number. If the spectroscopic constants are sufficiently reliable then this requirement limits values of n by the following inequalities

$$G(n+1) - G(n) > 0 \quad \text{for} \quad n < n_{max} \,, \tag{3.43}$$

and the limiting value of J is determined by

$$F_n(J+1) - F_n(J) > 0 \quad \text{for} \quad J < J_{max}(n) \,. \tag{3.44}$$

For conventional two-term expansions of the vibrational and rotational constants and neglecting the centrifugal distortion, these inequalities provide the following bounds, interpreting the right-hand side as the greatest integer

$$n_{max} = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} \,, \tag{3.45}$$

$$n'_{max} = \frac{B_e}{\alpha_e} - \frac{1}{2} \,. \tag{3.46}$$

The limit (3.41) usually results in the smallest values of n_{max} and J_{max}.

Considering the effect of rotation on the effective intramolecular potential energy curve Khachkuruzov (1966, 1967, 1971) provides a more sophisticated approach to determining upper bounds on the rotational quantum number for diatomic molecules. The approach is to consider the effect of molecular rotation to construct an effective potential energy function that includes the energy associated with rotational state J. The effective potential is a function of both the relative distance R and J

$$V_J(R) = V_o(r) + \frac{\hbar^2}{2\mu} \frac{J(J+1)}{r^2} \tag{3.47}$$

where V_o is the potential energy function for the non-rotating molecule. The key idea is that as J increases, the potential well depth becomes smaller and ultimately disappears as shown in Fig. 3.1. The highest possible value of J for a stable molecule is obtained when the effective potential well is just deep enough to accommodate a single vibrational state $n = 0$, the ground state. If the energy of this ground state is small compared to the well depth of the nonrotating molecule potential, then we can approximate $J_{max}(0)$ by J_{lim}, the value of J for which the effective potential has an inflection point at r_o. This requires solving the two simultaneous equations

$$\left. \frac{\mathrm{d}V_{J_{lim}}}{\mathrm{d}r} \right|_{r_o} = 0 \,, \tag{3.48}$$

$$\left. \frac{\mathrm{d}^2 V_{J_{lim}}}{\mathrm{d}r^2} \right|_{r_o} = 0 \,. \tag{3.49}$$

The result can be simplified by introducing the reduced distance $R = r/r_e$, measuring energies in terms of spectroscopic values (cm^{-1}) and using the definition of the rotational constant (3.10). The value of $R_o = r_o/r_e$ is found from the solution of the nonlinear equation

$$R_o V_o''(R_o) + 3V_o'(R_o) = 0 \,. \tag{3.50}$$

The value of the limiting rotational quantum number can then be computed as (assuming $J_{lim} \gg 1$) from (3.49)

$$J_{lim} \approx R_o^2 \sqrt{\frac{V_o''(R_0)}{6B_e}} \tag{3.51}$$

To proceed further, a representative form for the non-rotating potential has to be selected. A simple and widely used model is the *Morse* potential

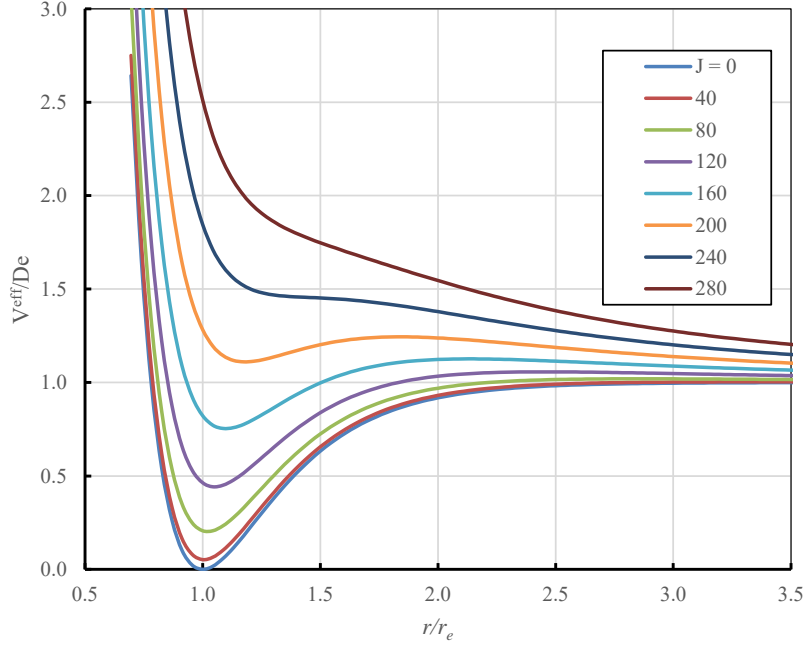$$V_o(R) = D^e \left[1 - \exp(-a(R-1)) \right]^2 \tag{3.52}$$

