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CHEETAH: A Fast Thermochemical Code for Detonation

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1 Overview

For more than 20 years, TIGER has been the benchmark thermochemical code in the energetic materials community. TIGER has been widely used because it gives good detonation parameters in a very short period of time. Despite its success, TIGER is beginning to show its age. The program's chemical equilibrium solver frequently crashes, especially when dealing with many chemical species. It often fails to find the C-J point. Finally, there are many inconveniences for the user stemming from the program's roots in pre-modern FORTRAN. These inconveniences often lead to mistakes in preparing input files and thus erroneous results. We are producing a modern version of TIGER, which combines the best features of the old program with new capabilities, better computational algorithms, and improved packaging. The new code, which will evolve out of TIGER in the next few years, will be called "CHEETAH"

CHEETAH owes an obvious debt to M. Cowperwaithe and W. H. Zwisler, the developers of TIGER. Many of the capabilities that will be put into CHEETAH are inspired by the thermochemical code CHEQ, written by A. Nichols III and F. Ree. Clark Souers first advanced the idea of improving TIGER, and has been instrumental in testing the program. Craig Tarver has made several insightful suggestions. Finally, I have had many useful conversations with Al Nichols III, whose help has been invaluable.

New Capabilities

- Calculate trace levels of chemical compounds for environmental analysis.
- Kinetics capability: CHEETAH will predict chemical compositions as a function of time given individual chemical reaction rates. Initial application: carbon condensation.
- CHEETAH will incorporate partial reactions.
- CHEETAH will be based on computer-optimized JCZ3 and BKW parameters. These parameters will be fit to over 20 years of data collected at LLNL. We will run CHEETAH thousands of times to determine the best possible parameter sets.
- CHEETAH will fit C-J data to JWL's, and also predict full-wall and half-wall cylinder velocities.

Improved Algorithms

- The old TIGER used a two-step solver. We have derived new thermodynamic equations for a single-step solver that will be faster and more reliable.
- CHEETAH will use dynamic memory allocation to handle a large number of species in as little memory as possible.
- CHEETAH will recognize long species name, to avoid confusion between similar compounds.
- CHEETAH will employ a “smart” initial guess of the concentrations to make it faster and more reliable.
- The convergence to the C-J point will be improved.

Improved Packaging

- PC and UNIX versions will be produced that are algorithmically identical. The current state of affairs is that the PC version gives slightly different results and requires slightly different input than the UNIX version.
- A batch facility for multiple runs will be added.
- An output summary sheet will be given.
- The input will be made as user-friendly as possible.

2 Differences between CHEETAH and TIGER

In lieu of a complete manual, we will report the changes that have been made to TIGER. As CHEETAH matures, these changes will be incorporated into a self-contained user manual.

2.1 New input routines

TIGER was written before FORTRAN had character string types. Because of this, the authors translated character strings into floating point numbers. This had nightmarish consequences for the readability of the code. For instance, the

string 'ALPHA' appears as the number 1526302215.0 in TIGER. It also had subtle consequences for the user. Single-precision versions of TIGER, (like Dan Calef's PC version) were limited to recognizing only the first three characters of a string. This made the creation of constituent libraries very error-prone, since one had to be sure that no two constituents shared the same first three letters.

To solve this problem, a set of modifications were made to the entire code that replaced all the input with a modern token-based input system. While commands may be abbreviated to three letters, further letters are now significant. Spaces in words are now recognized. Thus,

```
set, bkw, alpha, 0.5
```

is valid input, as is

```
set, bkw, alp, 0.5.
```

But,

```
s e t, bkw, a l p, 0.5
```

worked with the old program, but not with the new input. Similarly,

```
set, bkw, alphalfa, 0.7
```

worked with the old program, but not with the new one.

Although commands can be abbreviated, user-defined names cannot. This is to help reduce errors in library files. For instance, previously

```
for, petn, -128700., ....
```

would conflict with

```
for, petroleum, -128700, .....
```

Now ALL the characters in a user-defined name are significant.

You can have spaces in user-defined names if you want.

```
for, alpha olefin, ....
```

is valid input.

CHEETAH keeps a "dictionary" of strings that it has learned in previous runs and while loading the library, in the file string.tig. You should probably delete string.tig before loading a new library to avoid overfilling the dictionary. The maximum dictionary length is currently 5000 words.

2.2 Comments in input files

Any input line beginning with a “#” character is a comment. Comments are echoed into the output file but are otherwise ignored.

2.3 Load file command

The command

```
load file, myfile.in
```

instructs CHEETAH to execute the commands contained in `myfile.in`. After the commands are executed, it returns to running commands from the original input file. The `load file` command is particularly useful in conjunction with relative units (see below). For instance, the input file

```
c-j, p, 1.0, rho, 1.894  
load, cylinder.in
```

with the file `cylinder.in` containing

```
units, v,  
point, s, , v, 1.5  
point, s, , v, 2.0  
point, s, , v, 2.5
```

would run a standard set of points along the C-J adiabat at 1.5, 2.0, and 2.5 times the C-J volume.

