, free energy, heat capacity, and entropy as functions of temperature. Optionally, the program also reports the pure-species viscosity, pure-species thermal conductivity, and the binary diffusion coefficient as functions of temperature in the same table. The binary diffusion coefficient is reported at the bath gas pressure. The "binary" pair referred to is the carrier gas and the species listed in the table. The values for the viscosity and thermal conductivity do not depend on the specification of the bath gas. Keyword input parameters control how many temperatures are included in these tables. Similar thermochemical information is given for surface and bulk species, without transport-property information.

2.8 Summary Table of Thermodynamic Functions for Gas-Phase Reactions

Next, SURFTHERM prints kinetic and thermochemical information about gas-phase reactions. A summary table gives the change in free energy, enthalpy, and entropy for each gas-phase reaction at the specified bath-gas temperature.

2.9 Detailed Information about Each Gas-Phase Reaction

Following the summary table for all reactions, more detailed information is reported in tables for each gas-phase reaction. The program reports the change in the number of moles in the reaction, whether the reaction includes third-body effects, any enhanced third-body collision efficiencies, whether the reaction is reversible, and the number of reactant and product species. The table includes a modified Arrhenius

rate expression for the rate constant, including the units of the parameters. This is represents all of the information that the CHEMKIN Linking File contains about the reaction.

The next table gives rate constant information in the high-pressure limit. As a function of temperature, SURFTHERM prints the forward rate constant, the forward pre-exponential constant and activation energy (calculated at each temperature), the change in free energy, enthalpy, and entropy, the reverse rate constant, the reverse pre-exponential and activation energy, and k^* (the uniform-dimensional rate constant) for the forward and reverse directions.

2.10 Fall-Off Behavior for Special Classes of Reactions

If the rate constant's low-pressure fall-off is specified in the CHEMKIN Interpreter input (via Lindemann, Troe, or SRI expressions) , these parameters are printed next. The low-pressure and high-pressure limits of the rate constant are specified in CHEMKIN as follows:

$$k_0 = A_0 T^{\beta_0} \exp(-E_0 / R_c T) \tag{4}$$

$$k_\infty = A_\infty T^{\beta_\infty} \exp(-E_\infty / R_c T) \tag{5}$$

The rate constant as a function of pressure is then

$$k = k_\infty \left(\frac{P_r}{1+P_r} \right) F \tag{6}$$

where the reduced pressure P_r is

$$P_r = \frac{k_0 [M]}{k_\infty} \tag{7}$$

In equation (7) [M] is the "effective" concentration of collision partners

$$[M] = \sum_i \varepsilon_i [M_i] \tag{8}$$

where [M_i] is the concentration of gas-phase species i, and ε_i is the collision efficiency of that species (assumed to be unity, unless specified in the CHEMKIN Interpreter input). In the Troe form, F is given by

$$\log F = \left[1 + \left\{ \frac{\log P_r + c}{n - d(\log P_r + c)} \right\}^2 \right]^{-1} \log F_{cent}\,, \tag{9}$$

where the constants are

$$c = -0.4 - 0.67 \log F_{cent}$$
$$n = 0.75 - 1.27 \log F_{cent}$$
$$d = 0.14$$

and

$$F_{cent} = (1-a)\exp(-T/T^{***}) + a\exp(-T/T^{*}) + \exp(-T^{**}/T) \tag{10}$$

For reactions with pressure fall-off behavior, two tables are presented. The first table varies the gas temperature at the specified bath-gas pressure, and the second table varies the gas pressure at the specified bath-gas temperature. Each of these tables gives the calculated value of the rate constant, the pre-exponential and activation energy, k/k_{∞} (a measure of how far into the fall-off region this reaction is), the low-pressure limit of the rate constant k_0, the reduced pressure P_r, the fall-off parameter F, the effective concentration [*M*], and the reverse reaction rate constant, pre-exponential, and activation energy.

An additional table includes reactions in which a third body is explicitly included as a reactant, such as reaction 4 in the sample input file (Chapter 5). This table lumps the effective concentration [*M*] together with the rate constant to make a new, "effective" rate constant. In reaction 4 of the sample, this calculation converts the third-order rate constant into a second order rate constant for comparison purposes. The table includes a column containing the total gas-phase concentration (at the specified bath temperature and pressure), as well as the calculated effective concentration, as in Eq. (8).

2.11 Summary of Thermochemical Information for Surface Reactions

The program next analyzes each surface reaction in the mechanism. It first presents a summary table of the net thermochemistry of each surface reaction, evaluated at the specified bath temperature. Thermodynamic functions reported are the net changes in the free energy, enthalpy, and entropy.

2.12 Detailed Information About Each Surface Reaction

The next tables give of rate constant information for each surface reaction. The table reports the net molar change in the gas, surface, and bulk phases for the reaction. If the rate constant is modified by site-coverage parameters (in the SURFACE CHEMKIN Interpreter input file), those parameters are summarized. The listing includes the number of gas, surface, and bulk species present as reactants and as products, whether the reaction is reversible, and the types of reactants and products for the reaction.

SURFTHERM reports whether the reaction's rate constant was input via a sticking coefficient form or via the regular form. Within the SURFACE CHEMKIN input file, the rate constant for the forward reaction can be optionally specified as a sticking coefficient. In this case, the sticking coefficient parameters are printed by SURFTHERM, but also Arrhenius coefficients are derived for a rate constant, which would yield an

identical rate. SURFACE CHEMKIN actually converts all sticking coefficient expressions to rate constants internally, but this is hidden from the user. Alternatively, if a rate constant was used in the Interpreter input but if a sticking coefficient was a legal option, i.e., there was exactly one gas-phase reactant species in the reaction, SURFTHERM reports parameters for an equivalent sticking coefficient expression. The program derives and reports Arrhenius coefficients for the reverse reaction and, if applicable, effective sticking-coefficient parameters. These options are very useful for uncovering physically impossible reaction rate constants. For example, it is normally physically impossible for a surface reaction to have a sticking coefficient greater than one. However, in practice, it can happen that a user unknowingly specifies thermochemical information for a reversible reaction such that the reverse reaction would have an effective sticking coefficient greater than one.

In SURFACE CHEMKIN, the sticking probability γ can be specified in the three-parameter form

$$\gamma = aT_b \exp(-c / R_c T) \tag{11}$$

and the rate constant k is derived from γ as

$$k = \left(\frac{\gamma}{1-\gamma/2}\right)\left(\frac{1}{\Gamma_{\text{tot}}^m}\right)\sqrt{\frac{RT}{2\pi W}} \tag{12}$$

If more than one type of surface phase exists, there is an additional correction term, discussed below. In equation (12), m is the total number of surface species that appear as reactants in the reaction, Γ_{tot} is the total surface site density, and W is the molecular weight of the gas reactant species.

SURFTHERM next prints a table reporting the following rate information as a function of surface temperature: the rate constant, pre-exponential and activation energy for both the forward and reverse reaction, the net change in free energy, enthalpy, and entropy, and the uniform-dimensional rate constant k^* for the forward and reverse directions. All conditions other than the temperature are assumed to be given by the bath-gas conditions.

2.13 Coverage Dependent Surface Reaction Rates

SURFACE CHEMKIN allows modification of the rate constant expression for a surface reaction due to coverage of surface species in the following manner

$$k' = k\prod_i 10^{\eta_i Z_i} Z_i^{\mu_i} \exp(-\varepsilon_i Z_i / RT) \tag{13}$$

$$k = AT^{\beta} \exp(-E_a / RT) \tag{14}$$

In equation (13), the product runs over just the surface species. Z_i is the site fraction of surface species *i*. If coverage-dependence parameters are supplied for the reaction, an additional table is generated by SURFTHERM. This table gives the net rate constant k', and a local fit to that k' to a two-parameter Arrhenius form, i.e., a pre-exponential and activation energy. Also given is the rate constant k for Eq. (14). The product in Eq. (13), i.e., k'/k is listed in the table as "Cov_fac." The table also includes analogous information about the reverse reaction rate constants.

2.14 Breakdown of the Sticking Coefficient Surface Reaction Rate

If a sticking coefficient can describe the surface reaction, SURFTHERM also prints a table of information about γ as a function of surface temperature. The line labeled "Surface site density divisor" gives the quantity Γ_{tot} raised to the *m* power. The table prints γ at each temperature, and the sticking coefficient is fit to a two-parameter Arrhenius form, i.e., just using the constants *a* and *c* in Eq. (11). The column labeled "Eff_Veloc" is the square-root term in Eq. (12). The column labeled "Veloc_Corr" is

$$v_c = \frac{1}{1-\frac{\gamma}{2}}, \tag{15}$$

which is the correction to the effusive flux to the surface due to the breakdown of the Maxwell-Boltzmann distribution of species velocities near to a surface with a high sticking coefficient. The column labeled "Sden_Ratio" is a subtle term arising when more than one surface phase exists. It is best illustrated by an example. Suppose two types of surface phase were declared (phases α and ω), which each occupy part of the surface. If these phases have site densities of Γ_α and Γ_ω, respectively, then a molecule colliding with the surface has a probability

$$P_\alpha = \frac{\Gamma_\alpha}{\Gamma_\alpha + \Gamma_\omega} \tag{16}$$

of colliding with a species in phase α. A multiplicative term like this P_α modifies the conversion between a sticking coefficient and a rate constant, as in equation (12). It is this term that appears as "Sden_Ratio" in the sticking-coefficient table. The last column in the table is the rate constant corresponding to this sticking coefficient, and the next-to-the-last column is the rate constant times the site-density term. If the reverse reaction can be described with a sticking coefficient, an analogous table for the reverse reaction is also given by the program.

3. PROGRAM STRUCTURE AND CONTROL

The CHEMKIN Application User Interface runs the SURFTHERM program automatically through a mouse-driven interface. The SURFTHERM 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, SURFTHERM depends on data obtained from the CHEMKIN Gas-phase, SURFACE CHEMKIN and TRANSPORT packages. Therefore, to solve a SURFTHERM problem the user must first execute the three preprocessor programs, "chem", "tran" and "surf", which have access to thermodynamic and transport-property databases. SURFTHERM then reads input from the user (described in Chapter 4), 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 1 shows the relationships between these components. For more information about the CHEMKIN Application User Interface, please see the CHEMKIN Getting Started manual.

The first step is to execute the CHEMKIN Interpreter, "chem". The CHEMKIN Interpreter first reads user-supplied 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 SURFTHERM 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 SURFTHERM computation.