Figure 3.1: Effective potential energy as a function of radial distance r and rotational quantum number J. This example uses the Morse potential and parameters of the NO ground state.

where the parameter a can be determined from the spectroscopic constants

$$a = \frac{\omega_e}{2\sqrt{B_e D_e}} \tag{3.53}$$

The details of computation of J_{lim} with this potential are discussed by Khachkuruzov (1967), Khachkuruzov claims that for each electronic state, the maximum rotational quantum number is approximately a linear function of the vibrational quantum number

$$J_{max}(n) = J_{max}(0)\left(1 - \frac{n}{n_{max}}\right) . \tag{3.54}$$

Using the ground state NO spectroscopic data to calibrate the Morse potential, we compute $R_o = 1.435$ from (3.50), $J_{lim} = 234$ from (3.51) and direct computation of the stationary energy eigenstates of the effective potential (3.47) using numerical solution of the Schrödinger equation yields $J_{max}(0) = 178$, the spectroscopic condition (3.41) also give $J_{max}(0) = 178$. For $J = 0$, the maximum number of vibrational levels possible is $n_{max} = 39$ from the spectroscopic condition (3.42), 67 by (3.45), and 52 from numerical solution of the Schrödinger equation for the Morse potential.

3.3 Thermodynamic Properties from Partition Functions

The internal energy, E relative to that of the ground state E_0, can be calculated for a system of N molecules by summing over all states and weighting the energy of each state by the expected number of molecules in that state.

$$E - E_0 = \sum_j N_j \epsilon_j \tag{3.55}$$

N_j is the number of molecules in state j with an energy of ϵ_j relative to the ground state. This equation can be expressed in terms of the molecular partition function by using the *Boltzmann distribution* to define the expected fraction of the molecules in that state for a system that is in thermodynamic equilibrium

$$\frac{N_i}{N} = \frac{\exp\left(-\dfrac{\epsilon_i}{k_B T}\right)}{\sum_k \exp\left(-\dfrac{\epsilon_k}{k_B T}\right)} \tag{3.56}$$

Substituting this into (3.55), we can write the internal energy in terms of the molecular partition function as

$$E - E_0 = N k_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V \tag{3.57}$$

Since $q(T, V)$, the number of molecules N does not enter in to the computation of the partial derivative.

The enthalpy, specific heats, and entropy can be computed using thermodynamic relationships and the relationship (3.1). To express the results in terms of the molecular partition function we will first observe that for a large number of molecules, Stirlings' approximation for the factorial can be used to simply the expressions.

$$\lim_{N\to\infty} \ln N! \approx N \ln N - N \tag{3.58}$$

The Helmholtz energy can be approximated as

$$A - A_0 = N k_B T \left(\ln q - \ln N + 1\right) \tag{3.59}$$

The fundamental relation of thermodynamics for a fixed number of molecules can be written

$$dA = -SdT - PdV \tag{3.60}$$

which leads directly to the following expressions

$$S = -\left(\frac{\partial A}{\partial T}\right)_V \tag{3.61}$$

$$= N k_B \left[\left(\frac{\partial(T \ln q)}{\partial T}\right)_V - \ln N + 1\right] \tag{3.62}$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \tag{3.63}$$

$$= N k_B T \left(\frac{\partial \ln q}{\partial V}\right)_T \tag{3.64}$$

Enthalpy is defined as

$$H = E + PV \tag{3.65}$$

$$= A - TS + PV \tag{3.66}$$

and for ideal gases

$$PV = N k_B T \tag{3.67}$$

so that

$$H - H_0 = N k_B T \left[T \left(\frac{\partial \ln q}{\partial T}\right)_V + 1\right] \tag{3.68}$$

The definition for specific heat at constant pressure is

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \tag{3.69}$$

$$= N k_B \left[T \left(\frac{\partial^2}{\partial T^2} (T \ln q) \right)_V + 1 \right] \tag{3.70}$$