2.4 Startup file

Any commands in the file `startup.tig` will be executed before the regular input file. Favorite input units, equation of state `set` commands, or frequently used reactants are good candidates for inclusion into the startup file.

2.5 Spreadsheet output

CHEETAH can create an auxiliary output file consisting of specified thermodynamic variables, in a form readable by most spreadsheets and plotting packages. For example,

```
spreadsheet, myfile.dat, p, v, t, s, tab
isoline, s, v, , 10 0.5
spreadsheet, close
point, t, 3000, p, 20000
spreadsheet, myfile2.dat, h, e
point, t, 1200, p, 200000
stop
```

specifies that a spreadsheet file `myfile.dat` be created, containing values of `p`, `v`, `t`, and `s`. The columns in the file are to be separated by tabs. Other separator options are comma and space. By default, columns are separated by commas. The first argument to `spreadsheet` must be either a filename or `close`.

The `close` command is necessary to make sure that unwanted points do not end up in the spreadsheet file. In the above example, the point at 3000K and 20000 atm would be put in the spreadsheet file were it not for the `close` command. Spreadsheet commands can follow one another without an intervening `close`, in which case the set of variables used in the first spreadsheet command is inherited by the second. Spreadsheet can report the following variables: `p`, `t`, `v`, `h`, `s`, `e`, v_{gas} , α , β , C_v , and κ .

2.6 Improvements to the freeze command

The freeze command in TIGER used an algorithm that was susceptible to roundoff errors. The consequence of this to the user was that TIGER would frequently refuse to freeze concentrations, so that freezing had to be done in multiple steps. The freezing algorithm was modified in CHEETAH to make it more reliable.

2.7 Reformulated concentration solver

For every calculation type (point, c-j, isoline), TIGER solves at least once for the concentrations of the non-frozen constituents at a specified thermodynamic state (e.g. P, T). The original solver would often fail to converge. This occurred for two

reasons: the two-step solver used in TIGER could get trapped in local minima that a single-step solver would avoid. Secondly, the Newton solvers in TIGER used a poor backtracking mechanism that often led to poor convergence.

In the two-step solver the concentrations were adjusted at fixed η values (the η were related to chemical potentials), then the η s were adjusted. The problem with the two-step scheme is that if a difficult or unphysical set of η 's was chosen, the inner concentration solver would fail.

The η s have now been eliminated as basic variables in CHEETAH. Instead, the log concentrations, temperature, and specific volume are adjusted simultaneously in a single solver. The new solver implements a different set of equations than TIGER. The new equations are given below. The new thermo solver also incorporates bounds so that no concentration can exceed the maximum allowed by stoichiometry. The new solver is more robust than the TIGER solver, and maintains the exceptional speed of the original TIGER solver.

2.8 New point types

CHEETAH allows the user to specify the thermodynamic state ("point") by giving any two functions from the list (p,v,t,e,h,s,Hugoniot). See section 2.10 for information on Hugoniot points. Most notably, T-S points can be given. This should be useful for freezing along an isentrope. Other exotica, such as H-S points, are possible. Currently, the new point types require that you first run an ordinary point, such as p-t, p-v, etc. Sometimes the state specified does not exist (e.g., not all p-v states are attainable), in which case CHEETAH will be unable to find a solution. The following new point types are possible: p-e, v-h, t-s, t-h, t-e, h-s, h-e, s-e.

2.9 New isoline types

Corresponding to the new point types, isolin accepts new variables. Any thermodynamic variable from the list (p,v,t,e,h,s,Hugoniot) can be held constant, while any other variable from the list can be changed. Isentrope integrals are only calculated for p-s or v-s lines, as in TIGER.

2.10 New Hugoniot solver

TIGER used a simple iteration scheme to find a point on a shock Hugoniot. The same iteration was used within the C-J solver. Unfortunately, iterative methods

don't always converge; the C-J and Hugoniot solvers in TIGER often ran into difficulties. CHEETAH implements a Hugoniot point in a different way than TIGER: rather than solving for a successive number of (p, v) points, it uses the equation

$$e_1 - e_0 = (p_1 + p_0)(v_0 - v_1)/2 \quad (1)$$

as an implicit definition of the thermodynamic state. Thus, saying that we are on the Hugoniot plays the same role in CHEETAH as saying that the pressure is 100kBar.

The reference state (p_0, v_0, e_0) is specified through the new `hug0` command. It behaves very similarly to the specification of the reference state in TIGER's `c-j` or `hugoniot` command. The syntax is

```
hug0, p, 1, v, 0.529
hug0, p, 1, rho, 1.890
hug0, p, 1, rho, 1.5, e, 66.0
hug0, p, , rho, , e,
hug0, p, 1, vs,
```

The first command sets the reference pressure and volume. The second command specifies the inverse reference volume `rho`. By default, the reference energy is calculated from the heats of formation given in the `formula` instruction. The third command overrides this default and sets the reference energy. The fourth command sets the reference state to be the current thermodynamic state. The fifth command sets the reference volume to be the standard volume of the explosive.