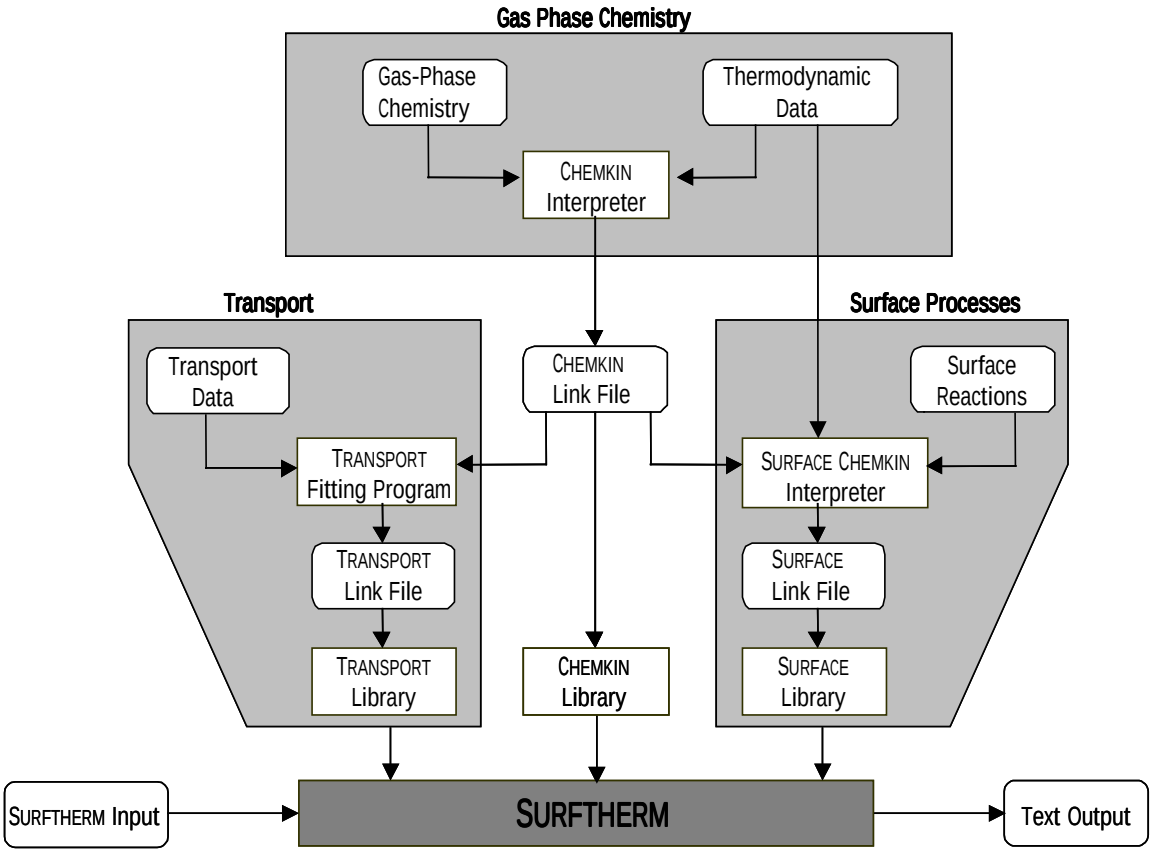

Figure 1. Relationship of the SURFTHERM program to the CHEMKIN, SURFACE CHEMKIN, and TRANSPORT preprocessors and the associated input and output files.

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 SURFTHERM 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 SURFTHERM program can then be executed. Since the CHEMKIN, SURFACE CHEMKIN, and TRANSPORT subroutine libraries must be initialized before use, the SURFTHERM 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. SURFTHERM then reads the user input that defines a the kind of information to be tabulated. This input is read in Keyword format from the input file (e.g. “surftherm.inp”), described in Chapter 4.

4. PROGRAM INPUT

4.1 Keyword Syntax and Rules

The SURFTHERM 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 (such as a species name or a number) is required. Some keywords have default values associated with them and in such cases the Keyword line is optional. The order of the keyword lines is generally unimportant, except that if the same keyword is given more than once (with conflicting values), the last one read will be operative. The rules governing the syntax of the keyword lines are listed below:

1. The first four columns of the line are reserved for the keyword, which must begin in the first column.
2. Any further input associated with the keyword can appear anywhere in columns 5 through 80. The specific column in which the information begins is unimportant.
3. When more than one piece of information is required, the order in which the information appears is important.
4. When numbers are required as input, they may be stated in either integer, floating point, or E format. The program converts the numbers to the proper type.
5. When gas-phase species names or chemical reactions are given as input, they must appear exactly as they were specified in the CHEMKIN Interpreter input. When surface or bulk species names or surface reactions are used as input, they must appear exactly as they were specified in the SURFACE CHEMKIN input.
6. When more than one piece of information is given on a line, the pieces must be delimited by one or more blank spaces.
7. If more information is input than required, then the last-read entries supercede earlier keywords.
8. Two types of "comment" lines can be included. If one inserts either a period (.) or an exclamation point (!) in the first column, the input line will be ignored by the program and this line will not be echoed in the output file. If a slash (/) is placed in column one, the input line will be ignored by the program, but will be echoed in the printed output file.
9. Any characters appearing on a line after an exclamation point (!) are considered to be comments and are not processed as keyword input. They are, however, echoed in the printed output file.

4.2 General keywords

ALL Turns on all output from all SURFTHERM tables. Use this keyword if you want to activate all features and tables. Note, the usual default for each of the other output options is for all output to be given.

Example usage: `ALL`

NONE Turns default output off for all of SURFTHERM's tables. One can use this keyword in combination with another keyword below, to turn on output from only one feature. This keyword will also turn-off all previously specified output from keywords given before it.

Example usage: `NONE`

END Signals end of the current keyword input. The keyword is optional, and an end of file condition serves the same purpose.

Example usage: `END`

CNTR Signals that another set of outputs will be requested. After the current set of output tables is processed by the program, the program will continue to process more keywords. Upon continuation, the NONE keyword is automatically assumed on later sets of input keywords.

Example usage: `CNTR`

4.3 Keywords that Control Functionality

GEN [ALL] [NONE]

Controls the printing of general information about the mechanism. It also controls the printing of summary tables about the reaction thermodynamics. The ALL option produces all of the general information tables. NONE will suppress this output. If only GEN is given on the input line, ALL is assumed (the default). The GEN information is printed by default unless explicitly turned off.

Example usage:

```
GEN ALL
GEN NONE
```

TSUM [ALL] [NONE] [SPECIES] [GAS] [SUR]

Controls the printing of summary tables for the thermodynamic functions at the bath gas conditions (see TBTH, TBTH, and XBTH, below). There are three sets of thermodynamic tables: one for the species, one for the gas reactions, and one for the surface reactions. The last three options turn on each table individually. The default is ALL, which will print all three thermodynamic tables. They may all be suppressed with NONE.

Example usage:

```
TSUM ALL
TSUM NONE
TSUM SPECIES
TSUM GAS
TSUM SUR
```

THRM [ALL] [GAS] [SUR] [BULK] [NONE] [Species_Name] [Species_number]

Prints out individual thermodynamics tables for the species in the mechanism. The default is ALL, which generates the tables for all species in the mechanism. The GAS, SUR, and BULK options will cause thermodynamic tables for only species in the specified phase to be printed. Listing individual species by their name or by their number (as listed in the CHEMKIN or SURFACE CHEMKIN Interpreter output files) will generate thermodynamic tables for the specified species. The keyword NONE will suppress all of the species thermodynamic tables.

Example usage:

```
THRM  ALL
THRM  NONE
THRM  GAS
THRM  SUR
THRM  BULK
THRM  3
THRM  CH4
THRM  CH(S)
THRM  D
```

TRAN [ALL] [NONE]

Prints out the transport data base properties (intermolecular potential parameters) for each gas-phase species in the mechanism. This feature also expands the thermo table to create a table of transport properties as a function of temperature. The NONE option turns off printing of this table. The transport data base, TRANDAT, must exist in the current directory, unless the NONE option is used.

Example usage:

```
TRAN  ALL
TRAN  NONE
```

NDIM [ALL] [GAS] [SUR] [NONE]

Prints out a table for the uniform-dimensional reaction rate constants for gas and surface reactions. The ALL option will produce output for both sets of reactions. Specifying either GAS or SUR will produce reaction rate information for only the given type of reaction. The NONE option suppresses all of these tables. Note that forming the NDIM print-out may require the bath gas quantities XBTH, PBTH, and TBTH, below.

Example usage:

```
NDIM  ALL
NDIM  GAS
NDIM  SUR
NDIM  NONE
```

GRXN [ALL] [NONE] [Gas_Reaction_Number...] [Gas_Reaction_Expression]

Prints out a table of reaction rates and other pertinent information for each gas-phase reaction. The ALL option is the default and produces tables for every gas-phase reaction. The NONE option suppresses output for all of the reactions. If reaction information is desired for only certain reactions, they may be optionally specified by their number (given in the Interpreter output) or by typing an exact duplicate of the reaction expression (see example input).

Example usage:

```
GRXN  ALL
GRXN  NONE
GRXN  1
GRXN  2  5
GRXN  CH4+H<=>CH3+H2
```

PFAL [ALL] [NONE] [Gas_Reaction_Number ...] [Gas_Reaction_Expression]

Analyze the pressure fall-off of a gas phase reaction, i.e., creates a table of reaction rates versus total gas pressure at a constant temperature. Optional keyword usage is the same as in GRXN, above.

Example usage:

```
PFAL ALL
PFAL NONE
PFAL 1
PFAL 2  5
PFAL 2CH3(+M)<=>C2H6(+M)
```

TFAL [ALL] [NONE] [Gas_Reaction_Number ...] [Gas_Reaction_Expression]
Analyze the fall-off of a gas-phase reaction with respect to changes in the temperature, i.e., create a table of reaction rates versus temperature at a constant pressure. The pressure and gas composition are assumed to be that of the bath gas. Optional keyword usage is the same as in GRXN, above.
Example usage:

```
TFAL  ALL
TFAL  NONE
TFAL  1
TFAL  2    5
TFAL  2CH3(+M)<=>C2H6(+M)
```

GTHB [ALL] [NONE] [Gas_Reaction_Number ...] [Gas_Reaction_Expression]
Create an extra table of the reaction rates for those reactions which involve third bodies. This option employs the bath-gas composition (specified by the XBTH keyword) to yield effective reaction rates. Optional keyword usage is the same as in GRXN, above.
Example usage:

```
GTHB  ALL
GTHB  NONE
GTHB  4
GTHB  2 5
GTHB  2H+M<=>H2+M
```

SRXN [ALL] [NONE] [Surf_Reaction_Number ...] [Surf_Reaction_Expression]
Prints out a table of reaction rates and other pertinent information for a surface reaction. Optional keyword usage is the same as in GRXN, above.
Example usage:

```
SRXN  ALL
SRXN  NONE
SRXN
SRXN  2    5
SRXN  CH(S)+H<=>C(S,R)+H2
```

STCK [ALL] [NONE] [Surf_Reaction_Number ...] [Surf_Reaction_Expression]
Analyzes the forward and reverse surface reaction's sticking coefficient, if applicable. Optional keyword usage is the same as in GRXN, above.
Example usage:

```
STCK  ALL
STCK  NONE
STCK  1
STCK  2    5
STCK  CH(S)+H<=>C(S,R)+H2
```

SCOV [ALL] [NONE] [Surf_Reaction_Number ...] [Surf_Reaction_Expression]
Analyze the coverage dependence of a surface reaction, i.e., create a table of effective reaction rates versus temperature. Surface coverage is assumed to be that of the bath-gas composition. Optional keyword usage is the same as in GRXN, above.
Example usage:

```
SCOV  ALL
SCOV  NONE
SCOV  1
SCOV  2    5
SCOV       CH(S)+H<=>C(S,R)+H2
```

4.4 Keywords that Control Bath Gas Quantities

XBTH Species_Name/Species_Number Value
Specifies the bath gas composition. The Species_Name (or number as it appears in the Interpreter output) and desired mole fraction are required parameters. If at least one species in a phase has been set with the XBTH keyword, then all of the specified mole fractions for that phase are summed and normalized so that they add up to one. If no XBTH parameters have been specified for any species in the phase, then mole fractions for all species in that phase are set equal to one another.
Example usage:

```
XBTH H2    1.0
XBTH 3     1.0
XBTH CH(S)       0.5
XBTH C(S,R) 0.5
```

PBTH Value
Set the total bath gas pressure in Torr. The default is 760 torr.
Example usage:

```
PBTH 1000. ! (torr)
```

TBTH Value
Set the bath gas temperature in Kelvin. This temperature is used wherever a single temperature is needed. The default is 298.15 K.
Example usage:

```
TBTH 900.  ! (Kelvin)
```

4.5 Keywords that Control the Composition of Tables

TLOW Value
Set the lower limit of the temperature range (K) in all tables where the temperature is varied. The default is 300 K.
Example usage:

```
TLOW 100.  ! (Kelvin)
```

THIG Value

Set the upper limit of the temperature range (K) in all tables where the temperature is varied. The default is 1500 K.