We can further simplify the result by using the splitting of the molecular partition function into translation and internal modes (3.7) and use (3.8) to compute the contribution of translation explicitly. The contribution of translation states to the thermodynamic function is equivalent to the thermodynamic properties of a monoatomic gas. The final results for the nondimensional temperature-dependent properties are found by considering one mole of substance ($N = N_A$) and expressing the properties in the same nondimensional form as used in the NASA polynomial representations:

$$\frac{c_P(T)}{R} = \frac{5}{2} + T \frac{d^2 (T \ln q_i)}{dT^2} , \tag{3.71}$$

$$\frac{h(T) - h_0}{RT} = \frac{5}{2} + T \frac{d(\ln q_i)}{dT} , \tag{3.72}$$

$$\frac{s(T)}{R} = \frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) + \frac{5}{2} \ln(k_B T) - \ln P + \frac{d}{dT} (T \ln q_i) . \tag{3.73}$$

The last term on the right-hand side of each of these expressions contains the contribution of all the internal degrees of freedom. The derivatives involving $\ln q_i$ can be expanded as follows:

$$T \frac{d(\ln q_i)}{dT} = \frac{T}{q_i} \frac{dq_i}{dT} , \tag{3.74}$$

$$\frac{d(T \ln q_i)}{dT} = \frac{T}{q_i} \frac{dq_i}{dT} + \ln q_i , \tag{3.75}$$

$$T \frac{\partial^2}{\partial T^2} (T \ln q_i) = \frac{2T}{q_i} \frac{dq_i}{dT} - \left(\frac{T}{q_i} \frac{dq_i}{dT} \right)^2 + \frac{T^2}{q_i} \frac{d^2 q_i}{dT^2} . \tag{3.76}$$

The first and second temperature derivatives of the internal partition function are:

$$\frac{dq_i}{dT} = \frac{1}{T} \sum_{k=1}^{k_{max}} \sum_{n=0}^{n_{max}} \sum_{J=\Lambda}^{J_{max}} g_\Lambda (2S+1)(2J+1) \frac{E(k,n,J)}{k_B T} \exp\left(-\frac{E(k,n,J)}{k_B T} \right) , \tag{3.77}$$

$$\frac{d^2 q_i}{dT^2} = -\frac{2}{T} \frac{dq_i}{dT} + \frac{1}{T^2} \sum_{k=1}^{k_{max}} \sum_{n=0}^{n_{max}} \sum_{J=\Lambda}^{J_{max}} g_\Lambda (2S+1)(2J+1) \left(\frac{E(k,n,J)}{k_B T} \right)^2 \exp\left(-\frac{E(k,n,J)}{k_B T} \right) . \tag{3.78}$$

To derive the pressure-independent portion of the entropy, use the definition

$$\frac{s_\circ(T)}{R} = \frac{s(T,P)}{R} + \ln \left(\frac{P}{P^\circ} \right) \tag{3.79}$$

to obtain

$$\frac{s_\circ(T)}{R} = \frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) + \frac{5}{2} \ln(k_B T) - \ln P^\circ + \frac{d}{dT} (T \ln q_i) \tag{3.80}$$

For a monoatomic gas with a mass of 1 amu (a hydrogen atom), the value of nondimensional entropy at a reference temperature of 1 K is known as the *Sackur-Tetrode* constant

$$\frac{s_\circ(T = 1 \text{ K})}{R} = -1.1517047 \qquad P^\circ = 100 \text{ kPa} \qquad q_i = 1 \qquad m = 1 \text{ amu} \tag{3.81}$$

For a discussion of the evaluation of the contributions of the internal partition function, see the JANAF table documentation (Chase, 1998) or the documentation for the NASA fitting program (McBride and Gordon, 1992). The JANAF data are accessible online from the NIST kinetics website.

