for any arbitrary vector $\mathbf{x} = (x_1, x_2, \ldots, x_R)$. In particular this means that a potential equilibrium composition point ξ_0 where the gradient vanishes, the Gibbs potential Taylor expansion up to second order is

$$g(\xi) - g(\xi_0) = \sum_i \sum_j \frac{\partial^2 g}{\partial \xi_i \xi_j} d\xi_i d\xi_j \geq 0 . \tag{4.54}$$

This guarantees the Gibbs potential is a minimum at these points and with a bit more effort (Powers and Paolucci, 2008), that this point is the unique, physically realizable solution. This is true not only for the case of minimizing the Gibbs potential but is true in general for chemical equilibrium of ideal solutions under more general constraint conditions other than constant (T, P). The positive definite property of the Hessian has implications for the relationship between frozen and equilibrium sound speeds Fickett and Davis (1979).

There are some subtleties to the iteration procedure (see Smith and Missen, 1991, Section 6.4) when using reaction coordinates and unconstrained optimization.

1. The number of species and elements should be reduced by eliminating inert species. These are species that do not participate in any reactions but have fixed amounts that affect the total molar concentration. This will decrease the number of species and reactions coordinates and increase the efficiency of the computation.

2. A procedure like `sqp` should be used to get good initial estimates to initialize the Newton-Raphson iteration, which will only converge reliably if started in the neighborhood of the correct solution.

3. The Newton-Raphson iteration has to be modified to include a damping factor Λ to prevent any species amounts from ever becoming negative. The modified iteration is

$$\delta \boldsymbol{\xi}^m = -\Lambda^m \left(\frac{\partial^2 g}{\partial \xi^2} \right)^{-1}_{\mathbf{n}^m} \left(\frac{\partial g}{\partial \boldsymbol{\xi}} \right)_{\mathbf{n}^m} , \tag{4.55}$$

where the value of Λ^m is selected to be the maximum value less than one such that

$$n_k^m > 0 \quad \text{for all } k . \tag{4.56}$$

Well-behaved equilibrium problems for which the Newton-Raphson method converges will typically start with values of $\Lambda < 1$ which increase with increasing m. The Newton-Raphson algorithm converges quadratically if $\Lambda = 1$ and is often poorly behaved for $\Lambda > 1$ so the goal should be to set convergence criteria so that some specified tolerance on δg to achieve quadratic convergence with a minimum number of total iterations. Cantera uses a default tolerance of $\max |\delta g| < \times 10^{-9}$ for the standard `equilibrate` function.

4. The Hessian will be difficult to invert for systems with a large number of species that have values that vary over a large range, i.e., problems with a combination of major ($O(10^{-3})$ or larger) and minor species present in much smaller amounts ($O(10^{-8})$ or less). The difficulty is signaled by the Hessian having a reciprocal *condition number* that is too small, i.e., typically less than 10^{-15}. The reciprocal condition number needs to be larger than the smallest change that can be represented by the floating point arithmetic in order for standard inversion methods to be reliable. For double precision with 64-bit representation, the smallest change for $O(1)$ numbers is on the order of 10^{-15}.

A solution to this is to limit the application of the Newton-Raphson iteration to a set of species larger than some threshold value. This can be accomplished by sorting the starting guess in decreasing order of concentration and partitioning the species accordingly. This idea is also a key step in the VCS procedure. After sorting the species and constructing a proper set of basis vectors for the stoichiometric coefficient matrix $\mathbf{N}$, the inverse Hessian is approximated analytically assuming that it is diagonal in this basis. This approximation is sketched out in Smith and Missen (1991) who give references to the original papers which contain the details.

For mixtures that have exceptionally disparate values of composition variables, a continuation method has been developed by Pope (2004). This technique is also applicable when additional constraints on composition are employed. The method has been extended to multiphase mixtures by Scoggins and Magin (2015) and applied to ionized gases and re-entry situations.

> Provide code example using Cantera of how to carry out equilibrium computation using the methods described above.

4.7 Element Potentials

A technique popularized by Reynolds and used in the STANJAN program (Reynolds, 1981, 1986) then later incorporated into CHEMKIN (Lutz et al., 1996), starts from the observation that at equilibrium (4.26) can be interpreted as a method for computing the chemical potentials of each species as a weighted sum of *element potentials* which are equal to the Lagrange multipliers λ_j

$$\mu_k = \sum_{j=1}^{J} a_{jk} \lambda_j \ . \tag{4.57}$$

If the element potentials are known, then the molar concentrations of each species can be computed as

$$n_k = n \exp\left(-\mu_k^* + \sum_{j=1}^{J} a_{jk} \lambda_j\right) \tag{4.58}$$

where from (4.28) we have defined

$$\mu_k^* = \mu_k^\circ(T) + \mathcal{R}T \ln(P/P^\circ) \ . \tag{4.59}$$

The composition constraints (4.27) becomes

$$b_j = n \sum_{k=1}^{K} a_{jk} \exp\left(-\mu_k^* + \sum_{j=1}^{J} a_{jk} \lambda_j\right) , \tag{4.60}$$

and the computation (4.29) of n requires

$$1 = \sum_{k=1}^{K} \exp\left(-\mu_k^* + \sum_{j=1}^{J} a_{jk} \lambda_j\right) \ . \tag{4.61}$$

The solution method developed by Reynolds is to formulate an initial guess for the composition and element potentials, then to use the method of steepest descents followed by Newton-Raphson iteration to solve for the equilibrium values of the element potentials. His solution method treats a mixture of ideal gases and solid phases, treating the solid phases as incompressible and with negligible volume.