Once the reference state is set, the `hugoniot` keyword specifies that the given state is to be on the Hugoniot. The `hugoniot` point always takes an empty argument. For example,

```
## Don't forget to set the initial state !
hug0, p, 1, v, 0.529
## Point along the Hugoniot at 400kBar
point, p, 400000, hugoniot,
## Give me points along the Hugoniot up to 1800 K.
isolin, hugoniot, t, , 10, 1800
```

TIGER's `hugoniot` command can still be used in CHEETAH, but it is made obsolete by the use of `isolin, hugoniot`.

2.11 New C-J solver

CHEETAH has a new C-J solver that should be more robust than TIGER's solver. CHEETAH's solver takes advantage of the `hugoniot` point type. A series of `p`, `hugoniot` calculations are performed until a pressure is found that satisfies the equation

$$v = v_0[(1 - p_0/p)/\kappa + 1]^{-1} \quad (2)$$

is satisfied. Here, v is the volume at the specified pressure on the Hugoniot line, and κ is the adiabatic exponent. The detonation pressure is assumed to be between the constant volume explosion point and 500kBar. Using these points as brackets, it finds the root of Eq. (2) with Brent's method.

The `c-j` command also has a new syntax. The reference point on the Hugoniot is specified with the `hug0` command described in Sec. 2.10. The `c-j` command doesn't take any arguments. For example,

```
hug0, p, 1, rho, 1.890
c-j
```

2.12 User-defined units

Units to use when entering pressures or volumes can be specified with the `units` commands

```
units, p, 100
units, v, 2
units, p,
```

The first command sets the input unit of pressure to be 100 Atm. The second command sets the input unit of relative volume to be 2 cc / gm. The third command sets the unit of pressure to be the current pressure. This is particularly useful when specifying pressures or volumes relative to the last thermodynamic state in the calculation. The units in the output file are unaffected by the `units` command.

Units can be set for p , v , ρ , E and T . If E units are specified, all quantities with the dimensions of energy (E , H , G) are input with the new E units. The unit of S is the unit of E divided by the unit of T .

2.13 New gas eos command

The old `geos` command has been given the less cryptic name `gas eos`.

2.14 Summary sheet output

A file summarizing the run can be generated by using the command:

```
summary, myfile.sum
```

where `myfile.sum` is the name of the summary file. The summary file contains the initial composition, C-J parameters, and the volumes and energies of any subsequent S-V points. The S-V points correspond to cylinder test results. Subsequent `summary` commands close the previous summary file. The `summary` command with a blank argument closes the current summary file.

3 The thermochemical equations used in CHEETAH

3.1 Overview

CHEETAH solves the same physical model as TIGER: there are t chemical species present, composed of c elements. A single gaseous phase composed of s species is in chemical equilibrium with $t - s$ condensed phases. Each condensed phase is comprised of a single chemical species. Condensed phases may undergo solid-liquid phase transitions. Of the t condensed species (referred to as “constituents” in the TIGER documentation, p are assumed to have nonzero concentrations at equilibrium, while the remaining $t - p$ condensed constituents are assumed absent.

CHEETAH solves for the concentrations in the gaseous phase given the guesses about the presence or absence of condensed constituents, then checks if these guesses are valid. Stoichiometry is then used to determine the mole numbers of the condensed constituents. CHEETAH uses the following variables to describe the gaseous phase: the mole numbers of each gaseous constituent n_i , the temperature T , and the inverse volume of gas per unit mass of mixture $\hat{p}$.

The Newton solver in CHEETAH operates with logarithmic variables, so the quantities $\xi_i \equiv \ln n_i$, $\ln T$, and $\ln \hat{p}$ are the independent variables in the solver. CHEETAH has the capability to freeze the mole numbers of given species, in which case the corresponding ξ_i are simply omitted from the solver. We will establish

the notation that F_i is the i th equation in the Newton solver. The variables in CHEETAH must satisfy stoichiometric equations, balance of chemical potentials, and two thermodynamic conditions. These equations are discussed in more detail below.

3.2 Stoichiometry

There are c equations which express the conservation of the mole number of each element. Stoichiometry is usually expressed in terms of the total amount of each element:

$$\sum_{j=1}^s \alpha_{i,j} n_i + \sum_{j=1}^{t-s} \alpha_{i,j+s} N_j = Q_i, \quad (3)$$

where $\alpha_{i,j}$ is the formula matrix, N_j is the mole number of condensed constituent j , and Q_i is the number of moles of element i .

In CHEETAH, however, stoichiometry is handled through the selection of c reference species. This is the same scheme used in TIGER. These species are referred to as “components”. The formulas of the component species serve as basis vectors for the description of the stoichiometry. Matters are further specialized by the convention that condensed constituents assumed to have nonzero concentrations are always chosen to be components. We have:

$$\begin{aligned} \sum_{m=p+1}^{p'} \beta_{i(m),j} N_m + \sum_{i=1}^s \beta_{i,j} n_i + N_j &= q_j \quad j = 1 \cdots p \\ \cdots &= q_j \quad j = p+1 \cdots c. \end{aligned} \quad (4)$$

Here, $p' - p$ is the number of frozen condensed constituents. CHEETAH solves for Eq. (5) as part of the Newton solver, while Eq. (4) is used to determine the N_j for each set of $\{n_j\}$. This gives us

$$F_j \equiv q_j - \sum_{m=p+1}^{p'} \beta_{i(m),j} N_m - \sum_{i=1}^s \beta_{i,j} n_i = 0, \quad j = 1 \cdots c - p \quad (6)$$

In TIGER, Eq. (6) is substituted into the equations for the η s.