The evaluation of the partition function for heteronuclear molecules and the resulting thermodynamics properties has been implemented in a SDT MATLAB script partition_rotvib.m. The spectroscopic data needed to compute the energy levels is provided in files for three molecules NO NO_rotvib.m, OH OH_rotvib.m and CH CH_rotvib.m. The calculated nondimensional heat capacities C_p/R are given in Figs. 3.2, 3.4 and 3.3 for the ground state (X), the first electronic state (A), a full set of energy levels and compared to the NASA fits from McBride et al. (2002). For a single energy level such as the A or X state, the heat capacity at low temperature has the classical value (for a linear rigid rotor) of $C_p/R = 3.5$. With increasing temperature, the heat capacity approaches the classical value (for a harmonic oscillator and rigid rotor) of $C_p/R = 4.5$ at 4000 K and then decreases with increasing temperature. The decrease is due to the finite number of rotational and vibrational states associated with the finite depth potential well that characterizes actual electronic states as opposed to the infinite number of states that are available in the rigid-rotator harmonic-oscillator approximation. With increasing temperature, the quantum states up to the dissociation level are increasing populated and eventually the internal energy approaches a constant value so that subsequent increases in temperature only result in changes to the translational temperature. More realistically, at high temperatures, a substantial fraction of the molecules become dissociated into atoms and the atoms are ionized so that the high temperature limit of the specific heat of the molecule is no longer meaningful. The differences between the NASA fits and the partition function results at high temperature is due to different choices of spectroscopic constants and number of energy levels included in the partition function summation.
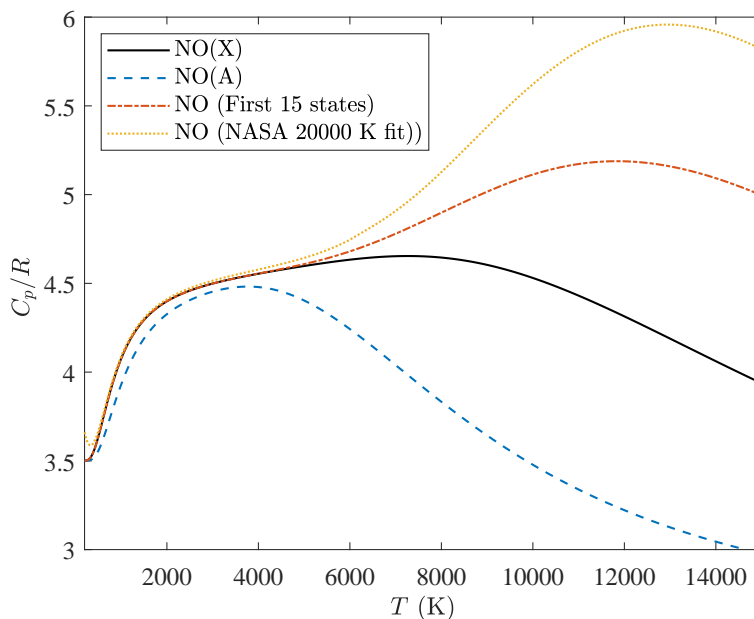