4.8 Equilibrium Constants

The equilibrium condition (4.37) leads to the following set of equations that must be satisfied at equilibrium

$$0 = \sum_{k=1}^{K} \mu_i \nu_{ki} \quad \text{for} \quad i = 1, 2, \dots, R \ . \tag{4.62}$$

As discussed above, the numbers ν_{ki} are the *stoichiometric coefficients* for the ith reaction coordinate. In terms of the stoichiometric coefficients corresponding a reaction coordinate i and suppressing the reaction coordinate index, the equilibrium condition can be written

$$0 = \sum_{k=1}^{K} \nu_k \left(\mu_k^{\circ}(T) + \mathcal{R}T \ln P_k \right) \tag{4.63}$$

and this can be simplified to separate the pressure and temperature dependence as follows

$$P_1^{\nu_1} P_2^{\nu_2} \ldots P_K^{\nu_K} \equiv \prod_{k=1}^{K} P_k^{\nu_k} = \exp\left(-\frac{\Delta G^{\circ}}{\mathcal{R}T} \right) \qquad \Delta G^{\circ} = \sum_{k=1}^{K} \nu_k \mu_k^{\circ}(T) \ . \tag{4.64}$$

The expression on the right hand side is known as the equilibrium constant and is a function only of temperature

$$K_p(T) = \exp\left(-\frac{\Delta G^{\circ}}{\mathcal{R}T} \right) \ . \tag{4.65}$$

In order to apply these equations to solve for the equilibrium composition, the J element conservation constraints still need to be employed in order compute the species mole fractions (and partial pressures $P_k = X_k P$) from the reaction coordinates.

$$X_k = \frac{n_k}{n} \tag{4.66}$$

$$n_k = n_k^{\circ} + \sum_{i=1}^{R} \nu_{ki} \xi_i \tag{4.67}$$

$$n = \sum_{k=1}^{K} n_k = \sum_{k=1}^{K} n_k^{\circ} + \sum_{k=1}^{K} \sum_{i=1}^{R} \nu_{ki} \xi_i \tag{4.68}$$

The idea of reaction coordinates applies equally to individual reactions or a set of reaction for which the stoichiometric coefficients are determined by balanced reaction equations. For a single reaction, the computation of equilibrium constants is particularly straighforward and is used to relate forward and reverse reaction rates as discussed in Section 10.

> Add an example using Cantera for a realistic equilibrium reaction such as water-gas shift, dissociation-recombination of diatomic and polyatomic species. Discuss van't Hoff equation and L'Chatelier's rule to equilibrium constants.

4.9   Partition Function Method

The statistical treatment of an ideal gas mixture is a straightforward extension of the statistical treatment of single molecules. The molecules are non-interacting so the system partition function for a mixture of K distinct molecules is simply the product of the molecular partition functions q_k for the N_k molecules of species k in the volume V

$$Q = \prod_{k=1}^{K} \frac{q_k^{N_k}}{N_k!} \ . \tag{4.69}$$

Using the definition of Helmholtz energy (3.1) and chemical potential (2.37) and applying Stirling's approximation $\ln N! \sim N \ln N - N$ we obtain

$$\mu_k = -k_b T \ln\left(\frac{q_k}{N_k} \right) \ . \tag{4.70}$$

For a single equilibrium relation, the equilibrium condition

$$\sum_k \nu_k \mu_k = 0 \,, \tag{4.71}$$

is equivalent to

$$\prod_k q_k^{v_k} = \prod_k N_k^{\nu_k} \tag{4.72}$$

Each molecular partition function has the form of the product of the translational function $q_t r$ and the internal function q_{int}. The translational functions all have the form

$$q_{tr,k} = V \left(\frac{2\pi m_k k_B T}{h^2} \right)^{3/2} \tag{4.73}$$

and the internal function $q_{int,k}$ depends on the specific molecular or atomic structure as discussed previously.

Example   A particularly simple case is the ionization of an atom, for example argon

$$\text{Ar} \; \rightleftarrows \; \text{Ar}^+ + \text{e}^- \tag{E1}$$

The dissociation and subsequent recombination of Ar behind strong shock waves has been extensively investigated and used as a light source in high explosive experimentation (Davis et al., 2006). If we disregard the electronic excitation states of Ar and Ar$^+$, the internal partition functions are $q_{int,Ar} = g_{Ar}$, q_{int,Ar^+} $= g_{Ar^+} \exp(-\varepsilon_I/k_B T)$, and $q_{int,e^-} = g_{e^-}$; where ε_I is the ionization energy, The conservation of charge implies that $N_{e^-} = N_{Ar^+}$ and expressing the concentrations in terms of partial pressures, the equilibrium relationship can be written as

$$\frac{P_{Ar^+} P_{e^-}}{P_{Ar}} = k_B T \left(\frac{2\pi m_e k_B T}{h^2} \right)^{3/2} \frac{g_{Ar^+} g_{e^-}}{g_{Ar}} \exp(-\varepsilon_I/k_B T) = K_p(T) \,, \tag{4.74}$$

where K_p is equilibrium constant for this reaction. Using the classical thermodynamic approach, this is equivalent to the equilibrium constant computed as

$$K_p = \exp\left(-\frac{\sum_i \nu_i \mu_i^\circ}{\mathcal{R}T} \right) \tag{4.75}$$

Alternatively, in terms of the fraction ϕ of ionized atoms and the total pressure P, the partition function solution is

$$\frac{\phi^2}{1 - \phi^2} = \frac{k_B T}{P} \left(\frac{2\pi m_e k_B T}{h^2} \right)^{3/2} \frac{g_{Ar^+} g_{e^-}}{g_{Ar}} \exp(-\varepsilon_I/k_B T) \,. \tag{4.76}$$

The numerical values for the degeneracy factors can be obtained by evaluating the symmetry of the electronic states $g_{Ar} = 1$, $g_{Ar^+} = 6$, $g_{e^-} = 2$. The ionization energy is 15.76 eV, equivalent to 182,879 K. These formulas are a specific case of the *Saha* relation for ionization equilibrium. Similar expressions can be derived for molecular reactions by using the appropriate internal partition functions and degeneracies, examples are given in McQuarrie (1976).

Chapter 5

Thermodynamic Property Representation

"Thermodynamics is useless without data or correlations intended to approximate data." - Van Ness and Abbott (1982)

This chapter describes how the ideal gas thermodynamic properties are represented as a function of temperature in the Cantera program and procedures for deriving polynomial fits from tabulated data.