3.3 Chemical potential balance

CHEETAH solves for chemical equilibrium between the constituents by balancing chemical potentials. The balance equations can be understood by constructing a

set of fictitious decomposition reactions:

$$Y_j \Leftrightarrow \sum_{i=1}^c \beta_{j,i} Y_i \quad j = 1 \cdots t. \quad (7)$$

The final chemical equilibrium obtained is unaffected by the use of fictitious reactions, as long as t linearly independent reactions are used. The decomposition reaction is trivial if constituent j is a component:

$$Y_j \Leftrightarrow Y_j \quad \text{if } j \text{ is a component} \quad (8)$$

Gibb's condition for chemical equilibrium of these reactions is

$$\mu_j = \sum_{i=1}^c \beta_{j,i} \mu_i \quad j = 1 \cdots t. \quad (9)$$

CHEETAH uses the non-trivial chemical potential balance equations for in the Newton solver:

$$F_{j+c-p} = \mu_{j'} - \sum_{i=1}^c \beta_{j',i} \mu_i \quad \text{if } j' \text{ is not a component,} \quad (10)$$

where $j = 1 \cdots s - c + p$, and $j' = j + c - p$.

3.4 Thermodynamic state

The last two equations in CHEETAH defines the thermodynamic state. CHEETAH allows the user to specify any two variables from the list (p, v, T, E, H, S) . Depending on what variables are specified, CHEETAH evaluates the appropriate thermodynamic function. The following equations are used:

3.4.1 p specified

The equation to be solved is

$$F_j = \ln(p/p_0), \quad (11)$$

where p_0 is the specified value of p . p is evaluated in subroutine STATEG through the equation of state relation:

$$p = \frac{nRT}{M_0} \hat{p}\Phi(\hat{p}, T, n_1, \dots, n_s), \quad (12)$$

where n is the total mole number, M_0 is the total mass of the sample, and Φ is the gas imperfection factor.

3.4.2 v specified

The equation to be solved is

$$F_j = \frac{pM_0}{RT}(v - v_0), \quad (13)$$

where the specific volume v is evaluated as:

$$\frac{pM_0v}{RT} = \frac{pM_0}{\hat{p}RT} + \sum_{j=1}^{p'} N_j \phi_j^*, \quad (14)$$

where ϕ_j^* is the reduced molar volume of the j th condensed constituent, defined by

$$\phi_j^* = \frac{pV_j^*}{RT}, \quad (15)$$

where V_j^* is the molar volume of the j th condensed constituent.

3.4.3 T specified

In this case the equation is simply

$$F_j = \ln T - \ln T_0 \quad (16)$$

3.4.4 H specified

The equation is

$$F_j = \frac{M_0}{RT}(h - h_0), \quad (17)$$

where h_0 is the specified enthalpy and

$$\frac{M_0h}{RT} = \sum_{j=1}^p N_j \chi_j^* + \sum_{i=1}^s n_i \chi_i^0 + \frac{pM_0}{RT} + \epsilon - n. \quad (18)$$

$\chi_j^* \equiv H_j^*/RT$ is the reduced molar enthalpy of condensed constituent j . χ_j^0 is the reduced enthalpy of the j th gaseous constituent at the standard pressure of 1 Atm. ϵ is the nonideality correction factor for the enthalpy, defined as

$$\epsilon = \int_0^{\hat{p}} \frac{M_0}{RT\hat{p}^2} \left[p - \frac{\partial p}{\partial \ln T} \right] d\hat{p}, \quad (19)$$

where the integral is along an isotherm.

3.4.5 S specified

The equation used is

$$F_j = \frac{M_0}{RT} (TS_0 - H + G), \quad (20)$$

where the Gibbs free energy is evaluated with

$$M_0G = \sum_{j=1}^{p'} N_j \mu_j^* + \sum_{i=1}^s n_i \mu_i. \quad (21)$$

3.4.6 E specified

The equation used is

$$F_j = \frac{M_0}{RT} (H - pv - E_0), \quad (22)$$

where E_0 is the specified energy.

3.5 The Jacobian matrix

The partial derivatives of the F_j with respect to system variables χ_i , $\ln T$, $\ln \hat{\rho}$ are called the Jacobian matrix. The Jacobian matrix, used in the Newton solver, is evaluated analytically in CHEETAH. This subsection gives the formulas used in evaluating the Jacobian matrix.