Example usage:

```
THIG 298.15      ! (Kelvin)
```

TDEL Value

Set the temperature increment in all tables where the temperature is varied. The default is 100 K.

Example usage:

```
TDEL 200.  ! (Kelvin)
```

PLOW Value

Set the lower limit of the pressure range (Torr) in all tables where the gas pressure is varied. The default is 1 Torr.

Example usage:

```
PLOW 1.0   ! (Torr)
```

PHIG Value

Set the upper limit of the pressure range (Torr) in tables where the gas pressure is varied. The de-fault is 1000 Torr.

Example usage:

```
PHIG 1000. ! (Torr)
```

PNUM Value

Set the total number of pressures in tables where the gas pressure is varied. The default is 10. Note that the changes in the pressure are determined on a logarithmic scale.

Example usage:

```
PNUM 10
```

CARR Gas_Species_Name / Gas_Species_Number

Specify the named species as the carrier gas. This keyword is used to identify the species in calculating binary diffusion coefficients for tables and for non-dimensionalizations that require a binary diffusion coefficient. The default is to use the gas species with the largest mole fraction (from the XBTH input) in the bath-gas composition. If the gas-phase bath-gas composition is not specified, the default is to use the first species in the mechanism.

Example usage:

```
CARR H2
CARR 3
```

MAJ Gas_Species_Name / Gas_Species_Number

Sets the "Major Species". This is only used to calculate an effective diffusion coefficient when non-dimensionalizing the reaction rate constants. The default is to use the gas species with the second largest mole fraction (from the XBTH input) in the bath-gas composition. If the gas-phase bath-gas composition is not specified, the default is to use the second species in the mechanism.

Example usage:

```
MAJ  CH4
MAJ  1
```

LSCL Value

Sets the length scale (cm) for the calculation of gas and surface Damköhler numbers. The default is 1 cm.

Example usage:

```
LSCL 3.     ! (cm)
```

5. SURFTHERM SAMPLE ANALYSIS

The next several pages give example input and output files from a sample execution of the SURFTHERM program. In the order in which they appear, the example files are: the keyword input file for SURFTHERM, the input to the Transport Properties Fitting code, the input to the CHEMKIN Interpreter, the output from the CHEMKIN Interpreter, the input to the SURFACE CHEMKIN Interpreter, the output from the SURFACE CHEMKIN Interpreter, and the output from SURFTHERM.

The SURFTHERM sample input file has been designed to illustrate as many of the features as possible. As such, a lengthy output file was generated. In practice, by selecting only the options desired, the output length can be shortened considerably.

The CHEMKIN and (especially the) SURFACE CHEMKIN input files were contrived to illustrate many features of SURFTHERM. As such they should not be considered as a source for kinetic rate information for Carbon / Hydrogen systems.

The printed output from SURFTHERM has been augmented in a number of places by comments, which appear in bold-faced font. The additional comments explain which keyword controls a given portion of the output.

5.1 Sample Input File for SURFTHERM Sample

```
NONE
GEN   ALL
TSUM  SPECIES   GAS    SUR
THRM  CH3  CH4  CH(S)  CH2(S) BULK
TRAN  ALL
NDIM  GAS  SUR
GRXN  ALL
PFAL  ALL
TFAL  ALL
GTHB  ALL
SRXN  ALL
STCK  ALL
SCOV  ALL
XBTH  H2  0.90
XBTH  H   0.02
XBTH  CH4 0.05
XBTH  CH3 0.03
PBTH  20.
TBTH  1100.
TLOW  300.
THIG  1200.
TDEL  400.
PLOW  100.
PHIG  700.
PNUM  3
CARR  H2
MAJ   CH4
LSCL  1.3
CNTR

END
PBTH  1000.
NDIM  ALL
END
```

5.2 Sample Input Data for the TRANSPORT Preprocessor

```
CH3              1   144.000     3.800     0.000     0.000                0.000
C2H6             2   252.300     4.302     0.000     0.000                1.500
CH4              2   141.400     3.746     0.000     2.600               13.000
H                0   145.000     2.050     0.000     0.000                0.000
H2               1    38.000     2.920     0.000     0.790              280.000
```

5.3 Sample Input File for the CHEMKIN Interpreter

```
ELEMENTS   H  C
SPECIES
   CH3 C2H6 CH4 H H2
END
THERMO
CH3               121286C   1H   3          G  0300.00   5000.00  1000.00      1
 2.84405160E+00 6.13797410E-03-2.23034522E-06 3.78516080E-10-2.45215903E-14    2
 1.64378086E+04 5.45269728E+00 2.43044281E+00 1.11240987E-02-1.68022034E-05    3
 1.62182872E-08-5.86495262E-12 1.64237813E+04 6.78979397E+00                   4
C2H6               51090C   2H   6    0    0G   300.000  5000.000 2000.00    0 1
 0.13436084E+02 0.36325546E-02-0.24694586E-06-0.11228470E-09 0.15553612E-13    2
-0.18298318E+05-0.56480824E+02 0.81958778E-01 0.24148658E-01-0.12186742E-04    3
 0.31174958E-08-0.34426783E-12-0.11399086E+05 0.20696499E+02                   4
CH4               121286C   1H   4          G  0300.00   5000.00  1000.00      1
 1.68347883E+00 1.02372356E-02-3.87512864E-06 6.78558487E-10-4.50342312E-14    2
-1.00807871E+04 9.62339497E+00 7.78741479E-01 1.74766835E-02-2.78340904E-05    3
 3.04970804E-08-1.22393068E-11-9.82522852E+03 1.37221947E+01                   4
H                 120186H   1               G  0300.00   5000.00  1000.00      1
 2.50000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 2.54716270E+04-4.60117638E-01 2.50000000E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 2.54716270E+04-4.60117608E-01                   4
H2                121286H   2               G  0300.00   5000.00  1000.00      1
 2.99142337E+00 7.00064411E-04-5.63382869E-08-9.23157818E-12 1.58275179E-15    2
-8.35033997E+02-1.35511017E+00 3.29812431E+00 8.24944174E-04-8.14301529E-07    3
-9.47543433E-11 4.13487224E-13-1.01252087E+03-3.29409409E+00                   4
END
REACTIONS
2CH3(+M)=C2H6(+M)             0.903E+17 -1.180    654.000
 LOW/ 3.18E41 -7.03 2762./
 TROE/ .6041 6927. 132./
 H2/2/
CH4+H=CH3+H2                  0.220E+05  3.000   8750.000
CH3+H(+M)=CH4(+M)             0.600E+17 -1.000      0.000
 LOW/8.0E26 -3.0 0.0/
 H2/2/
H+H+M=H2+M                    0.100E+19 -1.000      0.000
   H2/0.0/
H+H+H2=H2+H2                  0.920E+17 -0.600      0.000
END
```

5.4 Output from the CHEMKIN Interpreter for the Sample Analysis

```
CHEMKIN-III GAS-PHASE MECHANISM INTERPRETER:
DOUBLE PRECISION Vers. 6.24 2000/06/18
Copyright 1995, Sandia Corporation.
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                        --------------------
                        ELEMENTS     ATOMIC
                        CONSIDERED   WEIGHT
                        --------------------
                         1. H       1.00797
                         2. C       12.0112
                        --------------------

--------------------------------------------------------------------------------
                        C
                      P H
                      H A
                      A R
SPECIES               S G  MOLECULAR  TEMPERATURE  ELEMENT COUNT
CONSIDERED            E E  WEIGHT     LOW    HIGH  H  C
--------------------------------------------------------------------------------
  1. CH3              G 0   15.03506   300   5000   3  1
  2. C2H6             G 0   30.07012   300   5000   6  2
  3. CH4              G 0   16.04303   300   5000   4  1
  4. H                G 0    1.00797   300   5000   1  0
  5. H2               G 0    2.01594   300   5000   2  0
--------------------------------------------------------------------------------


                                                        (k = A T**b exp(-E/RT))
     REACTIONS CONSIDERED                                 A        b        E

  1. 2CH3(+M)=C2H6(+M)                              9.03E+16   -1.2      654.0
     Low pressure limit:  0.31800E+42 -0.70300E+01  0.27620E+04
     TROE centering:      0.60410E+00  0.69270E+04  0.13200E+03
     H2              Enhanced by    2.000E+00
  2. CH4+H=CH3+H2                                   2.20E+04    3.0     8750.0
  3. CH3+H(+M)=CH4(+M)                              6.00E+16   -1.0        0.0
     Low pressure limit:  0.80000E+27 -0.30000E+01  0.00000E+00
     H2              Enhanced by    2.000E+00
  4. H+H+M=H2+M                                     1.00E+18   -1.0        0.0
     H2              Enhanced by    0.000E+00
  5. H+H+H2=H2+H2                                   9.20E+16   -0.6        0.0

 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:      193
   REAL:         184
   CHARACTER:      7
Total CPUtime (sec): 0.125
```

5.5 Sample Input File for the SURFACE CHEMKIN Interpreter

```
SITE/DIAMOND/   SDEN/5.22E-09/
   CH(S)      C(S,R)   CH3(S)
   CH2(S)     CH2(S,R)   CH(S,R)
END
BULK
   D /3.515/
END
THERMO ALL
   300.     600.         3000.
CH(S)              71291C   1H   1    0    0G   300.000  3000.000 1000.00    0 1
 0.14872259E+01 0.33000924E-02-0.28411702E-06-0.34383971E-09 0.76660243E-13    2
-0.97217761E+03-0.10147021E+02-0.18660052E+01 0.90233106E-02 0.29339509E-06    3
-0.52555964E-08 0.20409182E-11 0.16202820E+03 0.81504984E+01                    4
C(S,R)             71291C   1    0    0    0G   300.000  3000.000 1000.00    0 1
 0.16900997E+01 0.11069085E-02-0.12616481E-06-0.11996654E-09 0.28811839E-13    2
 0.21028852E+05-0.10340458E+02-0.12628431E+01 0.73135700E-02-0.72650602E-06    3
-0.57274971E-08 0.29829661E-11 0.21889631E+05 0.52818985E+01                    4
CH3(S)             71291C   1H   3    0    0G   300.000  3000.000 1000.00    0 1
 0.22271934E+01 0.64840489E-02-0.50900690E-06-0.66263206E-09 0.14445464E-12    2
 0.72205317E+04-0.13843549E+02-0.23782465E+01 0.14169827E-01 0.60410139E-06    3
-0.75244326E-08 0.28128064E-11 0.87938271E+04 0.11347555E+02                    4
CH2(S)             71291C   1H   2    0    0G   300.000  3000.000 1000.00    0 1
 0.17394471E+01 0.51764320E-02-0.42153641E-06-0.53463645E-09 0.11763388E-12    2
-0.70305313E+04-0.12329198E+02-0.25071146E+01 0.12199585E-01 0.59056043E-06    3
-0.66420434E-08 0.24363521E-11-0.55698042E+04 0.10931940E+02                    4
CH2(S,R)          100191C   1H   2    0    0G   300.000  3000.000 1000.00    0 1
 0.17394471E+01 0.51764320E-02-0.42153641E-06-0.53463645E-09 0.11763388E-12    2
 0.24246523E+05-0.12329198E+02-0.25071146E+01 0.12199585E-01 0.59056043E-06    3
-0.66420434E-08 0.24363521E-11 0.25707254E+05 0.10931940E+02                    4
CH(S,R)            71291C   1H   1    0    0G   300.000  3000.000 1000.00    0 1
 0.14872259E+01 0.33000924E-02-0.28411702E-06-0.34383971E-09 0.76660243E-13    2
 0.15069210E+05-0.10147021E+02-0.18660052E+01 0.90233106E-02 0.29339509E-06    3
-0.52555964E-08 0.20409182E-11 0.16203417E+05 0.81504984E+01                    4
D                  71291C   1    0    0    0G   300.000  3000.000 1000.00    0 1
 0.16900997E+01 0.11069085E-02-0.12616481E-06-0.11996654E-09 0.28811839E-13    2
-0.56464282E+03-0.10340458E+02-0.12628431E+01 0.73135700E-02-0.72650602E-06    3
-0.57274971E-08 0.29829661E-11 0.29613477E+03 0.52818985E+01                    4
END
REACTIONS
 CH(S)     + H         <=> C(S,R)  + H2                  2.14     0.0  7300.0
    STICK   COV /CH(S)  0.1  0.0  -0.25/
 C(S,R)    + H          => CH(S)                         3.0E-1   0.0     0.0
    STICK
 C(S,R)    + CH3       <=> D       + CH3(S)             4.0E12   0.0  1200.0
      REV  /1.0E13  0.0  15000./
 CH2(S,R)  + CH(S,R)   <=> CH2(S)  + CH(S)              6.0E19   0.0  2000.0
END
```