For ideal gas mixtures, the thermodynamic properties are determined by the mixture composition and the molar properties of each species $(E, H, S, A, G)_i$. These properties can be derived from the molar specific heat $C_{P,i}(T)$ as a function of temperature, the enthalpy standard state value H_i° and the entropy standard state value S_i°. The mass specific properties are computed from the molar properties by dividing by the molar mass $\mathcal{W}_\rangle$. As discussed in the section on ideal gas thermodynamics, the construction of the thermodynamic properties can be accomplished by using the First Law of Thermodynamics and the definitions of the thermodynamic potentials. By basing all the properties on a minimal set of independent information, we ensure that the results are thermodynamically consistent.

The Cantera software allows several methods of specifying the thermodynamic properties. The most commonly used technique for high-temperature gases is a piecewise polynomial representation for the specific heat at constant pressure supplemented by values of enthalpy and entropy at the reference condition. The most common form of the polynomials are a pair of 4th-order polynomials that cover two temperature ranges. In non-dimensional form, the molar specific heat at constant pressure is represented by

$$\frac{C_P}{\mathcal{R}} = \begin{cases} \sum_{n=0}^{4} a_n T^n & T_{min} \leq T \leq T_{mid} \\ \\ \sum_{n=0}^{4} b_n T^n & T_{mid} \leq T \leq T_{max} \end{cases} \tag{5.1}$$

for each species. The constants a_n and b_n have to be determined by fitting the polynomial representation to tabular data that is either determined by experiment or computed from statistical mechanics. The values of the coefficients also have to be adjusted so that the specific heat is continuous at the midpoint temperature T_{mid}.

This polynomial representation of the specific heat dependence on temperature and the method used to derive the other properties was widely used in developing the database used with the NASA chemical equilibrium computer program (Gordon and McBride, 1976, McBride et al., 1993, Gordon and McBride, 1994, McBride and Gordon, 1996) and subsequently in the CHEMKIN software Kee et al. (1980, 1987) and adopted by many other researchers (e.g., the Burcat database at DLR) for representing ideal gas thermodynamic properties. For this reason, these are usually known as NASA-style polynomial representations of thermodynamic data. There are two versions, the original version (5.1) requires 7-coefficients per temperature interval and only allow 2 two intervals to cover the range from 200 or 300 to 5000-6000 K. A more flexible version was developed McBride et al. (2002) by NASA to enable fitting over a wider temperature range. This version is known as the NASA-9 format and uses 9 coefficients, 7 for the polynomial representation of specific heat and two for the reference data.

$$\frac{C_P}{\mathcal{R}} = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \tag{5.2}$$

The inclusion of negative exponents in the polynomial enables a higher quality of fit in some cases. For the 9-coefficient fits, any number of temperature ranges are allowed although usually three are sufficient to cover the range from 200 to 20000 K.

The ideal gas enthalpy can be found by integrating the specific heat since $\mathrm{d}\,H = C_P\,\mathrm{d}T$ for an ideal gas.

$$H(T) = \int_{T^\circ}^{T} C_P(T')\,\mathrm{d}T' + \Delta_f H^\circ \tag{5.3}$$

where the constant of integration is the heat of formation $\Delta_f H^\circ$ at the standard thermochemical state of $T^\circ = 298.15$ K, $P^\circ = 1$ bar (one atm in older data sets) for the ith species. Inserting the functional form of (5.1) and integrating the polynomial term-by-term, the nondimensional enthalpy is

$$\frac{H}{\mathcal{R}T} = \begin{cases} \sum_{n=0}^{4} \dfrac{a_n T^n}{n+1} + \dfrac{a_5}{T} & T_{min} \leq T \leq T_{mid} \\[3mm] \sum_{n=0}^{4} \dfrac{b_n T^n}{n+1} + \dfrac{b_5}{T} & T_{mid} \leq T \leq T_{max} \end{cases} \tag{5.4}$$

The constant a_{i5} is determined by evaluating the enthalpy at the standard state to obtain

$$\Delta_f H^\circ = H(T^\circ) \tag{5.5}$$

so that

$$a_5 = \frac{\Delta_f H^\circ}{\mathcal{R}} - \sum_{n=0}^{4} \frac{a_n}{n+1} (T^\circ)^{n+1} \tag{5.6}$$

The constant b_5 is determined by requiring continuity of the two representations at the midpoint temperature.

The entropy can be determined by using the fundamental relation of thermodynamics

$$\mathrm{d}H = T\,\mathrm{d}S - V\,\mathrm{d}P \tag{5.7}$$

This be written for an ideal gas as

$$\mathrm{d}S = \frac{C_P\,\mathrm{d}T}{T} - \mathcal{R}\frac{\mathrm{d}P}{P} \tag{5.8}$$

For a single species in a gas mixture, the pressure is interpreted as the partial pressure of that species $P_i = X_i P$, and the entropy differential is integrated to obtain

$$S(T, P_i) = S^\circ(T) - \mathcal{R}\ln\left(\frac{P_i}{P^\circ}\right) \tag{5.9}$$

The pressure-independent portion of the entropy is

$$S^\circ = \int_{T^\circ}^{T} \frac{C_P(T')}{T'}\,\mathrm{d}T' + S^\circ(T^\circ) \tag{5.10}$$

Using the polynomial representation of the specific heats and integrating term by term, we have

$$\frac{S^\circ}{\mathcal{R}} = \begin{cases} a_0 \ln(T) + \sum_{n=1}^{4} \dfrac{a_n T^n}{n} + a_6 & T_{min} \leq T \leq T_{mid} \\[3mm] b_0 \ln(T) + \sum_{n=1}^{4} \dfrac{b_n T^n}{n} + b_6 & T_{mid} \leq T \leq T_{max} \end{cases} \tag{5.11}$$

where a_6 is determined from the species entropy evaluated at the standard state.

$$S(T^\circ, P^\circ) = S^\circ(T^\circ) \tag{5.12}$$

$$a_6 = \frac{S^\circ(T^\circ)}{\mathcal{R}} - \left(a_0 \ln(T^\circ) + \sum_{n=1}^{4} \frac{a_n(T^\circ)^n}{n} \right) \tag{5.13}$$

The constant b_6 is determined by requiring continuity at the midpoint temperature. The preceding results illustrate the procedure for using the NASA-7 fits, the procedure for the NASA-9 fits is analogous.