Figure 3.2: NO (nitric oxide) Heat capacity computed from partition function and spectroscopic data for the ground state (X), the first electronic state (A), the first 15 electronic energy levels and compared to the NASA fits from McBride et al. (2002)
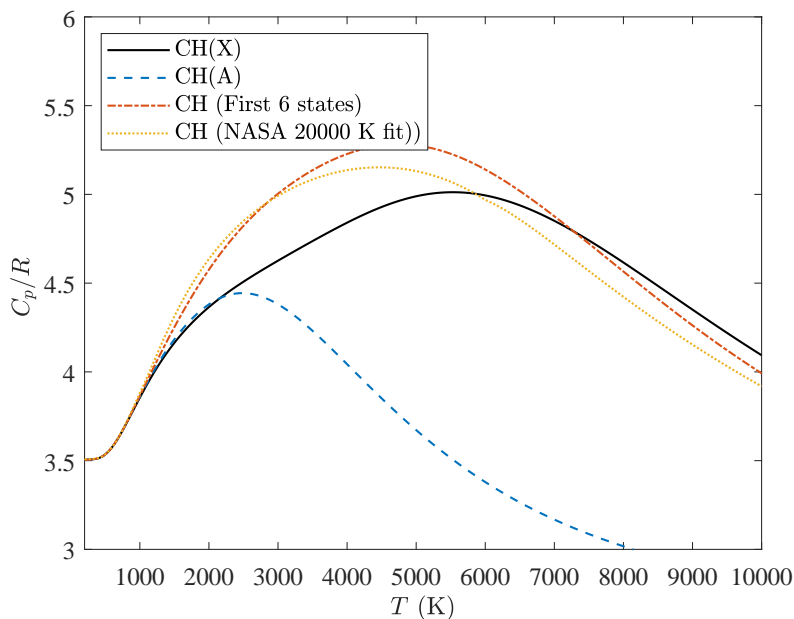
Figure 3.3: CH (methylidyne) Heat capacity computed from partition function and spectroscopic data for the ground state (X), the first electronic state (A), the first six electronic energy levels and compared to the NASA fits from McBride et al. (2002)
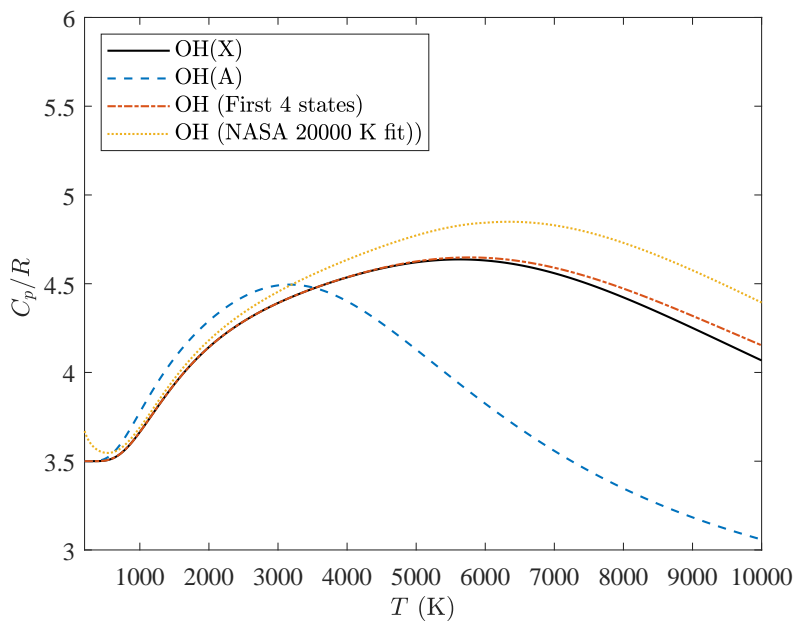

Figure 3.4: OH (hydroxyl) Heat capacity computed from partition function and spectroscopic data for the ground state (X), the first electronic state (A), the first four electronic energy levels and compared to the NASA fits from McBride et al. (2002)

3.4   Estimating Heat Capacities

Some basic heuristics apply for estimating both the low and high temperature limits of the specific heats. These are useful for extending each species' properties to higher temperatures or for visually evaluating the success or failure of a least squares fit.

The heuristic models presented come from the classical result known as the equipartition of energy. The rule is that at sufficiently high temperatures that quantum effects can be ignored, each degree of freedom (DOF) of a molecule contributes $\frac{1}{2}k_B T$ to the internal energy. If the total number of degrees of freedom are f, then the internal energy per molecule can be written as

$$\varepsilon = f\frac{1}{2}k_B T \tag{3.82}$$

and the internal energy per unit mass is

$$e = f\frac{1}{2}RT \tag{3.83}$$

The number of degrees of freedom f depends on the particular molecule. The effect of quantum mechanics is that the energy levels are discrete and for thermal energies ($k_B T$) that are comparable to or smaller than the energy level differences, the effective number of degrees of freedom will be a function of the temperature. Fewer degrees of freedom are excited at low temperatures and more are excited at higher temperatures. There are always three degrees of translational freedom for an atom, and similarly, there are three from the translation of the center of mass of a molecule. Equation 3.83 implies that the specific heat at constant volume is

$$c_v = \frac{f}{2}R \tag{3.84}$$

This is related to the specific heat at constant pressure through

$$c_P = c_v + R \tag{3.85}$$

$$\tag{3.86}$$

At low temperatures, the only contributions to a molecule's energy are the rotational and translational degrees of freedom. Therefore, with each atom fixed in the molecule (no vibrational energy), there are three degrees of translational freedom and two or three degrees of rotational freedom for the molecule as a whole. If the molecule is treated as a rotating rigid body, the total rotational degrees of freedom are two for linear molecules (e.g., O_2 or N_2) or 3 for non-linear molecules (e.g., H_2O or NH_3). The net result at low temperature but still high enough that rotation is fully excited is that