3.5.1 Stoichiometric equations

The derivatives are quite simple for these equations:

$$\frac{\partial F_j}{\partial \xi_k} = -\beta_{k,j} n_k \quad (23)$$

$$\frac{\partial F_j}{\partial \ln \hat{\rho}} = 0 \quad (24)$$

$$\frac{\partial F_j}{\partial \ln T} = 0 \quad (25)$$

3.5.2 Chemical potential balance

The relation

$$\mu_i/RT = \mu_i^0/RT + \xi_i + \Gamma_i + \ln(RT\hat{\rho}/M_0), \quad (26)$$

is used to re-write the chemical potential balance equations. Here, Γ_i is a non-ideality term. This leads to the form:

$$\begin{aligned} F_j = & \xi_j - \Gamma_j + \sum_{k=1}^p \beta_{jk} \frac{\mu_k^*}{RT} + \sum_{k=p+1}^c \beta_{jk} (\xi_{i^*(k)} + \Gamma_{i^*(k)}) \\ & + \beta_{j,c+1} \ln(RT\hat{\rho}/M_0) - \frac{\mu_j^0}{RT} + \sum_{k=p+1}^c \beta_{jk} \frac{\mu_k^0}{RT} \end{aligned} \quad (27)$$

Here $\beta_{i,c+1} \equiv \sum_{j=p+1}^c \beta_{ij}$. The resulting derivatives are

$$\frac{\partial F_j}{\partial \xi_k} = -\delta_{jk} - \frac{\partial \Gamma_j}{\partial \xi_k} + \sum_{l=1}^p \beta_{jl} \phi_l^* \frac{\partial \ln p}{\partial \xi_k} + \sum_{l=p+1}^c \beta_{jl} (\delta_{i^*(l),j} + \frac{\partial \Gamma_{i^*(l)}}{\partial \xi_l}) \quad (28)$$

$$\frac{\partial F_j}{\partial \ln \hat{\rho}} = -\frac{\partial \Gamma_j}{\partial \ln \hat{\rho}} + \frac{\partial \ln p}{\partial \ln \hat{\rho}} \sum_{k=1}^p \beta_{jk} \phi_k^* + \sum_{k=p+1}^c \beta_{jk} \frac{\partial \Gamma_{i^*(k)}}{\partial \ln \hat{\rho}} + \beta_{j,c+1} \quad (29)$$

$$\begin{aligned} \frac{\partial F_j}{\partial \ln T} = & \frac{\partial \Gamma_j}{\partial \ln T} - \sum_{k=1}^p \beta_{jk} \chi_k^* + \sum_{k=p+1}^c \frac{\partial \Gamma_{i^*(k)}}{\partial \ln T} \beta_{jk} + \beta_{j,c+1} + \chi_j^0 \\ & - \sum_{k=p+1}^c \beta_{jk} \chi_k^0 + \sum_{k=1}^p \beta_{jk} \phi_k^* \frac{\partial \ln p}{\partial \ln T} \end{aligned} \quad (30)$$

3.5.3 Thermodynamic state equations

The thermodynamic functions in CHEETAH are linear combinations of the variables p , v , H , and G . These variables serve as a basis for the evaluation of derivatives of thermodynamic functions. We begin with the pressure derivatives:

$$\frac{\partial \ln p}{\partial \xi_k} = n_k \left[\frac{\partial \ln \Phi}{\partial n_k} + 1/n \right] \quad (31)$$

$$\frac{\partial \ln p}{\partial \ln \hat{\rho}} = 1 + \frac{\partial \ln \Phi}{\partial \ln \hat{\rho}} \quad (32)$$

$$\frac{\partial \ln p}{\partial \ln T} = 1 + \frac{\partial \ln \Phi}{\partial \ln T} \quad (33)$$

where Φ is the equation of state imperfection factor, and n is the total gaseous mole number.

It is most convenient to express the volume derivatives in terms of the reduced volume $v^* \equiv pM_0v/RT$. The reduced volume is equal to

$$v^* = \frac{pM_0}{\rho RT} + \sum_{j=1}^{p'} N_j \phi_j^* \quad (34)$$

The partial derivatives are given by

$$\frac{\partial v^*}{\partial \xi_k} = \frac{pM_0}{\rho RT} \frac{\partial \ln p}{\partial \xi_k} - \sum_{j=1}^p \beta_{kj} n_k \phi_j^* + \sum_{j=1}^{p'} N_j \phi_j^* (1 + \beta_j^*) \frac{\partial \ln p}{\partial \xi_k} \quad (35)$$

$$\frac{\partial v^*}{\partial \ln \hat{p}} = \frac{pM_0}{\rho RT} \left(\frac{\partial \ln p}{\partial \ln \hat{p}} - 1 \right) + \sum_{j=1}^{p'} N_j \phi_j^* (1 + \beta_j) \quad (36)$$

$$\frac{\partial v^*}{\partial \ln T} = \frac{pM_0}{\rho RT} \left(\frac{\ln p}{\ln T} - 1 \right) + \sum_{j=1}^{p'} N_j \phi_j^* \left[\alpha_j - 1 + \frac{\partial \ln p}{\partial \ln T} (\beta_j + 1) \right] \quad (37)$$

The enthalpy equations are expressed in terms of the reduced enthalpy $H^* \equiv M_0H/RT$. We then have

$$H^* = \sum_{j=1}^p \chi_j^* (q_j - \sum_{i=1}^s \beta_{ij} n_i) + \sum_{i=1}^s n_i \chi_i^0 + \frac{pM_0}{\hat{p}RT} + \epsilon - n + \sum_{m=p+1}^{p'} N_m \chi_m^* \quad (38)$$