Using the definitions of the thermodynamic potentials, all other properties and potentials can be found. Specific heat at constant volume:

$$C_V = C_P - \mathcal{R} \tag{5.14}$$

Internal energy:

$$E = H - \mathcal{R}T \tag{5.15}$$

Gibbs energy:

$$G = H - TS \tag{5.16}$$

Helmholtz energy:

$$A = E - TS \tag{5.17}$$

5.1 Specification for Cantera input

The thermodynamic properties $C_P/\mathcal{R}$, $H/\mathcal{R}T$, and $S/\mathcal{R}$ for each species are specified in the Cantera mechanism (`.cti` file). For each species in the `.cti` file that uses the NASA-style polynomials, Cantera requires 14 coefficients and three temperatures (T_{min}, T_{mid}, T_{max}). The NASA-7 format of the data in the Cantera `.cti` file is

$$\begin{aligned} \text{thermo} \ = \ &(\, \text{NASA}(\, [T_{min}, \ T_{mid}], \ [a_0, \ a_1, \ a_2, \ a_3, \ a_4, \ a_5, \ a_6]), \\ &\ \ \text{NASA}(\, [T_{mid}, \ T_{max}], \ [b_0, \ b_1, \ b_2, \ b_3, \ b_{4i}, \ b_5, \ b_6]) \,) \end{aligned}$$

As an example, a set of NASA-7 coefficients for $CH_3CHCHCHO$ (2-Butenal) is shown in Figure 5.1. The

```
species( name = "CH3CHCHCHO",
    atoms = " C:4  H:6  O:1 ",
    thermo = (
       NASA( [  200.00,  2500.00], [ -2.696365560E-01,   4.341252850E-02,
               -3.073846170E-05,   1.115698570E-08,  -1.581997240E-12,
               -1.483378370E+04,   2.817336550E+01] ),
       NASA( [ 2500.00,  5000.00], [  8.318851910E+01,  -6.599805600E-02,
                2.896794850E-05,  -5.456349720E-09,   3.760599270E-13,
               -6.854568290E+04,  -4.704570180E+02] )
             ),
    note = "CIT/08" )
```

Figure 5.1: Example usage of NASA-7 thermodynamic coefficients with Cantera for 2-Butenal.

coefficients given in this example were obtained by performing a least-squares fit to tabulated data generated

by evaluating at fixed temperature intervals the statistical mechanical functions with inputs from a semi-empirical model of the molecular structure. The methodology behind the computation and fitting is described in the subsequent sections.

The NASA-9 format is similar to NASA-7 with two additional coefficients per temperature range and multiple ranges. The coefficients $a_7, b_7, \ldots$ are used for the enthalpy expression and $a_8, b_8, \ldots$ are for the entropy expression. These are determined as in the NASA-7 cases by using a combination of standard state values and enforcing continuity at the common boundaries of the temperature ranges.

$$
\begin{aligned}
\text{thermo} = (\, &\text{NASA9}(\,[T_1,\ T_2], \\
&\quad [a_0,\ a_1,\ a_2, \\
&\quad\ \ a_3,\ a_4,\ a_5, \\
&\quad\ \ a_6,\ a_7,\ a_8]), \\
&\text{NASA9}(\,[T_2,\ T_3], \\
&\quad [b_0,\ b_1,\ b_2, \\
&\quad\ \ b_3,\ b_{4i},\ b_5, \\
&\quad\ \ b_6,\ b_7,\ b_8]), \\
&\ldots
\end{aligned}
$$

As an example, a set of NASA-9 coefficients for O_2 is shown in Figure 5.2. These coefficients were obtained

```
thermo=(NASA9([200.00, 1000.00],
              [-3.425563420E+04,  4.847000970E+02,  1.119010961E+00,
                4.293889240E-03, -6.836300520E-07, -2.023372700E-09,
                1.039040018E-12, -3.391454870E+03,  1.849699470E+01]),
        NASA9([1000.00, 6000.00],
              [-1.037939022E+06,  2.344830282E+03,  1.819732036E+00,
                1.267847582E-03, -2.188067988E-07,  2.053719572E-11,
               -8.193467050E-16, -1.689010929E+04,  1.738716506E+01]),
        NASA9([6000.00, 20000.00],
              [ 4.975294300E+08, -2.866106874E+05,  6.690352250E+01,
               -6.169959020E-03,  3.016396027E-07, -7.421416600E-12,
                7.278175770E-17,  2.293554027E+06, -5.530621610E+02]))
```

Figure 5.2: Example usage of NASA-9 thermodynamic coefficients with Cantera for O_2.

from the compilation in McBride et al. (2002) and find use in computing high temperature equilibrium for high-speed flow, planetary re-entry, shock tube and shock tunnel applications.

In the reaction mechanisms distributed with the Toolbox, most species have NASA-7 fits with typical values of $T_{min} = 200$ K, $T_{mid} = 1000$ K, and $T_{max} = 5000$ to 6000 K. This temperature range is necessary for many shock and detonation problems, particularly in high-enthalpy flow. One of the motivations behind the present section is the need to create data sets that extend to the higher temperatures that occur in typical shock and detonation problems. There are two NASA-9 data sets provided as part of the SDT website, airNASA9noions.cti which includes all species for high-temperature air except ions and airNASA9ions.cti which includes the ions.

Cantera 2.5 YAML Format

The new standard format for input files introduced for Cantera 2.5 is based on the YAML syntax. Files based on the Chemkin legacy format or .cti format can be converted using the Cantera supplied utilities described in https://cantera.org/tutorials/legacy2yaml.html. The YAML format is more flexible than the .cti file format but input data for the NASA7 or NASA9 polynomials is identical to that used in the legacy formats. For example, the NASA7 thermo data for the $CH_3CHCHCHO$ (2-Butenal) example is represented as

```
species:
- name: CH3CHCHCHO
  composition: {C: 4, H: 6, O: 1}
  thermo:
    model: NASA7
    temperature-ranges: [200.0, 1000.0, 5000.0]
    data:
    - [4.81128032, 5.04043764e-03, 4.54497545e-05, -5.04331802e-08, 1.6700052e-11,
      1.12352054e+04, 9.54134078]
    - [1.11829874, 0.0317936187, -1.38771283e-05, 2.7330487e-09, -1.99493623e-13,
      1.14155759e+04, 24.4646241]
  note: Fit by JES 14-Jul-2018 12:06:24
```