5.6 Output from the SURFACE CHEMKIN Interpreter for the Sample Analysis

```
CHEMKIN-III SURFACE MECHANISM INTERPRETER:
DOUBLE PRECISION Vers. 7.20 2000/06/18
Copyright 1995, Sandia Corporation.
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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                          ELEMENT COUNT
 CONSIDERED             WEIGHT       Density    Nsites     H  C
 -------------------------------------------------------------------------------

 Gas phase species:
   1. CH3                15.03506                          3  1
   2. C2H6               30.07012                          6  2
   3. CH4                16.04303                          4  1
   4. H                   1.00797                          1  0
   5. H2                  2.01594                          2  0

 SITE: DIAMOND                    0.522E-08 moles/cm**2
   6. CH(S)              13.01912                    1     1  1
   7. C(S,R)             12.01115                    1     0  1
   8. CH3(S)             15.03506                    1     3  1
   9. CH2(S)             14.02709                    1     2  1
  10. CH2(S,R)           14.02709                    1     2  1
  11. CH(S,R)            13.01912                    1     1  1

 BULK: BULK1
  12. D                 12.01115 0.352E+01 g/cm**3         0  1

 -------------------------------------------------------------------------------
                                                        (k = A T**b exp(-E/RT))
     SURFACE REACTIONS CONSIDERED                         A        b        E

   1. CH(S)+H<=>C(S,R)+H2                              2.14E+00    0.0     7300.0
      Coverage parameters for species CH(S):
           1.000E-01 0.000E+00-2.500E-01
      Coefficients are sticking parameters...
   2. C(S,R)+H=>CH(S)                                  3.00E-01    0.0        0.0
      Coefficients are sticking parameters...
   3. C(S,R)+CH3<=>D+CH3(S)                            4.00E+12    0.0     1200.0
      Reverse Arrhenius coefficients:                  1.00E+13    0.0    15000.0
   4. CH2(S,R)+CH(S,R)<=>CH2(S)+CH(S)                  6.00E+19    0.0     2000.0

  NOTE:  A units mole-cm-sec-K, E units cal/mole
         Default Motz-Wise correction to sticking coefficients is turned ON.


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

 WORKING SPACE REQUIREMENTS ARE
    INTEGER:      293
    REAL:         328
    CHARACTER:     18
 Total CPUtime (sec): 0.046875
```

5.7 Sample Output from SURFTHERM

```
  SURFTHERM: Program to analyze gas/surface reaction mechanisms
                                                    surftherm.f, version 1.41, 1/6/94
                                                                 DOUBLE PRECISION
            Command File = example
  CKLIB:  Chemical Kinetics Library
                                                  CHEMKIN-II Version 4.0, October 1992
                                                                 DOUBLE PRECISION
  SKLIB:  Surface kinetics library
                                                  Copyright 1990, Sandia Corporation.
                           The U.S. Government retains a limited license in this software.
                                                  CHEMKIN-II Version 4.07, October 1992
                                                                 DOUBLE PRECISION
------------------------------------------------------------------------------------------------
                                                                        Command Lines read:

           KEYWORD INPUT
 NONE
 GEN   ALL
 TSUM  SPECIES   GAS    SUR
 THRM  CH3  CH4  CH(S)  CH2(S) BULK
 TRAN  ALL
 NDIM  GAS  SUR
 GRXN  ALL
 PFAL  ALL
 TFAL  ALL
 GTHB  ALL
 SRXN  ALL
 STCK  ALL
 SCOV  ALL
 XBTH  H2  0.90
 XBTH  H   0.02
 XBTH  CH4 0.05
 XBTH  CH3 0.03
 PBTH  20.
 TBTH  1100.
 TLOW  300.
 THIG  1200.
 TDEL  400.
 PLOW  100.
 PHIG  700.
 PNUM  3
 CARR  H2
```

```
 MAJ   CH4
 LSCL  1.3
 CNTR
 END
-----------------------------------------------------------------------------------------------


  CKLIB:  Chemical Kinetics Library
                                                CHEMKIN-II Version 4.0, October 1992
                                                           DOUBLE PRECISION

  SKLIB:  Surface kinetics library
                                                 Copyright 1990, Sandia Corporation.
                           The U.S. Government retains a limited license in this software.
                                               CHEMKIN-II Version 4.07, October 1992
                                                           DOUBLE PRECISION

 TRANLIB:  Multicomponent transport library,
           CHEMKIN-II Version 1.7, October 1992
           DOUBLE PRECISION
```

(GEN keyword produces this portion of printout)

```
 ================================================================================================================================================
 GENERAL INFORMATION CONCERNING THE SURFACE CHEMKIN PROBLEM:
          Total number of elements declared =  2 ( H C )
          Total number of species  =  12
          Total number of phases   =  3
          Total number of gas-phase reactions =   5
          Total number of surface-phase reactions =   4
          Universal gas constant = 8.31400E+07 ergs/(mole*K)
          Universal gas constant used for activation energies =  1.9870     cals/(mole*K)
          Pressure of one standard atmosphere = 1.01325E+06 dynes/cm**2

          GAS phase (Always phase # 1, with the name, "GAS"):
               Number of species =   5
               Number of surface reactions where the # of gas products is different than the # of gas reactants =  2
               Number of elements in the phase =  2 ( H C )

          SURFACE PHASES:
               Phase    Name of        SS Site Density   Number of  Number of  Site_changing    Elements:
               Number    Phase           (moles/cm**2)    Species   Elements     Surf_rxns
               ---------------------------------------------------------------------------------------
                 2      DIAMOND            5.2200E-09         6         2          0        ( H C )
               ---------------------------------------------------------------------------------------
```

```
     Tot SS Site Dens=   5.2200E-09 (mole/cm**2) (used in sticking coefficient express)

BULK PHASES:
     Phase    Name of              Number of   Number of   Mole_changing    Elements:
     Number    Phase               Species     Elements    Surf_rxns
     ---------------------------------------------------------------------------------
       3      BULK1                    1          1           1          ( C )
```

(GEN keyword produces this portion of printout)

```
 ================================================================================================================================

     SUMMARY OF SPECIES IN THE MECHANISM  with a DESCRIPTION OF BATH GAS COMPOSITION:
```

(PBTH keyword sets this pressure)

```
                Total pressure =    20.0     torr
```

(TBTH keyword set this temperature)

```
                Temperature (where needed) =   1100.E+00 Kelvin
```

(CARR keyword determines this species)

```
                Carrier Gas (used in diff. calcs) = H2
```

(MAJ keyword determines this species)

```
                Major Gas Species (used in nondim calcs) = CH4
```

(XBTH keyword sets these mole fractions)

```
                Number   Name         Mole_fraction      Concentration
                ------------------------------------------------------------------------
                  1.    CH3                .3000E-01             .8747E-08 mole/cm**3
                  2.    C2H6               .0000E+00             .0000E+00 mole/cm**3
                  3.    CH4                .5000E-01             .1458E-07 mole/cm**3
                  4.    H                  .2000E-01             .5831E-08 mole/cm**3
                  5.    H2                 .9000                 .2624E-06 mole/cm**3
                  6.    CH(S)              .1667                 .8700E-09 mole/cm**2
                  7.    C(S,R)             .1667                 .8700E-09 mole/cm**2
                  8.    CH3(S)             .1667                 .8700E-09 mole/cm**2
                  9.    CH2(S)             .1667                 .8700E-09 mole/cm**2

                 10.    CH2(S,R)           .1667                 .8700E-09 mole/cm**2
                 11.    CH(S,R)            .1667                 .8700E-09 mole/cm**2
                 12.    D                 1.000         .0000E+00 activity(unitless)
```

(TSUM keyword produces this portion of printout)

SUMMARY OF STANDARD STATE THERMODYNAMIC FUNCTIONS FOR SPECIES AT BATH GAS CONDITIONS:

Bath Gas Temperature = 1100. Kelvin

Number	Name	H(298 K) (kcal/mole)	H(T_bath) (kcal/mole)	Cp(T_bath) (cal/moleK)	S(T_bath) (cal/moleK)	G(T_bath) (kcal/mole)
1.	CH3	34.820	44.550	14.634	61.460	-23.056
2.	C2H6	-20.671	-2.1373	30.888	82.894	-93.321
3.	CH4	-17.898	-6.9959	18.067	60.830	-73.909
4.	H	52.093	56.076	4.9675	33.873	18.816
5.	H2	5.85426E-04	5.6653	7.3188	40.389	-38.762
6.	CH(S)	-1.85923E-04	4.8346	8.7987	7.1569	-3.0379
7.	C(S,R)	43.360	46.629	5.2408	5.1543	40.959
8.	CH3(S)	17.300	26.172	16.042	16.566	7.9494
9.	CH2(S)	-11.488	-4.6301	12.685	10.128	-15.771
10.	CH2(S,R)	50.659	57.517	12.685	10.128	46.376
11.	CH(S,R)	31.874	36.709	8.7987	7.1569	28.836
12.	D	.45374	3.7227	5.2408	5.1543	-1.9470

(GEN keyword produces this portion of printout)

SHORT DESCRIPTION OF GAS-PHASE REACTIONS

Number	Description	Gas_Mole Change	Gas_Mole Reactants
1.	2CH3(+M)<=>C2H6(+M)	-1	2
2.	CH4+H<=>CH3+H2	0	2
3.	CH3+H(+M)<=>CH4(+M)	-1	2
4.	2H+M<=>H2+M	-1	2
5.	2H+H2<=>2H2	-1	3

(GEN keyword produces this portion of printout)

SHORT DESCRIPTION OF SURFACE-PHASE REACTIONS

Number	Description	Gas Mole	Surf Mole	Bulk Mole	Surf_Site

```
                                                  Change    Change      Change       Change
  ------------------------------------------------------------------------------------------
    1.   CH(S)+H<=>C(S,R)+H2                          0         0          0                 0
    2.   C(S,R)+H=>CH(S)                            -1         0          0                 0
    3.   C(S,R)+CH3<=>D+CH3(S)                      -1         0          1                 0
    4.   CH2(S,R)+CH(S,R)<=>CH2(S)+CH(S)            0         0          0                 0
  ------------------------------------------------------------------------------------------
```