The resulting derivatives are

$$\begin{aligned} \frac{\partial H^*}{\partial \xi_k} = & - \sum_{j=1}^p \beta_{kj} n_k \chi_j^* + \sum_{j=1}^{p'} N_j \phi_j^* (1 - \alpha_j) \frac{\partial \ln p}{\partial \xi_k} \\ & + \frac{pM_0}{\rho RT} \frac{\ln p}{\xi_k} - n_k \frac{\partial \Gamma_k}{\partial \ln T} + n_k (\chi_i^0 - 1) \end{aligned} \quad (39)$$

$$\frac{\partial H^*}{\partial \ln \hat{p}} = \sum_{j=1}^{p'} N_j \phi_j^* (1 - \alpha_j) \frac{\partial \ln p}{\partial \ln \hat{p}} + \frac{pM_0}{\rho RT} \left(\frac{\partial \ln p}{\partial \ln \hat{p}} - \frac{\partial \ln p}{\partial \ln T} \right) + \frac{\partial \epsilon}{\partial \ln \hat{p}} \quad (40)$$

$$\frac{\partial H^*}{\partial \ln T} = \sum_{j=1}^{p'} N_j \left(\frac{C_{p,j}^*}{R} - \chi_j^* + \frac{\partial \ln p}{\partial \ln T} [\phi_j^* - phis_j \alpha_j] \right) \quad (41)$$

$$+ \sum_{i=1}^s n_i \left(\frac{C_p^0}{R} - \chi_i^0 \right) + \frac{pM_0}{\rho RT} \left(\frac{\partial \ln p}{\partial \ln T} - 1 \right) + \frac{\partial \epsilon}{\partial \ln T} \quad (42)$$

We finally consider the reduced Gibbs free energy $G^* \equiv M_0 G / RT$. We have

$$G^* = \sum_{j=1}^{p'} N_j \mu_j^* + \sum_{i=1}^s n_i \mu_i, \quad (43)$$

and the following derivatives:

$$\begin{aligned} \frac{\partial G^*}{\partial \xi_k} = & \sum_{j=1}^{p'} N_j \phi_j^* \frac{\partial \ln p}{\partial \xi_k} - \sum_{j=1}^p \beta_{kj} n_k \frac{\mu_j^*}{RT} \\ & + n_k \left(\frac{\mu_k^0}{RT} + \xi_k + \Gamma_k + \ln(RT \hat{\rho} / M_0) + \sum_{i=1}^s n_i \left(\delta_{ki} + \frac{\partial \Gamma_i}{\partial \xi_k} \right) \right) \end{aligned} \quad (44)$$

$$\frac{\partial G^*}{\partial \ln \hat{\rho}} = \sum_{j=1}^{p'} N_j \phi_j^* \frac{\partial \ln p}{\partial \ln \hat{\rho}} + \sum_{i=1}^s n_i \left(\frac{\partial \Gamma_i}{\partial \ln \hat{\rho}} + 1 \right) \quad (45)$$

$$\frac{\partial G^*}{\partial \ln T} = \sum_{j=1}^{p'} N_j \phi_j^* \frac{\partial \ln p}{\partial \ln T} + \sum_{i=1}^s n_i \left(\frac{\partial \Gamma_i}{\partial \ln T} - \chi_i^0 + 1 \right) - \sum_{j=1}^{p'} N_j \chi_j^* \quad (46)$$

4 Example runs

In the first example, we show usage of CHEETAH that is typical at LLNL. The C-J point of PETN is first found. From the C-J point, an adiabatic expansion is done up to 1800K. It has been found empirically at LLNL that TIGER BKWR compositions agree best with experimental results if the composition is frozen at 1800K. After freezing the composition, a series of point calculations are done for a standard set of relative specific volumes. The results of these point calculations are saved into a spreadsheet file.

```
# The first new feature you should note is that you can have
# comments in your input files. Comments are copied to the
# output, so you can use them to document your work.
# Comments start with a '#', in case you haven't noticed.

# You don't need the set, bkwr, ... commands because these
# are in your startup.tig file, so they are invoked automatically.

reactants
```

```

for, petn,      -128700., 177.61, 0., c, 5, h, 8, n, 4, o, 12
comp, petn, 100

# This specifies the hugoniot reference state.
hug0, p, 1.0, rho, 1.763

# C-J doesn't take any arguments any more.
c-]

## This moves directly down the adiabat to 1800 K.
point, s, , t, 1800.0

## It is standard practice at LLNL to freeze the composition
## at 1800K.
freeze

## Put volumes and temperatures along the adiabat in the file
## plot.dat for plotting or incorporation into a spreadsheet.
spreadsheet, plot.dat, v, t

## Now we do a set of points along the adiabatic that
## correspond to cylinder shots. Note the use of
## relative volumes.

units, rho, 1.763
point, s, , v, 2.2
point, s, , v, 4.1
point, s, , v, 6.5
point, s, , v, 10.0
point, s, , v, 20.0
stop