The NASA9 thermo data for the O_2 (2-Butenal) example is represented as

```
species:
- name: O2
  composition: {O: 2}
  thermo:
    model: NASA9
    temperature-ranges: [200.0, 1000.0, 6000.0, 2.0e+04]
    data:
    - [-3.42556342e+04, 484.700097, 1.119010961, 4.29388924e-03, -6.83630052e-07,
      -2.0233727e-09, 1.039040018e-12, -3391.45487, 18.4969947]
    - [-1.037939022e+06, 2344.830282, 1.819732036, 1.267847582e-03, -2.188067988e-07,
      2.053719572e-11, -8.19346705e-16, -1.689010929e+04, 17.38716506]
    - [4.9752943e+08, -2.866106874e+05, 66.9035225, -6.16995902e-03, 3.016396027e-07,
      -7.4214166e-12, 7.27817577e-17, 2.293554027e+06, -553.062161]
  note: Ref-Elm. Gurvich,1989 pt1 p94 pt2 p9. [tpis89]
```

5.2   Resources for Thermodynamic Data

The thermodynamic parameters for each species are specified in the Cantera mechanism file and based on the NASA format (McBride and Gordon, 1992, McBride et al., 1993, 2002). Compilations of this data have been made for many species through the JANAF-NIST project (Chase et al., 1998) and are available online as PDF file. Coefficients of fits are available from NASA, NIST, BURCAT[1], enthalpies of formation for many species relevant to combustion are available at ANL. Cantera provides a utility (ck2cti.py) to convert legacy data sets to its .cti file format. The original NASA format only used two temperature ranges for the polynomial fits and seven coefficients for each temperature range. The newer versions of the NASA polynomials use a larger number of terms (there are 9 coefficients per temperature interval instead of 7) and multiple temperature ranges. Cantera 2.3 and 2.4 can support both specifications.

The SDToolbox thermodynamic resource webpage has links to sources of data, documentation on computation of polynomial coefficients, multiple versions of the NASA databases and programs for checking, fitting, and updating databases of polynomial fits. The following programs are provided on the SDToolbox website.

thermo_check.py This Python script scans a Cantera .cti mechanism file to determine the size of jumps in thermodynamic properties and derivatives. Identifies species with largest Cp/R jump. Provides routines for finding all jumps and plotting thermodynamic properties of individual species. Only works for NASA-7 polynomials with the current version of Cantera 2.3 and 2.4

thermo_refit.m Refits thermodynamic data to eliminate jumps in properties at midpoint temperature. Works with a list of species created by thermo_check.py or individual species specified by user. Creates

---

[1]This database is now maintained by Dr. Elke Goos of the DLR Stuttgart

a new NASA-7 fit and data structure for polynomial coefficients, writes output files in three formats (cti, NASA-7 and NASA-9).

thermo_replace.m Reads new thermodynamic data fits generated by thermo_refit.m and batch processes replaces the data in the NASA format data file using the list generated by check_thermo.py. Currently only works for NASA-7 polynomials.

thermo_fit.m fit tabular thermodynamic data to generate NASA-7 polynomial fits and writes files in three formats. An example input file is provided for **2-butenal**

The .cti files provided on the SDToolbox reaction mechanism webpage were all checked and in some cases, selected species were refit to eliminate midpoint temperature discontinuities.

5.3   Least Squares Fit for Piecewise Thermodynamic Representation

Using the partition function definitions of thermodynamic properties, (3.71)-(3.73), we can calculate the specific heat, the enthalpy, and the pressure-independent portion of the entropy as functions of temperature. Since a large number of transcendental functions and sums have to be computed for each temperature, it is computationally expensive to evaluate the partition functions and derivatives each time a thermodynamic property is needed in a numerical computation. To circumvent this, the thermodynamic properties are evaluated ahead of time at fixed temperature increments over the range of interest and fit to an approximating polynomial that is computationally inexpensive to evaluate. For example, the tables in the JANAF compilation are generated directly from evaluating the partition function expressions and the NASA polynomial coefficients are obtained by fitting these data. In order to obtain reasonable fits of polynomials to specific heats over a wide temperature range, the temperature range is divided into segments and data on each segment fit separately. The method developed by NASA in the 1960s, which is still widely used today, is to divide the temperature range into two segments that share a common mid-point temperature T_{mid}.

Of the many ways of computing the polynomial fit coefficients, the most suitable method is to simultaneously optimize the fit to all three properties in the least-squares sense with the additional constraints of continuity at the matching temperature, T_{mid}. Other constraints, such as continuity of derivatives and high and low temperature limit boundary conditions, can also be considered. A common past practice has been to evaluate the properties from the partition function expressions at at 100 K intervals from 200 K to 3000-6000 K and match the two temperature ranges at 1000 K.

An example of the statistical thermodynamic data and the fit for c_P/R with $T_{min} = 200$ K, $T_{mid} = 2500$ K, and $T_{max} = 5000$ K is shown in Figure 5.3. This figure was constructed using the coefficients from the 2-Butenal ($CH_3CHCHCHO$) example shown in Figure 5.1. The piecewise function was fitted using a constrained least-squares method in MATLAB. All three piecewise functions for the non-dimensional properties, $c_{Pi}(T)/R$, $h_i(T)/RT$, and $s_i^\circ(T)/R$, were simultaneously optimized and constrained for the best overall fit. The constraints include continuity for $h_i(T)/RT$ and $s_i^\circ(T)/R$ and continuity for both $c_{Pi}(T)/R$ and its derivatives. Also, the boundary point constraints for $c_{Pi}(T)/R$ and $h_i(T)/RT$ are included. There are a number of different possible combinations of constraints; however, care must be taken not to over-constrain the system of equations to be optimized.