(NDIM keyword produces this portion of printout)

```
 ================================================================================================================================================
          NON-DIMENSIONAL GAS REACTION RATE CONSTANTS
                   AT THE BATH GAS CONDITIONS
                    Total Pressure =     20.0                                    torr
                    Temperature    =   1100.E+00 Kelvin

          Number             Description                      k_star      k_star_rev    |  Gas_Da_For          Gas_Da_Rev
                                                          (mole/cm**3 sec) (mole/cm**3 sec)|
          ------------------------------------------------------------------------------|------------------------------
            1.   2CH3(+M)<=>C2H6(+M)                          .270         4.280E-09     |    6.113E+03         9.677E-05
            2.   CH4+H<=>CH3+H2                            4.544E-02     2.095E-03     |    1.027E+03      47.4
            3.   CH3+H(+M)<=>CH4(+M)                       2.813E-02     1.535E-14     |     636.             3.470E-10
            4.   2H+M<=>H2+M                              2.253E-06     5.667E-20     |    5.095E-02         1.281E-15
            5.   2H+H2<=>2H2                              3.413E-05     8.585E-19     |     .772             1.941E-14
          ------------------------------------------------------------------------------------------------------------
                                          NOTE ON THE ABSOLUTE NUMBERS IN THIS TABLE:
                    The rate rate constants (mole/cm**3*sec) should be compared to rate of mass transport in order
                    to characterize their values as being fast or slow.  The nondimensionalization of the mass transport
                    involves the following multiplicative factor, which also has the units of mole/cm**3*sec:
                                       Total_Concentration * Diffusivity / Length_scale**2
                                         Using the binary diffusion coefficient between H2
                     and CH4, the following factors are calculated at bath gas conditions:
                              Total Concentration                  =  2.916E-07 mole/cm**3
                              Binary Diffusion Coefficient =   256.              cm**2/sec
```

(LSCL keyword sets this length scale)

```
                              Length scale                =  1.30                    cm
                    Therefore, the non-dimensionalization factor for gas reactions becomes:
                              Conc * Diff / Length**2          =  4.423E-05 mole/cm**3*sec
                                        Note that this number is independent of pressure
```

(NDIM keyword produces this portion of printout)

```
 ================================================================================================================================
         NON-DIMENSIONAL SURFACE REACTION RATE CONSTANTS
                 AT THE BATH GAS CONDITIONS
                  Total Pressure =     20.0     torr
                  Temperature    =   1100.E+00 Kelvin

         Number              Description                       k_star      k_star_rev    | Surf_Da_For           Surf_Da_Rev
                                                            (mole/cm**2 sec) (mole/cm**2 sec)|
         ---------------------------------------------------------------------------------|-----------------------------
           1.   CH(S)+H<=>C(S,R)+H2                          2.870E-03     5.747E-06     |     49.9              9.996E-02
           2.   C(S,R)+H=>CH(S)                             1.237E-02  [  1.553E-13]    |     215.      [  2.701E-09]
           3.   C(S,R)+CH3<=>D+CH3(S)                       3.516E-03      54.6         |     61.1              9.496E+05
           4.   CH2(S,R)+CH(S,R)<=>CH2(S)+CH(S)              655.         1.362E-16     |    1.139E+07          2.369E-12
         ---------------------------------------------------------------------------------------------------------------------
                           [  ] indicates that this reaction is not in mechanism

                                          NOTE ON THE ABSOLUTE NUMBERS IN THIS TABLE:
                    The rate rate constants (mole/cm**2*sec) should be compared to rate of mass transport to the surface in
                    to characterize their values as being fast or slow.  The nondimensionalization of the mass transport
                    involves the following multiplicative factor, which also has the units of mole/cm**2*sec:
                              Total_Concentration * Diffusivity / Length_scale
                                        Using the binary diffusion coefficient between H2
                     and CH4, the following factors are calculated at bath gas conditions:
                              Total Concentration                =  2.916E-07 mole/cm**3
                              Binary Diffusion Coefficient =   256.             cm**2/sec
                              Length scale                =  1.30                  cm
                    Therefore, the non-dimensionalization factor for surface reactions becomes:
                              Conc * Diff / Length            =  5.750E-05 mole/cm**2*sec
                                        Note that this number is independent of pressure
```

(THRM keyword produces this portion of printout)

```
 ------------------------------------------------------------------------
 THERMO TABLE FOR MOLECULE "CH3" IN PHASE "GAS"
                  Overall, this is the   1th species in the mechanism
                  It is the   1th species in phase GAS
                  Elemental Composition:

                                                                    H :  3
                                                                    C :  1
                  L-J Potential well depth =    144.                    K
                  L-J collision diameter   =    3.80                Angstroms
                  Dipole Moment =    .000E+00 Debye
                  Polarizability =                          .000E+00 Angstroms**3
                  Rotational Collision number at 298K =    .000E+00
```

```
                This molecule is linear
                Heat of Formation at 298 =                          34.820 kcal/mole
                Molecular Weight =    15.035                              gm/mole
```

(TRAN keyword is responsible for adding transport properties to the table)

```
-------------------------------------------------------------------------------------------------------------------------
|     Temp  |   (H-H298)          (G-H298)     '     Cp              S       |  Viscosity   Therm_Cond          Dif_Co_with_H2
|      (K)  |  (kcal/mole)    (kcal/mole)    (cal/mole*K)    (cal/mole*K)   | (gm/cm*sec) (erg/cm*sec*K)       (cm**2/sec)
|-----------|-------------------------------------------------------------|-----------------------------------------------
|    298.15 |    .00000E+00     -13.827          9.2137          46.375     |  1.069E-04     3.556E+03         28.0
|    300.00 |   1.70617E-02     -13.912          9.2313          46.432     |  1.074E-04     3.581E+03         28.3
|    700.00 |    4.3359         -34.449          12.198          55.406     |  2.032E-04     9.207E+03         119.
|   1100.00 |    9.7307         -57.876          14.634          61.460     |  2.767E-04     1.486E+04         253.
-------------------------------------------------------------------------------------------------------------------------
                           [Pressure for binary diffusion coeff. calc. =    20.0     torr]

-------------------------------------------------------------------------
THERMO TABLE FOR MOLECULE "CH4" IN PHASE "GAS"
                Overall, this is the                    3th species in the mechanism
                It is the   3th species in phase GAS
                                                          Elemental Composition:
                                                                       H :  4
                                                                       C :  1
                L-J Potential well depth =    141.                          K
                L-J collision diameter   =    3.75                    Angstroms
                Dipole Moment =    .000E+00 Debye
                Polarizability =    2.60                            Angstroms**3
                Rotational Collision number at 298K =    13.0
                This molecule is non-linear
                Heat of Formation at 298 =                         -17.898 kcal/mole
                Molecular Weight =    16.043                              gm/mole
-------------------------------------------------------------------------------------------------------------------------
|     Temp  |   (H-H298)          (G-H298)     '     Cp              S       |  Viscosity   Therm_Cond          Dif_Co_with_H2
|      (K)  |  (kcal/mole)    (kcal/mole)    (cal/mole*K)    (cal/mole*K)   | (gm/cm*sec) (erg/cm*sec*K)       (cm**2/sec)
|-----------|-------------------------------------------------------------|-----------------------------------------------
|    298.15 |    .00000E+00     -13.257          8.3985          44.465     |  1.143E-04     3.406E+03         28.4
|    300.00 |   1.55634E-02     -13.340          8.4268          44.517     |  1.148E-04     3.436E+03         28.7
|    700.00 |    4.4632         -33.078          13.701          53.630     |  2.167E-04     1.092E+04         121.
|   1100.00 |    10.902         -56.011          18.067          60.830     |  2.950E-04     1.879E+04         256.
-------------------------------------------------------------------------------------------------------------------------
                           [Pressure for binary diffusion coeff. calc. =    20.0     torr]

-------------------------------------------------------------------------
THERMO TABLE FOR MOLECULE "CH(S)" IN PHASE "DIAMOND"
```

```
                  Overall, this is the                     6th species in the mechanism
                  It is the                                1th species in phase DIAMOND
                                                                 Elemental Composition:
                                                                                H :  1
                                                                                C :  1
                                    Number of surface sites occupied by the species = 1
                  Heat of Formation at 298 =                                .000 kcal/mole
                  Molecular Weight =    13.019                                    gm/mole
-------------------------------------------------------------------------------
|     Temp  |   (H-H298)          (G-H298)          Cp              S                  |
|      (K)  |  (kcal/mole)      (kcal/mole)    (cal/mole*K)    (cal/mole*K)            |
|-----------|-------------------------------------------------------------------       |

|    298.15 |    .00000E+00     -.10646          1.4450          .35705                |
|    300.00 |   2.70042E-03     -.10712          1.4744          .36608                |
|    700.00 |    1.6955         -.85811          6.5202          3.6481                |
|   1100.00 |    4.8348         -3.0378          8.7987          7.1569                |
-------------------------------------------------------------------------------

-------------------------------------------------------------------------------
THERMO TABLE FOR MOLECULE "CH2(S)" IN PHASE "DIAMOND"
                  Overall, this is the                     9th species in the mechanism
                  It is the                                4th species in phase DIAMOND
                                                                 Elemental Composition:
                                                                                H :  2
                                                                                C :  1
                                    Number of surface sites occupied by the species = 1
                  Heat of Formation at 298 =                              -11.488 kcal/mole
                  Molecular Weight =    14.027                                    gm/mole
-------------------------------------------------------------------------------
|     Temp  |   (H-H298)          (G-H298)          Cp              S                  |
|      (K)  |  (kcal/mole)      (kcal/mole)    (cal/mole*K)    (cal/mole*K)            |
|-----------|-------------------------------------------------------------------       |
|    298.15 |    .00000E+00     -.15231          2.0385          .51086                |
|    300.00 |   3.80869E-03     -.15327          2.0790          .52359                |
|    700.00 |    2.3778         -1.2092          9.1973          5.1242                |
|   1100.00 |    6.8583         -4.2825          12.685          10.128                |
-------------------------------------------------------------------------------

-------------------------------------------------------------------------------
THERMO TABLE FOR MOLECULE "D" IN PHASE "BULK1"
                                  Overall, this is the  12th species in the mechanism
                  It is the   1th species in phase BULK1
                                                                 Elemental Composition:
                                                                                C :  1
                  Bulk Density =   3.5150     gm/cm**3
```

```
                  Activity (bath gas dependent) =                              1.0000
                  Heat of Formation at 298 =                               .454 kcal/mole
                  Molecular Weight =    12.011                                   gm/mole
-------------------------------------------------------------------------------
|     Temp  |   (H-H298)          (G-H298)          Cp             S              |
|      (K)  |  (kcal/mole)      (kcal/mole)    (cal/mole*K)    (cal/mole*K)       |
|-----------|-------------------------------------------------------------        |
|    298.15 |    .00000E+00     -.11272          1.4404          .37807           |
|    300.00 |   2.68391E-03     -.11343          1.4612          .38704           |
|    700.00 |    1.2896         -.76144          4.4754          2.9301           |
|   1100.00 |    3.2690         -2.4007          5.2408          5.1543           |
-------------------------------------------------------------------------------
```

(TSUM keyword produces this portion of printout)

```
================================================================================================================================================
         SUMMARY OF STANDARD STATE THERMODYNAMICS FUNCTIONS FOR GAS-PHASE REACTIONS:

                  Bath Gas Temperture =   1.100E+03

         Number                      Description           Delta_G        Delta_H             Delta_S
                                                         (kcal/mole)    (kcal/mole)    (cal/moleK)
         ------------------------------------------------------------------------------------------
           1.   2CH3(+M)<=>C2H6(+M)                        -47.209        -91.238             -40.026
           2.   CH4+H<=>CH3+H2                            -6.7249         1.1351             7.1455
           3.   CH3+H(+M)<=>CH4(+M)                      -69.668        -107.62             -34.504
           4.   2H+M<=>H2+M                              -76.393        -106.49             -27.358
           5.   2H+H2<=>2H2                              -76.393        -106.49             -27.358
         ------------------------------------------------------------------------------------------
```