```

The output is as follows:

```

CHEETAH CHEETAH CHEETAH CHEETAH CHEETAH CHEETAH CHEETAH CHEETAH
CHEETAH version 0.80
The time is Mon Nov 8 22:41:45 1993

```

```

Input from startup.tig> ## These are startup commands, which are
Input from startup.tig> ## run before every cheetah job.
Input from startup.tig> geos, bkw
Input from startup.tig> set, bkw, alpha, 0.5
Input from startup.tig> set, bkw, beta, 0.176
Input from startup.tig> set, bkw, kappa, 11.80
Input from startup.tig> set, bkw, theta, 1850
Input from startup.tig>
Input from startup.tig>
Input>
Input> # The first new feature you should note is that you can have
Input> # comments in your input files. Comments are copied to the
Input> # output, so you can use them to document your work.
Input> # Comments start with a '#', in case you haven't noticed.
Input>
Input> # You don't need the set, bkw, ... commands because these
Input> # are in your startup.tig file, so they are invoked automatically.

```

```

Input>
Input> reactants
Input> for, petn, -128700., 177.61, 0., c, 5, h, 8, n, 4, o, 12
Input> comp, petn, 100

```

The Composition

Name	% wt.	% mol	Heat of formation (cal/mol)	Standard volume (cc/mol)	Standard entropy (cal/K/mol)	Mol. wt.	Formula
petn	100.00	100.00	-128700.000	177.610	0.000	316.15	c5h8n4o12

```

Heat of formation = -407.090 cal/gm
Standard volume   = 0.562 cc/gm
Standard entropy   = 0.000 cal/k/gm
Standard energy    = -407.104 cal/gm

```

The elements and percent by mole

Element	Percent by mole
c	17.241
h	27.586
n	13.793
o	41.379

```

Input>
Input> # This specifies the hugoniot reference state.
Input> hug0, p, 1.0, rho, 1.763
Input>
Input> # C-J doesn't take any arguments any more.
Input> c-j

```

The C-J condition

```

The shock velocity = 8.32981e+03
The particle velocity = 2.11071e+03
The speed of sound = 6.21910e+03

```

P0 = 1.000000 atm, V0 = 0.567215 cc/gm, E0 = -407.104001 cal/gm

Reference state = reactants

H(R) = H--407.09, E(R) = E--407.10, S(R) = S- 0.00

	P (ATM)	V (CC/GM)	T (K)	H(R) (CAL/GM)	E(R) (CAL/GM)	S(R) (CAL/K/GM)	VGS (CC/GM)
1.)	305915.3	0.4235	3337.6	3669.88	532.42	1.557	0.4235

Product concentrations (mol/kg)

Name	Concentration (mol/kg)
CO2 GAS	.9994E+01
H2O GAS	.6683E+01
N2 GAS	.6171E+01
HCOOH GAS	.5465E+01
NH3 GAS	.3073E+00
CO GAS	.3510E+00
NO GAS	.2472E-02
H2 GAS	.3281E-01
O2 GAS	.1186E-03
CH3OH GAS	.2108E-02
CH4 GAS	.3245E-02

```

      HCN GAS      .9695E-08
      *C SOLID     .0000E+00
TOTAL   GAS              29.0125

```

```

Input>
Input> ## This moves directly down the adiabat to 1800 K.
Input> point, s,, t, 1800.0

```

```

      Reference state = reactants
      H(R) = H--407.09, E(R) = E--407.10, S(R) = S- 0.00

```

	P (ATM)	V (CC/GM)	T (K)	H(R) (CAL/GM)	E(R) (CAL/GM)	S(R) (CAL/K/GM)	VGS (CC/GM)
1.)	25117.8	1.0577	1800.0	-252.51	-895.88	1.557	1.0577

Product concentrations (mol/kg)

Name	Concentration
CO2 GAS	.1182E+02
H2O GAS	.1066E+02
N2 GAS	.6232E+01
CO GAS	.3560E+01
H2 GAS	.8882E+00
CH4 GAS	.3844E+00
NH3 GAS	.1885E+00
HCOOH GAS	.5320E-01
CH3OH GAS	.1263E-02
HCN GAS	.4857E-04
NO GAS	.2409E-06
O2 GAS	.1205E-09
*C SOLID	.0000E+00
TOTAL GAS	33.7809

```

Input>
Input> ## It is standard practice at LLNL to freeze the composition
Input> ## at 1800K.
Input> freeze
0CONSTITUENT      *C HAS BEEN INDIRECTLY FROZEN TO ZERO
Input>
Input> ## Put volumes and temperatures along the adiabat in the file
Input> ## plot.dat for plotting or incorporation into a spreadsheet.
Input> spreadsheet, plot.dat, v, t
Input>
Input> ## Now we do a set of points along the adiabatic that
Input> ## correspond to cylinder shots. Note the use of
Input> ## relative volumes.
Input>
Input> units, rho, 1.763
Input> point, s,, v, 2.2

```

```

      Reference state = reactants
      H(R) = H--407.09, E(R) = E--407.10, S(R) = S- 0.00