The constrained optimization problem for a piecewise fit is formulated in matrix form with two non-square systems of equations, one for the least squares minimization

$$Ax = b \tag{5.18}$$

and one for the constraint equations

$$A_{eq}x = b_{eq} \tag{5.19}$$

where x is the 14×1 vector of coefficients

$$x = [a_{0i}, a_{1i}, ..., a_{6i}, b_{0i}, b_{1i}, ..., b_{6i}]^T \tag{5.20}$$

with $[.]^T$ representing the transpose. After constructing the matrices A, A_{eq} b, and b_{eq}, MATLAB's *lsqlin()*, iterative constrained least-squares optimization function is used to find the best fit for the coefficient vector
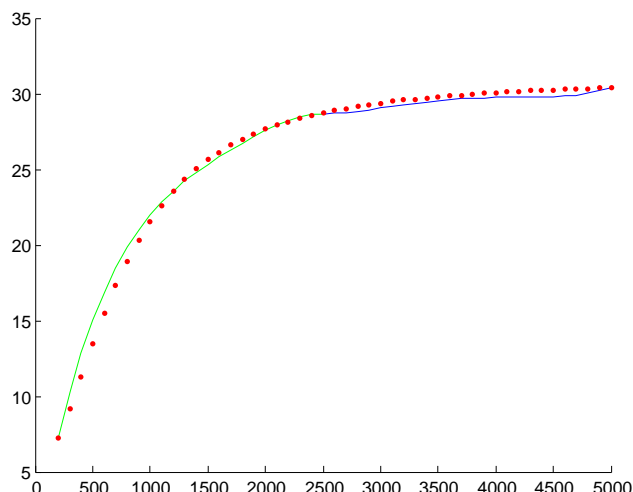
Figure 5.3: Comparison of c_P/R for 2-Butenal ($CH_3CHCHCHO$) calculated from the statistical mechanics representation (points) to the piecewise polynomial fit (solid lines).

x. The constraints are handled by the method of Lagrange multipliers and the solution is iterated until user-specified convergence criterion are met.

The general form of the linear least-squares problem without constraints can be written as the matrix equation

$$Ax = b \tag{5.21}$$

where A is dimension $m \times n$, x is dimension $n \times 1$, and b is dimension $m \times 1$. The dimension m depends on the number of temperature intervals that are used to evaluate the partition function expressions. The standard solution method is to construct a square ($n \times m$) linear system by augmenting the matrix A and using a standard numerical linear algebra routine to find the unknown vector x.

$$(A^T A)x = (A^T b) \tag{5.22}$$

However, for the constrained problem, additional steps are required, which MATLAB conveniently handles through the function `lsqlin()`.

The user-defined input for the fitting program includes the temperature ranges, the standard state enthalpy of formation and standard state entropy, the species name, and the species molecular composition.

The program is only available as a MATLAB script thermo_fit.m, which uses a routine poly_cp.m to carry out the constrained optimization to fit the specific heat polynomial coefficients (NASA-7 form only). Input for the program is tabular thermodynamic data[2] and molecular constants in a MATLAB script. The thermodynamic input data for the example molecule 2-Butenal is in the script twobutenal.m. The output from the program fitting program includes the coefficients a_{ni} and b_{ni}, optimization diagnostics, and goodness of fit measures. The output files for the example are CH3CHCHCHO_NASA7.dat and CH3CHCHCHO_NASA9.dat, in the NASA formats and CH3CHCHCHO.cti in the Cantera .cti file format.

All of these files can be found at the Shock and Detonation Toolbox website. By independently obtaining thermodynamic data from tables, molecular modeling and statistical mechanics software such as LINGRAF, one may easily adapt this MATLAB program for constructing fits for any desired species.

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[2]We thank Siddharth Dasgupta of Caltech for computing this data using the Lingraf program developed by the Goddard group.
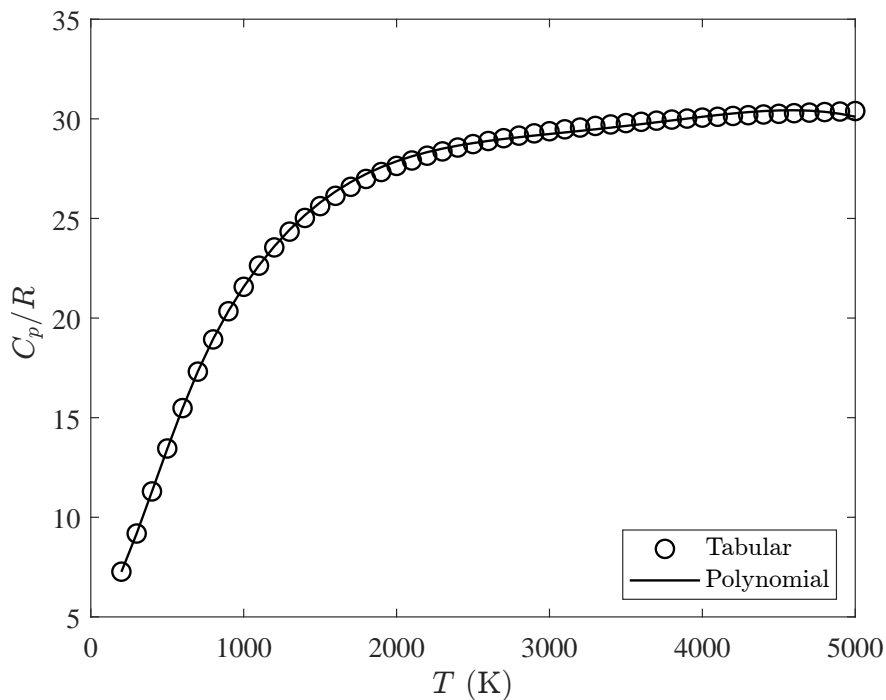
Figure 5.4: Comparision of tabulated and polynomial fit to reduced heat capacity C_p/R for 2-butenal (CH3CHCHCHO).
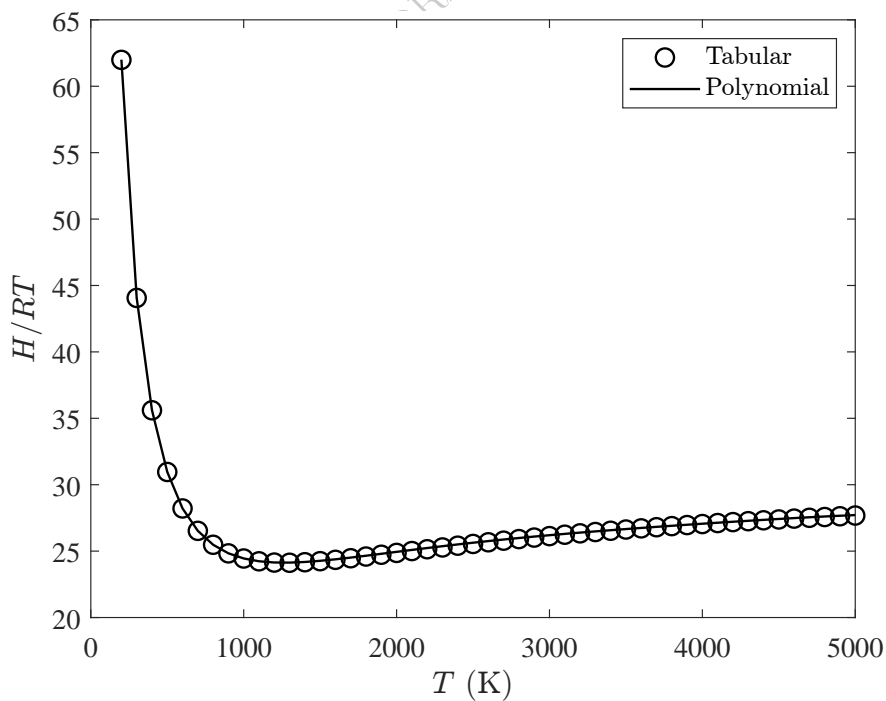