(GRXN keyword produces this portion of printout)

```
================================================================================================================================================

Gas Reaction #   1          2CH3(+M)<=>C2H6(+M)

                                              Change in moles in the reaction =-1
                  This reaction does have third body effects.  1 modified enhanced third body efficiencies were input
                           Species "H2", modified enhanced third body efficiency for the reaction =   2.000
                  This is a reversible reaction, having 2 reactant species
                                         and 1 product species

                           k (cm**3/(mole sec)) =  9.0300E+16 T**( -1.180    ) exp( - .6540     kcal/mole / RT)
```

```
                  Reaction has a fall-off behavior with a 6 parameter Troe function form:
                       klow (cm**6/(mole**2 sec)) =   3.180E+41 T**( -7.030    ) exp( -  2.76     kcal/mole / RT)
                            a =    .6041
                            T*** =                                    6927.E+00 Kelvin
                            T*   =    132.                                   Kelvin
-------------------------------------------------------------------------------------------------------------------------------
                            HIGH PRESSURE GAS REACTION RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

                                                                                                          |UnifDimensnal Rate
```

(TLOW keyword makes the table start at 300 K; the printout at 298.15 K is automatically given)

(TDEL keyword determines the 400 degree increment between lines of printout)

(THIG keyword cuts off the table at the last temperature below 1200, in this case 1100 K)

```
  T     |    k      A_factor    Ea      |  DeltaG     DeltaH    DeltaS   | k_rev   A_factor_rev  Ea_rev   | k_star     k_star
 (K) (cm**3/(mole sec))     (kcal/mol)  |(kcal/mol)(kcal/mole)(cal/moleK)|       (sec-1)        (kcal/mol)|   (mole/cm**3*sec)
--------|------------------------------|------------------------------|------------------------------|----------------------
        |                              |                              |                              |
 298.15 |  3.60E+13  3.34E+13 **********| -79.15     -90.31    -37.41    |  1.38E-49   7.55E+16  89.67    |    39.            1.
 300.00 |  3.60E+13  3.31E+13 **********| -79.09     -90.32    -37.45    |  3.52E-49   7.59E+16  89.68    |    38.            3.
 700.00 |  2.48E+13  1.22E+13 -.9873    | -63.30     -91.51    -40.30    |  7.41E-12   5.02E+16  89.13    |    2.8             1.
1100.00 |  1.73E+13  7.15E+12 -1.925    | -47.21     -91.24    -40.03    |  7.96E-02   1.63E+16  87.13    |    .27             4.
================================================================================================================================
```

(TFAL keyword produces this portion of printout)

```
-------------------------------------------------------------------------------------------------------------------------------
                        FALL-OFF BEHAVIOR AS A FUNCTION OF TEMPERATURE: Reaction #    1
                                  Bath Gas Pressure =    20.0     torr

Temperature   k         A_factor    Ea     |   k/kinf     klow     Reduc_Press   F       C_eff    |   k_rev     A_factor_rev
  (K)    (cm**3/(mole sec))    (kcal/mole) |       (cm**6/(mole**2 sec))            (mole/cm**3) |       (sec-1)
-----------------------------------------|----------------------------------------------------|------------------------------
  298.     3.3493E+13  2.644E+13 -.1402    |   .930      1.209E+22   686.      .931     2.04E-06 | 1.2869E-49  5.983E+16  89
  300.     3.3443E+13  2.615E+13 -.1466    |   .929      1.191E+22   672.      .931     2.03E-06 | 3.2697E-49  5.992E+16  89
  700.     1.3480E+13  1.279E+12 -3.276    |   .544      4.355E+20   15.3      .579     8.71E-07 | 4.0297E-12  5.264E+15  86
================================================================================================================================
```

(PFAL keyword produces this portion of printout)

```
 ------------------------------------------------------------------------------------------------------------------------------------------
                        FALL-OFF BEHAVIOR AS A FUNCTION OF PRESSURE: Reaction #    1
                                  Bath Gas Temperature =   1100.E+00 K
                                  Low Pressure Limiting Reaction Rate = klow =  3.7379E+19 (cm**6/(mole**2 sec))
```

(PHIG keyword controls the maximum pressure in this table)

(PLOW keyword controls the minimum pressure in this table)

(PNUM keyword controls the number of pressures included in this table)

```
  Pressure    k         A_factor    Ea     |   k/kinf  klow*C_eff  Reduc_Press   F       C_eff   |   k_rev     A_factor_rev
 (torr)  (cm**3/(mole sec))    (kcal/mole) |        (cm**3/(mole sec))             (mole/cm**3) |       (sec-1)
-----------------------------------------|-----------------------------------------------------|---------------------------------
  700.     1.1510E+13  1.447E+12 -4.532    |   .667      7.247E+14   42.0      .683     1.94E-05 | 5.3126E-02  3.306E+15  84
  265.     9.1063E+12  5.942E+11 -5.966    |   .528      2.739E+14   15.9      .561     7.33E-06 | 4.2032E-02  1.357E+15  83
  100.     6.4504E+12  2.165E+11 -7.419    |   .374      1.035E+14   6.00      .436     2.77E-06 | 2.9773E-02  4.945E+14  81
==========================================================================================================================================
==========================================================================================================================================
Gas Reaction #   2          CH4+H<=>CH3+H2

                                              Change in moles in the reaction = 0
                    This reaction does not have any third body effects
                                 This is a reversible reaction, having 2 reactant species
                                                        and 2 product species

                             k (cm**3/(mole sec)) =  2.2000E+04 T**(  3.000    ) exp( - 8.750           kcal/mole / RT)

 ------------------------------------------------------------------------------------------------------------------------------------------
                             HIGH PRESSURE GAS REACTION RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

                                                                                                                |UnifDimensnal Rate
  T     |    k      A_factor    Ea      |  DeltaG     DeltaH    DeltaS   | k_rev   A_factor_rev  Ea_rev   | k_star     k_star
 (K) (cm**3/(mole sec))     (kcal/mol)  |(kcal/mol)(kcal/mole)(cal/moleK)| (cm**3/(mole sec))   (kcal/mol)|    (mole/cm**3*sec)
--------|-------------------------------|--------------------------------|--------------------------------|----------------------
        |                               |                                |                                |
 298.15 |  2.25E+05  1.17E+13  10.53    | -1.083      .6252     5.731    |  3.61E+04   6.55E+11  9.902    |   2.60E-07        4.
 300.00 |  2.51E+05  1.19E+13  10.54    | -1.094      .6303     5.748    |  4.00E+04   6.61E+11  9.908    |   2.86E-07        4.
 700.00 |  1.40E+10  1.52E+14  12.92    | -3.810      1.310     7.313    |  9.04E+08   3.82E+12  11.61    |   2.94E-03        1.
1100.00 |  5.35E+11  5.88E+14  15.31    | -6.725      1.135     7.145    |  2.46E+10   1.61E+13  14.17    |   4.54E-02        2.
```

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Gas Reaction #   3          CH3+H(+M)<=>CH4(+M)

                                                Change in moles in the reaction =-1
                    This reaction does have third body effects.  1 modified enhanced third body efficiencies were input
                              Species "H2", modified enhanced third body efficiency for the reaction =   2.000
                                  This is a reversible reaction, having 2 reactant species
                                                          and 1 product species

                              k (cm**3/(mole sec)) =  6.0000E+16 T**( -1.000    ) exp( -         .00E+00 kcal/mole / RT)

                    Reaction has a fall-off behavior with a Lindeman function form:
                         klow (cm**6/(mole**2 sec)) =   8.000E+26 T**( -3.000    ) exp( -  .000E+00 kcal/mole / RT)

------------------------------------------------------------------------------------------------------------------------------------------------
                              HIGH PRESSURE GAS REACTION RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

                                                                                                                    |UnifDimensnal Rate
  T     |    k      A_factor    Ea      |  DeltaG     DeltaH    DeltaS   | k_rev   A_factor_rev  Ea_rev   | k_star     k_star
 (K) (cm**3/(mole sec))     (kcal/mol)  |(kcal/mol)(kcal/mole)(cal/moleK)|       (sec-1)        (kcal/mol)|    (mole/cm**3*sec)
--------|------------------------------|------------------------------|------------------------------|----------------------

        |                              |                              |                              |
 298.15 |  2.01E+14  7.40E+13 -.5924    | -96.08     -104.8    -29.30    |  3.05E-61   2.82E+15  103.6    |    55.            7.
 300.00 |  2.00E+14  7.36E+13 -.5961    | -96.02     -104.8    -29.33    |  8.96E-61   2.84E+15  103.6    |    53.            2.
 700.00 |  8.57E+13  3.15E+13 -1.391    | -83.30     -106.7    -33.40    |  1.46E-17   4.04E+15  103.9    |    .42            1.
1100.00 |  5.45E+13  2.01E+13 -2.186    | -69.67     -107.6    -34.50    |  8.68E-06   2.84E+15  103.3    |   2.81E-02        1.
================================================================================================================================================
```

(TFAL keyword produces this portion of printout)

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------------------------------------------------------------------------------------------------------------------------------------------------
                        FALL-OFF BEHAVIOR AS A FUNCTION OF TEMPERATURE: Reaction #    3
                                  Bath Gas Pressure =    20.0                        torr

Temperature   k         A_factor    Ea     |   k/kinf     klow     Reduc_Press   F       C_eff    |   k_rev     A_factor_rev
  (K)    (cm**3/(mole sec))    (kcal/mole) |       (cm**6/(mole**2 sec))            (mole/cm**3) |       (sec-1)
-----------------------------------------|----------------------------------------------------|------------------------------
  298.     4.7217E+13  1.748E+12 -1.953    |   .235      3.018E+19   .307      1.00     2.04E-06 | 7.1502E-62  6.660E+13  102
  300.     4.6263E+13  1.696E+12 -1.971    |   .231      2.963E+19   .301      1.00     2.03E-06 | 2.0730E-61  6.537E+13  102
  700.     1.9834E+12  3.894E+10 -5.467    |  2.314E-02  2.332E+18  2.369E-02  1.00     8.71E-07 | 3.3862E-19  4.990E+12  99
================================================================================================================================================
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(PFAL keyword produces this portion of printout)

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                       FALL-OFF BEHAVIOR AS A FUNCTION OF PRESSURE: Reaction #         3
                                Bath Gas Temperature =                      1100.E+00 K
                                Low Pressure Limiting Reaction Rate = klow =  6.0105E+17 (cm**6/(mole**2 sec))

  Pressure    k         A_factor    Ea      |   k/kinf  klow*C_eff  Reduc_Press   F       C_eff    |   k_rev      A_factor_rev
 (torr)  (cm**3/(mole sec))    (kcal/mole) |        (cm**3/(mole sec))             (mole/cm**3) |       (sec-1)
-----------------------------------------|-----------------------------------------------------|--------------------------------
  700.     9.6022E+12  2.982E+11 -7.588    |   .176      1.165E+13   .214      1.00     1.94E-05 | 1.5272E-06  4.228E+13  97
  265.     4.0756E+12  9.340E+10 -8.253    |  7.472E-02  4.405E+12  8.075E-02  1.00     7.33E-06 | 6.4820E-07  1.324E+13  97
  100.     1.6155E+12  3.234E+10 -8.549    |  2.962E-02  1.665E+12  3.052E-02  1.00     2.77E-06 | 2.5694E-07  4.585E+12  96
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Gas Reaction #   4          2H+M<=>H2+M

                  Change in moles in the reaction =-1
                  This reaction does have third body effects.  1 modified enhanced third body efficiencies were input
                           Species "H2", modified enhanced third body efficiency for the reaction =   .0000E+00
                  This is a reversible reaction, having 3 reactant species
                                          and 2 product species (including the third body)

                           k (cm**6/(mole**2 sec)) =  1.0000E+18 T**( -1.000    ) exp( -   .00E+00 kcal/mole / RT)

------------------------------------------------------------------------------------------------------------------------------------
                           HIGH PRESSURE GAS REACTION RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

                                                                                                          |UnifDimensnal Rate
  T     |    k      A_factor    Ea      |  DeltaG     DeltaH    DeltaS   | k_rev   A_factor_rev  Ea_rev   | k_star     k_star
 (K)(cm**6/(mole**2 sec))   (kcal/mol)  |(kcal/mol)(kcal/mole)(cal/moleK)| (cm**3/(mole sec))   (kcal/mol)|   (mole/cm**3*sec)
--------|------------------------------|--------------------------------|--------------------------------|----------------------
        |                              |                                |                                |
 298.15 |  3.35E+15  1.23E+15 -.5924    | -97.16     -104.2    -23.57    |  8.16E-61   2.63E+15  103.0    |   4.18E-04        9.
 300.00 |  3.33E+15  1.23E+15 -.5961    | -97.12     -104.2    -23.59    |  2.38E-60   2.62E+15  103.0    |   4.07E-04        2.
 700.00 |  1.43E+15  5.26E+14 -1.391    | -87.11     -105.4    -26.09    |  1.58E-17   1.70E+15  102.6    |   1.37E-05        3.
1100.00 |  9.09E+14  3.34E+14 -2.186    | -76.39     -106.5    -27.36    |  6.67E-06   1.30E+15  102.1    |   2.25E-06        5.
====================================================================================================================================
```