```


	P (ATM)	V (CC/GM)	T (K)	H(R) (CAL/GM)	E(R) (CAL/GM)	S(R) (CAL/K/GM)	VGS (CC/GM)
1.)	16402.9	1.2479	1631.9	-493.71	-989.41	1.557	1.2479

Product concentrations (mol/kg)

Name	Concentration
* CO2 GAS	.1182E+02
* H2O GAS	.1066E+02
* N2 GAS	.6232E+01
* CO GAS	.3560E+01
* H2 GAS	.8882E+00
* CH4 GAS	.3844E+00
* NH3 GAS	.1885E+00
* HCOOH GAS	.5320E-01
* CH3OH GAS	.1263E-02
* HCN GAS	.4857E-04
* NO GAS	.2409E-06
* O2 GAS	.1205E-09
* *C SOLID	.0000E+00
TOTAL GAS	33.7809

Input> point, s,, v, 4.1

Reference state = reactants
H(R) = H--407.09, E(R) = E--407.10, S(R) = S- 0.00

	P (ATM)	V (CC/GM)	T (K)	H(R) (CAL/GM)	E(R) (CAL/GM)	S(R) (CAL/K/GM)	VGS (CC/GM)
1.)	3808.4	2.3256	1182.7	-980.14	-1194.62	1.557	2.3256

Product concentrations (mol/kg)

Name	Concentration
* CO2 GAS	.1182E+02
* H2O GAS	.1066E+02
* N2 GAS	.6232E+01
* CO GAS	.3560E+01
* H2 GAS	.8882E+00
* CH4 GAS	.3844E+00
* NH3 GAS	.1885E+00
* HCOOH GAS	.5320E-01
* CH3OH GAS	.1263E-02
* HCN GAS	.4857E-04
* NO GAS	.2409E-06
* O2 GAS	.1205E-09
* *C SOLID	.0000E+00
TOTAL GAS	33.7809

Input> point, s,, v, 6.5

Reference state = reactants
H(R) = H--407.09, E(R) = E--407.10, S(R) = S- 0.00

P	V	T	H(R)	E(R)	S(R)	VGS
---	---	---	------	------	------	-----

```

      (ATM)      (CC/GM)      (K)      (CAL/GM)      (CAL/GM)      (CAL/K/GM)      (CC/GM)
1.)    1475.5      3.6869      968.7    -1140.46    -1272.19      1.557      3.6869
Product concentrations (mol/kg)
      Name
*   CO2 GAS      .1182E+02
*   H2O GAS      .1066E+02
*    N2 GAS      .6232E+01
*    CO GAS      .3560E+01
*    H2 GAS      .8882E+00
*   CH4 GAS      .3844E+00
*   NH3 GAS      .1885E+00
*  HCOOH GAS      .5320E-01
*  CH3OH GAS      .1263E-02
*   HCN GAS      .4857E-04
*    NO GAS      .2409E-06
*    O2 GAS      .1205E-09
*   *C SOLID      .0000E+00
TOTAL   GAS      33.7809

```

Input> point, s,, v, 10.0

```

                        Reference state = reactants
                        H(R) = H--407.09, E(R) = E--407.10, S(R) = S- 0.00

      P      V      T      H(R)      E(R)      S(R)      VGS
      (ATM)   (CC/GM)   (K)   (CAL/GM)   (CAL/GM)   (CAL/K/GM)   (CC/GM)
1.)    661.6     5.6721   820.1   -1228.44   -1319.31     1.557     5.6721
Product concentrations (mol/kg)
      Name
*   CO2 GAS      .1182E+02
*   H2O GAS      .1066E+02
*    N2 GAS      .6232E+01
*    CO GAS      .3560E+01
*    H2 GAS      .8882E+00
*   CH4 GAS      .3844E+00
*   NH3 GAS      .1885E+00
*  HCOOH GAS      .5320E-01
*  CH3OH GAS      .1263E-02
*   HCN GAS      .4857E-04
*    NO GAS      .2409E-06
*    O2 GAS      .1205E-09
*   *C SOLID      .0000E+00
TOTAL   GAS      33.7809

```

Input> point, s,, v, 20.0

```

                        Reference state = reactants
                        H(R) = H--407.09, E(R) = E--407.10, S(R) = S- 0.00

      P      V      T      H(R)      E(R)      S(R)      VGS
      (ATM)   (CC/GM)   (K)   (CAL/GM)   (CAL/GM)   (CAL/K/GM)   (CC/GM)

```

```

1.1      207.3      11.3443      642.4  -1312.14  -1369.07      1.557      11.3443
Product concentrations (mol/kg)
      Name
*   CO2 GAS      .1182E+02
*   H2O GAS      .1066E+02
*    N2 GAS      .6232E+01
*    CO GAS      .3560E+01
*    H2 GAS      .8882E+00
*   CH4 GAS      .3844E+00
*   NH3 GAS      .1885E+00
*  HCOOH GAS      .5320E-01
* CH3OH GAS      .1263E-02
*   HCN GAS      .4857E-04
*    NO GAS      .2409E-06
*    O2 GAS      .1205E-09
*   *C SOLID      .0000E+00
TOTAL   GAS      33.7809

```

```

Input> stop

```

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