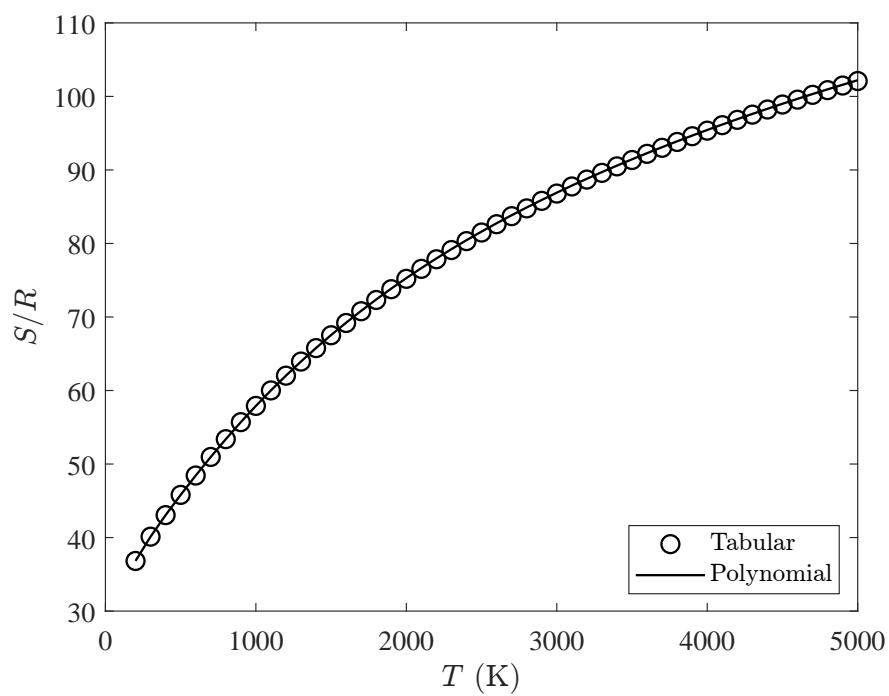Figure 5.5: Comparision of tabulated and polynomial fit to reduced enthalpy H/RT for 2-butenal (CH3CHCHCHO).

Figure 5.6: Comparision of tabulated and polynomial fit to reduced entropy S/R for 2-butenal (CH3CHCHCHO).

Part II

Equilibrium and Frozen Flows

This part of these notes describes numerical methods and applications for flows that can be treated using the approximation of either complete chemical equilibrium or fixed (frozen) chemical composition. These are situations that can be modeled using mass, momentum and energy conservation without considering chemical kinetics or transfer of energy between molecular and translation motions. The methods can be used to model shock waves and detonation waves as jumps or discontinuities. Expansion waves can be modeled when the flow either remains in chemical equilibrium through shifting composition or else the composition remains fixed. These basic wave processes can be combined to create approximate but very useful models for many applications such as shock tubes, shock tunnels, propulsion systems based on detonation waves, rocket motors, and various wave configurations that can be analyzed using either steady flows or simple wave matching methods.

Chapter 6

Jump Conditions

We present a brief summary of the shock jump conditions and the standard formulation of the graphical solutions. As discussed in classical texts on gas dynamics, Courant and Friedrichs (1948), Shapiro (1953), Liepmann and Roshko (1957), Becker (1968), Thompson (1972), Zel'dovich and Raizer (1966), an ideal shock or detonation wave has no volume and locally can be considered a planar wave if we ignore the structure of the reaction zone.

6.1 Introduction

A wave propagating with speed U into gas at state 1 moving with velocity u_1 is shown in Fig. 6.1a. This can be transformed into a stationary wave with upstream flow speed w_1 and downstream flow speed w_2, Fig. 6.1b.

$$w_1 = U_s - u_1 \tag{6.1}$$

$$w_2 = U_s - u_2 \tag{6.2}$$

Using a control volume surrounding the wave and any reaction region that we would like to include in our
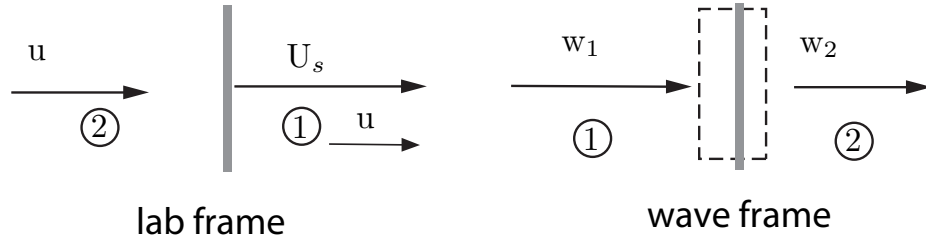

Figure 6.1: Cartoon depiction of the transformation from the laboratory to the wave fixed reference frame.