(GTHB keyword produces this portion of printout)

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                           ANALYSIS OF THIRD BODY REACTIONS: LUMPING [M] WITH RATE CNST
```

```
                          Reaction #   4
                               Bath Gas Pressure =    20.0     torr

Temperature   k         A_factor    Ea     |   Concentration         C_eff   |   k_rev   A_factor_rev  Ea_rev          |
  (K)    (cm**3/(mole sec))    (kcal/mole) |   (mole/cm**3)     (mole/cm**3) |       (sec-1)            (kcal/mole)  |
-----------------------------------------|-------------------------------|--------------------------------      |
  298.     3.6079E+08  4.883E+07 -1.185    |     1.076E-06       1.076E-07   |   8.7743E-68  1.040E+08  102.4          |
  300.     3.5635E+08  4.823E+07 -1.192    |     1.069E-06       1.069E-07   |   2.5477E-67  1.030E+08  102.4          |
  700.     6.5453E+07  8.858E+06 -2.782    |     4.582E-07       4.582E-08   |   7.2218E-25  2.861E+07  101.2          |
 1100.E+00 2.6506E+07  3.587E+06 -4.371    |     2.916E-07       2.916E-08   |   1.9437E-13  1.395E+07  99.93          |
=============================================================================================================================
=============================================================================================================================


Gas Reaction #   5          2H+H2<=>2H2

                  Change in moles in the reaction =-1
                  This reaction does not have any third body effects
                  This is a reversible reaction, having 3 reactant species
                                        and 2 product species

                           k (cm**6/(mole**2 sec)) =  9.2000E+16 T**( -.6000    ) exp( -   .00E+00 kcal/mole / RT)

-----------------------------------------------------------------------------------------------------------------------------
                           HIGH PRESSURE GAS REACTION RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

                                                                                                          |UnifDimensnal Rate
  T     |    k      A_factor    Ea      |  DeltaG     DeltaH    DeltaS   | k_rev   A_factor_rev  Ea_rev   | k_star    k_star
 (K)(cm**6/(mole**2 sec))   (kcal/mol)  |(kcal/mol)(kcal/mole)(cal/moleK)| (cm**3/(mole sec))   (kcal/mol)|   (mole/cm**3*sec)
--------|------------------------------|--------------------------------|--------------------------------|----------------------
        |                              |                                |                                |
 298.15 |  3.01E+15  1.65E+15 -.3555    | -97.16     -104.2    -23.57    |  7.33E-61   3.52E+15  103.2    |   3.75E-03        8.
 300.00 |  3.00E+15  1.65E+15 -.3577    | -97.12     -104.2    -23.59    |  2.15E-60   3.52E+15  103.2    |   3.67E-03        2.
 700.00 |  1.81E+15  9.91E+14 -.8345    | -87.11     -105.4    -26.09    |  1.99E-17   3.20E+15  103.1    |   1.74E-04        4.
1100.00 |  1.38E+15  7.56E+14 -1.311    | -76.39     -106.5    -27.36    |  1.01E-05   2.94E+15  103.0    |   3.41E-05        8.
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```

(TSUM keyword produces this portion of printout)

```
 ============================================================================================================
          SUMMARY OF STANDARD STATE THERMODYNAMICS FUNCTIONS FOR SURFACE-PHASE REACTIONS:

                    Bath Gas Temperture =   1.100E+03

          Number                      Description           Delta_G       Delta_H             Delta_S
                                                           (kcal/mole)    (kcal/mole)    (cal/moleK)
```

```
-----------------------------------------------------------------------------------------
  1.   CH(S)+H<=>C(S,R)+H2                        -13.581        -8.6166              4.5127
  2.   C(S,R)+H=>CH(S)                           -62.813        -97.871              -31.871
  3.   C(S,R)+CH3<=>D+CH3(S)                     -11.901        -61.285              -44.895
  4.   CH2(S,R)+CH(S,R)<=>CH2(S)+CH(S)           -94.022        -94.022        8.88178E-16
-----------------------------------------------------------------------------------------
```

(SRXN keyword produces this portion of printout)

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 ================================================================================================================================================

 Surface Reaction #   1          CH(S)+H<=>C(S,R)+H2

                   Change in gas                                  moles in the reaction = 0
                                          Change in surface moles in the reaction = 0
                   Change in bulk                                 moles in the reaction = 0

                   This reaction has  1 species whose surface coverage modify the rate constant
                        Each of these species has three parameters that multiplicatively modify the rate constant as follows:

                              k_prime = k * 10**(Z_k*nu_ki) * Z_k**mu_ki *  exp[ - eps_ki*Z_k / Rc*T ]
                                  where Z_k = Site Fraction of species k
                        Species = CH(S)
                             nu_ki  =   .1000     (cm**2/mole)
                             mu_ki  =   .0000E+00
                             eps_ki =  -.2500     (cal*cm**2/mole**2)

                   This is a reversible surface reaction, having the following types of reactant species:
                                                                1 gas-phase species
                                                              1 surface-phase species
                                                                0 bulk-phase species
                        and the following types  of product species:
                                                                1 gas-phase species
                                                              1 surface-phase species
                                                                0 bulk-phase species
                   The reaction rate constant was input via a sticking coefficient in the interpretor input file

                             Sticking Coeff = MIN(   2.140     exp( - 7.300     kcal/mole / RT)  , 1 )

                               It can be fit to the following general rate constant form:

                             k (cm**3/ mole sec) =  5.3977E+11 T**(  .6423    ) exp( - 7.180            kcal/mole / RT)

                   The reverse rate constant can be fit to the following form:
```

k(rev) (cm**3/ mole sec) = 1.4822E+11 T**(.5045) exp(- 15.83 kcal/mole / RT)

The reverse rate constant can also be expressed in a sticking coefficient form:

Sticking Coeff(rev) = .3031 T**(3.9764E-03) exp(- 15.83 kcal/mole / RT)

FORWARD AND REVERSE SURFACE REACTION RATE CONSTANTS									Bath Gas Dependent UnifDimensnal Rate	
T (K)	k (cm**3/ mole sec)	A_factor	Ea (kcal/mol)	DeltaG (kcal/mol)	DeltaH (kcal/mole)	DeltaS (cal/moleK)	k_rev (cm**3/ mole sec)	A_factor_rev	Ea_rev (kcal/mol)	k_star (mole/cm**2*sec)	k_star
298.15	1.14E+08	4.23E+13	7.596	-9.878	-8.732	3.842	6.5	6.12E+12	16.33	6.66E-07	3.
300.00	1.24E+08	4.24E+13	7.598	-9.885	-8.729	3.854	7.8	6.10E+12	16.33	7.17E-07	4.
700.00	2.08E+11	6.71E+13	8.037	-11.70	-8.327	4.819	4.62E+07	5.94E+12	16.36	5.16E-04	1.
1100.00	1.81E+12	9.63E+13	8.681	-13.58	-8.617	4.513	3.63E+09	9.94E+12	17.30	2.87E-03	5.

(SCOV keyword produces this portion of printout)

ANALYSIS OF FORWARD AND REVERSE COVERAGE DEPENDENT
SURFACE RATE CONSTANTS AT BATH GAS CONDITIONS:

T (K)	k_prime (cm**3/ mole sec)	A_factor	Ea (kcal/mole)	k (cm**3/ mole sec)	Cov_fac (cgs)	k_rev (cm**3/ mole sec)	krev_prime (cm**3/ mole sec)	A_factor_rev	
298.15	1.186E+08	4.394E+13	7.575	1.1417E+08	1.039	6.550	6.806	6.3545E+12	16
300.00	1.284E+08	4.408E+13	7.577	1.2357E+08	1.039	7.763	8.067	6.3362E+12	16
700.00	2.159E+11	6.975E+13	8.016	2.0772E+11	1.039	4.6164E+07	4.7972E+07	6.1700E+12	16
1100.00	1.886E+12	1.001E+14	8.660	1.8148E+12	1.039	3.6340E+09	3.7762E+09	1.0327E+13	17

(STCK keyword produces this portion of printout)

BREAKDOWN OF FORWARD REACTION'S STICKING COEFFICIENT

Surface site density divisor = 5.2200E-09 mole**1/cm**2

T (K)	Stck_Coeff (unitless)	A_factor	Ea	Eff_Veloc (cm/sec)	Veloc_Corr	Sden_Ratio	k* (cm/sec)	k (cm**3/ mole sec)

```
------------------------------------------------------------------------------------------------------------------------------------

  298.15   9.5263E-06   2.140       7.300      6.2562E+04   1.000       1.000       .5960              1.1417E+08
  300.00   1.0278E-05   2.140       7.300      6.2756E+04   1.000       1.000       .6450              1.2357E+08
  700.00   1.1248E-02   2.140       7.300      9.5861E+04   1.006       1.000      1084.               2.0772E+11
 1100.00   7.5843E-02   2.140       7.300      1.2017E+05   1.039       1.000      9473.               1.8148E+12
------------------------------------------------------------------------------------------------------------------------------------

                                BREAKDOWN OF REVERSE REACTION'S STICKING COEFFICIENT

                                     Surface site density divisor =   5.2200E-09 mole**1/cm**2

  T        Stck_Coeff    A_factor     Ea       Eff_Veloc   Veloc_Corr   Sden_Ratio      k*             k
  (K)      (unitless)                          (cm/sec)                                (cm/sec)    (cm**3/ mole sec)
------------------------------------------------------------------------------------------------------------------------------------

  298.15   7.7283E-13   .4377       16.03      4.4238E+04   1.000       1.000      3.4189E-08          6.550
  300.00   9.1318E-13   .4351       16.03      4.4375E+04   1.000       1.000      4.0522E-08          7.763
  700.00   3.5551E-06   .2773       15.67      6.7784E+04   1.000       1.000       .2410              4.6164E+07
 1100.00   2.2322E-04   .3700       16.20      8.4971E+04   1.000       1.000       18.97              3.6340E+09
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====================================================================================================================================


Surface Reaction #   2          C(S,R)+H=>CH(S)

                  Change in gas                                  moles in the reaction =-1
                                              Change in surface moles in the reaction = 0
                  Change in bulk                                 moles in the reaction = 0
                  This is an irreversible surface reaction, having the following types of reactant species:
                                                                        1 gas-phase species
                                                                  1 surface-phase species
                                                                     0 bulk-phase species
                       and the following types  of product species:
                                                                        0 gas-phase species
                                                                  1 surface-phase species
                                                                     0 bulk-phase species
                  The reaction rate constant was input via a sticking coefficient in the interpretor input file

                            Sticking Coeff = MIN(   .3000     exp( - .0000E+00 kcal/mole / RT)  , 1 )

                       It can be fit to the following general rate constant form:

                            k (cm**3/ mole sec) =  2.4498E+11 T**(  .5000    ) exp( -121.25E-13 kcal/mole / RT)

                  Even though this reaction is IRREVERSIBLE, the reverse rate constant will also be analysed:
```

The reverse rate constant can be fit to the following form:

k(rev) (1 / sec) = 9.0324E+10 T**(1.096) exp(- 94.69 kcal/mole / RT)

FORWARD AND REVERSE SURFACE REACTION RATE CONSTANTS
(note: reverse rate constant is not in mechanism)

T (K)	k (cm**3/ mole sec)	A_factor	Ea (kcal/mol)	DeltaG (kcal/mol)	DeltaH (kcal/mole)	DeltaS (cal/moleK)	k_rev	A_factor_rev (1 / sec)	Ea_rev (kcal/mol)	Bath Gas Dependent UnifDimensnal Rate k_star	k_star (mole/cm**2*sec)
298.15	4.23E+12	6.97E+12	.2962	-87.28	-95.45	-27.41	1.79E-56	1.03E+14	95.16	2.38E-02	9.
300.00	4.24E+12	7.00E+12	.2981	-87.23	-95.46	-27.44	4.83E-56	1.04E+14	95.16	2.37E-02	2.
700.00	6.48E+12	1.07E+13	.6955	-75.41	-97.04	-30.91	3.22E-16	3.90E+14	96.35	1.55E-02	1.
1100.00	8.12E+12	1.34E+13	1.093	-62.81	-97.87	-31.87	2.98E-05	5.05E+14	96.78	1.24E-02	1.

BREAKDOWN OF FORWARD REACTION'S STICKING COEFFICIENT

Surface site density divisor = 5.2200E-09 mole**1/cm**2

T (K)	Stck_Coeff (unitless)	A_factor	Ea	Eff_Veloc (cm/sec)	Veloc_Corr	Sden_Ratio	k* (cm/sec)	k (cm**3/ mole sec)
298.15	.3000	.3000	.0000E+00	6.2562E+04	1.176	1.000	2.2081E+04	4.2300E+12
300.00	.3000	.3000	.0000E+00	6.2756E+04	1.176	1.000	2.2149E+04	4.2431E+12
700.00	.3000	.3000	.0000E+00	9.5861E+04	1.176	1.000	3.3833E+04	6.4814E+12
1100.00	.3000	.3000	.0000E+00	1.2017E+05	1.176	1.000	4.2412E+04	8.1249E+12

Surface Reaction # 3 C(S,R)+CH3<=>D+CH3(S)

Change in gas moles in the reaction =-1
Change in surface moles in the reaction = 0
Change in bulk moles in the reaction = 1
This is a reversible surface reaction, having the following types of reactant species:
1 gas-phase species
1 surface-phase species
0 bulk-phase species
and the following types of product species:
0 gas-phase species
1 surface-phase species
1 bulk-phase species
A sticking coefficient was not used though the forward reaction could have used one

k (cm**3/ mole sec) = 4.0000E+12 exp(- 1.200 kcal/mole / RT)

The forward rate constant can be fit to the following sticking coefficient expression:

Sticking Coeff = 13.56 T**(-.4623) exp(- 1.082 kcal/mole / RT)

The reverse rate constant can be fit to the following form:

k(rev) (1 / sec) = 1.0000E+13 T**(-6.8718E-12) exp(- 15.00 kcal/mole / RT)

k(rev) (1 / sec) = 1.0000E+13 exp(- 15.00 kcal/mole / RT)

FORWARD AND REVERSE SURFACE REACTION RATE CONSTANTS

T (K)	k (cm**3/ mole sec)	A_factor	Ea (kcal/mol)	DeltaG (kcal/mol)	DeltaH (kcal/mole)	DeltaS (cal/moleK)	k_rev	A_factor_rev (1 / sec)	Ea_rev (kcal/mol)	Bath Gas Dependent UnifDimensnal Rate k_star	k_star (mole/cm**2*sec)	
298.15	5.28E+11	4.00E+12	1.200	-47.78	-60.43	-42.42	1.01E+02	1.00E+13	15.00	2.96E-03		5.
300.00	5.34E+11	4.00E+12	1.200	-47.70	-60.44	-42.46	1.18E+02	1.00E+13	15.00	2.98E-03		6.
700.00	1.69E+12	4.00E+12	1.200	-29.94	-61.57	-45.19	2.07E+08	1.00E+13	15.00	4.04E-03		1.
1100.00	2.31E+12	4.00E+12	1.200	-11.90	-61.28	-44.89	1.05E+10	1.00E+13	15.00	3.52E-03		55

BREAKDOWN OF FORWARD REACTION'S STICKING COEFFICIENT

Surface site density divisor = 5.2200E-09 mole**1/cm**2

T (K)	Stck_Coeff (unitless)	A_factor	Ea	Eff_Veloc (cm/sec)	Veloc_Corr	Sden_Ratio	k* (cm/sec)	k (cm**3/ mole sec)
298.15	.1567	.6394	.8330	1.6199E+04	1.085	1.000	2754.	5.2767E+11
300.00	.1581	.6369	.8307	1.6249E+04	1.086	1.000	2789.	5.3430E+11
700.00	.3015	.4103	.4285	2.4821E+04	1.178	1.000	8811.	1.6880E+12
1100.00	.3246	.3383	8.9753E-02	3.1114E+04	1.194	1.000	1.2058E+04	2.3101E+12

Surface Reaction # 4 CH2(S,R)+CH(S,R)<=>CH2(S)+CH(S)

Change in gas moles in the reaction = 0

```
                                  Change in surface moles in the reaction = 0
          Change in bulk                          moles in the reaction = 0
          This is a reversible surface reaction, having the following types of reactant species:
                                                      0 gas-phase species
                                                    2 surface-phase species
                                                      0 bulk-phase species
               and the following types  of product species:
                                                      0 gas-phase species
                                                    2 surface-phase species
                                                      0 bulk-phase species

                    k (cm**2/ mole sec) =  6.0000E+19 exp( - 2.000     kcal/mole / RT)

          The reverse rate constant can be fit to the following form:

                    k(rev) (cm**2/ mole sec) =  5.9991E+19 T**( 2.0901E-05) exp( - 96.02     kcal/mole / RT)
```

FORWARD AND REVERSE SURFACE REACTION RATE CONSTANTS									Bath Gas Dependent UnifDimensnal Rate	
T (K)	k (cm**2/ mole sec)	A_factor	Ea (kcal/mol)	DeltaG (kcal/mol)	DeltaH (kcal/mole)	DeltaS (cal/moleK)	k_rev (cm**2/ mole sec)	A_factor_rev	Ea_rev (kcal/mol)	k_star (mole/cm**2*sec)	k_star
298.15	2.05E+18	6.00E+19	2.000	-94.02	-94.02	**********	2.43E-51	6.00E+19	96.02	56.	6.
300.00	2.09E+18	6.00E+19	2.000	-94.02	-94.02	.0000E+00	6.62E-51	6.00E+19	96.02	57.	1.
700.00	1.42E+19	6.00E+19	2.000	-94.02	-94.02	4.4409E-16	6.26E-11	6.00E+19	96.02	3.88E+02	1.
1100.00	2.40E+19	6.00E+19	2.000	-94.02	-94.02	8.8818E-16	5.0	6.00E+19	96.02	6.55E+02	1.

```
          Continuation Command Lines Read from surfkey.inp:
```

(CNTR keyword controls printout of this second set of tables; in this case we changed the pressure of the bath gas and printed another set of non-dimensional rates)

```
         KEYWORD INPUT
 PBTH  1000.
 NDIM  ALL
 END
```

NON-DIMENSIONAL GAS REACTION RATE CONSTANTS

AT THE BATH GAS CONDITIONS

Total Pressure = 1000.E+00 torr

Temperature = 1100.E+00 Kelvin

Number	Description	k_star (mole/cm**3 sec)	k_star_rev (mole/cm**3 sec)	Gas_Da_For	Gas_Da_Rev
1.	2CH3(+M)<=>C2H6(+M)	2.602E+03	8.239E-07	2.057E+08	6.514E-02
2.	CH4+H<=>CH3+H2	114.	5.24	8.982E+06	4.141E+05
3.	CH3+H(+M)<=>CH4(+M)	2.711E+03	2.957E-11	2.143E+08	2.338E-06
4.	2H+M<=>H2+M	.282	1.417E-16	2.227E+04	1.120E-11
5.	2H+H2<=>2H2	4.27	2.146E-15	3.373E+05	1.697E-10

NOTE ON THE ABSOLUTE NUMBERS IN THIS TABLE:

The rate rate constants (mole/cm**3*sec) should be compared to rate of mass transport in order to characterize their values as being fast or slow. The nondimensionalization of the mass transport involves the following multiplicative factor, which also has the units of mole/cm**3*sec:

Total_Concentration * Diffusivity / Length_scale**2

Using the binary diffusion coefficient between O2 and N2, the following factors are calculated at bath gas conditions:

Total Concentration = 1.458E-05 mole/cm**3

Binary Diffusion Coefficient = 1.47 cm**2/sec

Length scale = 1.30 cm

Therefore, the non-dimensionalization factor for gas reactions becomes:

Conc * Diff / Length**2 = 1.265E-05 mole/cm**2*sec

Note that this number is independent of pressure

NON-DIMENSIONAL SURFACE REACTION RATE CONSTANTS

AT THE BATH GAS CONDITIONS

Total Pressure = 1000.E+00 torr

Temperature = 1100.E+00 Kelvin

Number	Description	k_star (mole/cm**2 sec)	k_star_rev (mole/cm**2 sec)	Surf_Da_For	Surf_Da_Rev
1.	CH(S)+H<=>C(S,R)+H2	.144	2.874E-04	8.727E+03	17.5
2.	C(S,R)+H=>CH(S)	.618	[1.553E-13]	3.760E+04	[9.445E-09]
3.	C(S,R)+CH3<=>D+CH3(S)	.176	54.6	1.069E+04	3.320E+06
4.	CH2(S,R)+CH(S,R)<=>CH2(S)+CH(S)	655.	1.362E-16	3.982E+07	8.282E-12

[ ] indicates that this reaction is not in mechanism

NOTE ON THE ABSOLUTE NUMBERS IN THIS TABLE:

The rate rate constants (mole/cm**2*sec) should be compared to rate of mass transport to the surface in to characterize their values as being fast or slow. The nondimensionalization of the mass transport

```
     involves the following multiplicative factor, which also has the units of mole/cm**2*sec:
               Total_Concentration * Diffusivity / Length_scale
                         Using the binary diffusion coefficient between O2
       and N2, the following factors are calculated at bath gas conditions:
               Total Concentration                 =  1.458E-05 mole/cm**3

               Binary Diffusion Coefficient =   1.47     cm**2/sec
               Length scale                 =  1.30     cm
Therefore, the non-dimensionalization factor for surface reactions becomes:
               Conc * Diff / Length         =  1.644E-05 mole/cm**3*sec
                          Note that this number is independent of pressure
```

6. REFERENCES

1. M. E. Coltrin and H. K. Moffat, "SURFTHERM: A Program to Analyze Thermochemical and Kinetic Data in Gas-phase and Surface Chemical Reaction Mechanisms" Sandia National Laboratories Report SAND94-0219 (1994).
2. S. Gordon and B. J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks and Chapman-Jouguet Detonations" NASA Report SP-273 (1971).