computation, the integral versions of the conservation relations can be used to derive the jump conditions relating properties at the upstream and downstream ends of the control volume. The simplest way to carry out this computation is in a *wave-fixed* coordinate system considering only the velocity components normal to the wave front. The resulting relationships are the conservation of mass

$$\rho_1 w_1 = \rho_2 w_2 \, , \tag{6.3}$$

momentum

$$P_1 + \rho_1 w_1^2 = P_2 + \rho_2 w_2^2 \, , \tag{6.4}$$

and energy

$$h_1 + \frac{\text{w}_1^2}{2} = h_2 + \frac{\text{w}_2^2}{2} \ . \tag{6.5}$$

These equations apply equally to moving and stationary waves as well as to oblique waves as long as the appropriate transformations are made to the wave-fixed coordinate system. In addition to the conservation equations (6.3-6.5), an entropy condition must also be satisfied.

$$s_2 \geq s_1 \tag{6.6}$$

For reacting flows in ideal gases, the entropy condition is usually automatically satisfied and no additional constraint on the solution of (6.3-6.5) is imposed by this requirement. Considerations about entropy variation as a function of wave speed do enter into the analysis of detonation waves and these are discussed in the subsequent section on detonation analysis.

In general, an equation of state in the form $h = h(P, \rho)$ is required in order to complete the equation set. We will consider the specific case of an ideal gas. The equation of state for this case is given by combining the usual $P(\rho, T)$ relationship with a representation of the enthalpy. The usual $P(\rho, T)$ relationship is

$$P = \rho R T \tag{6.7}$$

where the gas constant is

$$R = \frac{\mathcal{R}}{\mathcal{W}} \tag{6.8}$$

and the average molar mass is

$$\mathcal{W} = \left(\sum_{i=1}^{K} \frac{Y_i}{\mathcal{W}_i} \right)^{-1} \tag{6.9}$$

with the gas compositions specified by the mass fractions Y_i. The enthalpy of an ideal gas can be expressed as

$$h = \sum_{i=1}^{K} Y_i h_i(T) \tag{6.10}$$

The enthalpy of each species can be expressed as

$$h_i = \Delta_f h_i + \int_{T^\circ}^{T} c_{P,i}(T') \, dT' \tag{6.11}$$

where $\Delta_f h_i$ is the heat of formation, $c_{p,i}$ is the specific heat capacity, and T° is a reference temperature, usually taken to be 298.15 K. The thermodynamic parameters for each species are specified in the Cantera data input file. The methodology and software for the generation of thermodynamic data and polynomial fits is described in detail in Section 5.

Formulation of Jump Conditions in Terms of Density Ratio

An alternate way to look at the jump conditions is to write them as a set of equations for pressure and enthalpy at state 2 in terms of the density ratio ρ_2/ρ_1 and the normal shock speed w_1

$$P_2 = P_1 + \rho_1 \text{w}_1^2 \left(1 - \frac{\rho_1}{\rho_2} \right) \tag{6.12}$$

$$h_2 = h_1 + \frac{1}{2} \text{w}_1^2 \left[1 - \left(\frac{\rho_1}{\rho_2} \right)^2 \right] \tag{6.13}$$

The equation of state $h(P, T)$ (6.10) provides another expression for h_2. This naturally leads to the idea of using functional iteration or implicit solution methods to solve for the downstream state 2. A method based on solving these equations for a given value of w_1 and state 1 is discussed in Section 8.1.

6.2 Chemical Composition

In order to completely determine the state of the gas and solve the jump conditions, we need to know the composition of the gas $(Y_1, Y_2, \ldots, Y_k)$. In the context of jump condition analysis, we only consider two possible cases, either a nonreactive shock wave or complete reaction to an equilibrium state. (The more general problem of finite rate chemical reaction rates and reaction zone structure is considered in Section 9.) Although this assumption may seem quite restrictive, these two cases are actually very useful in analyzing many situations. Frozen composition is usually presumed to correspond to the conditions just behind any shock front prior to chemical reaction taking place. Equilibrium composition is usually presumed to occur if the reactions are fast and the reaction zone is thin in comparison with the other lengths of interest in the problem.

   The two possibilities for the downstream state 2 are:

1. Nonreactive or frozen composition

$$Y_{2i} = Y_{1i}$$

   The frozen composition case assumes that the composition does not change across the shock, which is appropriate for nonreactive flows (moderately strong shocks in inert gases or gas mixtures like air) or the conditions just downstream of a shock that is followed by a reaction zone. In this case, from the equation for enthalpy (6.10), the state 2 enthalpy will just be a function of temperature

$$h_2 = h(T_2) = \sum_{i=1}^{K} Y_{1i} h_i(T_2) \tag{6.14}$$

2. Completely reacted, equilibrium composition.

$$Y_{2i} = Y_i^{eq}(P, T)$$

   The case of a completely reacted state 2, the equilibrium mixture is used to treat ideal detonation waves or other reactive waves like bow shocks on re-entry vehicles. In order to determine the equilibrium composition, an iterative technique must be used to solve the system of equations that define chemical equilibrium of a multi-component system. In the present software package, we use the algorithms built into Cantera to determine the equilibrium composition. In this case, the state 2 enthalpy will be a function of both temperature and pressure

$$h_2 = h(T_2, P_2) = \sum_{i=1}^{K} Y_{2i}^{eq}(P_2, T_2) h_i(T_2) \tag{6.15}$$

6.3 Rayleigh Line and Hugoniot

The jump conditions are often transformed so that they can be represented in P-v thermodynamic coordinates. The *Rayleigh line* is a consequence of combining the mass and momentum conservation relations

$$P_2 = P_1 - \rho_1^2 w_1^2 (v_2 - v_1) \tag{6.16}$$

The slope of the Rayleigh line is

$$\frac{P_2 - P_1}{v_2 - v_1} = \frac{\Delta P}{\Delta v} = -\left(\frac{w_1}{v_1}\right)^2 = -\left(\frac{w_2}{v_2}\right)^2 \tag{6.17}$$

where $v = 1/\rho$ and $\Delta P = P_2 - P_1$, etc. The slope of the Rayleigh line is proportional to the square of the shock velocity w_1 for a fixed upstream state 1. The Rayleigh line must pass through both the initial state 1 and final state 2.