$$c_P \to \frac{7}{2}R \quad \text{linear} , \tag{3.87}$$

$$c_P \to 4R \quad \text{nonlinear} . \tag{3.88}$$

At high temperatures, all the vibrational modes of oscillation are excited in additional to rotation and vibration. Contributions from electronic excitation are usually small in the 3000 to 6000 K range and we will neglect these. The number of vibration modes can be computed by considering the atoms to move independently at high temperatures. There are a total of $3n_a$ independent motions per molecule with n_a atoms and if we subtract center of mass translation and rotation, then we expect that at high temperatures there are $3n_a - 5$ vibrational modes for linear molecules and $3n_a - 6$ modes for nonlinear molecules. Each vibrational mode contributes two degrees of freedom, one for kinetic energy and one for potential energy. The total number of degrees of freedom for the high temperature limit is obtained by summing the translational, rotational, and vibrational degrees of freedom. The final result can be used to express the high temperature specific heat limits as

$$\lim_{T \to \infty} c_P = \frac{6n_a - 3}{2} R \quad \text{linear} \tag{3.89}$$

$$\lim_{T \to \infty} c_P = \frac{6n_a - 4}{2} R \quad \text{nonlinear} \tag{3.90}$$

Note that if we neglect the electronic excitation of monatomic species, the specific heat is independent of temperature

$$(c_P)_{monatomic} = \frac{5}{2} R \, . \tag{3.91}$$

This is a good approximation for the temperatures of interest in ordinary combustion.

The utility of the limits for heat capacity are that these are a convenient way to check the validity of thermodynamic data and also provide limiting values that can be used for extrapolating data originally given over a limited range of temperature. It is preferred but not always possible to recompute the thermodynamic functions using statistical mechanics if the polynomial fits are not valid to sufficiently high temperatures. It is possible in some cases to extrapolate the data from the fits to higher temperatures. The idea behind the extrapolation is that given a specific heat function $c_p(T)$ defined on $T_{min} \leq T \leq T_{max}$, the specific heat can be extrapolated using

$$\frac{1}{c_p} = \frac{1}{c_p(\infty)} - \frac{T_{max}}{T} \left(\frac{1}{c_p(\infty)} - \frac{1}{c_p(T_{max})} \right) \quad \text{for} \quad T \geq T_{max} \tag{3.92}$$

This method is simpler but less accurate than the more general extrapolation method developed by Wilhoit and implemented in the NASA code PAC91 (McBride and Gordon, 1992, see p. 7). It will work only if there are no low-lying electronic states that contribute significantly to the specific heat. Above 5000 K, these states almost always have to be taken into consideration.

3.5   RRHO Model Thermodynamics

The thermodynamics of a model gas described by the RRHO approximation (neglecting electronic excitation) can be computed using the statistical thermodynamics prescription (Section 3.3) and the model partition functions of Section 3.1. The starting point for computing the thermodynamic energy is (3.57) which can be written for a single molecule as

$$\varepsilon = k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \, . \tag{3.93}$$

Consistent with the RRHO approximation, assume that all the modes of the molecular excitation are independent. This means that the quantum states for translation, rotation, vibration can be separately computed and the total molecular partition function can be written as a product of the partition function for each mode. Omitting the nuclear partition function, we have

$$q = q_t q_r q_v \tag{3.94}$$

With this approximation, the energy of a molecule can be written as the sum of the energies for each mode

$$\varepsilon = k_B T^2 \sum_{t,r,v} \frac{1}{q_j} \left(\frac{\partial q_j}{\partial T} \right)_V , \tag{3.95}$$

$$\varepsilon = \sum_{t,r,v} \varepsilon_j , \tag{3.96}$$

where the energy of mode j is

$$\varepsilon_j = k_B T \frac{T}{q_j} \left(\frac{\partial q_j}{\partial T} \right)_V . \tag{3.97}$$

Using the partition functions computed in Section 3.1, we obtain the contributions to energy for a single molecule:

$$\text{translation} \quad \varepsilon_t = \frac{3}{2} k_B T ; \tag{3.98}$$

$$\text{rotation} \quad \varepsilon_r = k_B T \qquad \text{linear molecule } T \gg \Theta_r ; \tag{3.99}$$

$$\text{rotation} \quad \varepsilon_r = \frac{3}{2} k_B T \qquad \text{nonlinear molecule } T \gg \Theta_r ; \tag{3.100}$$

$$\text{vibration} \quad \varepsilon_v = \sum_{i=1}^{n_v} k_B \Theta_{v,i} \left(\frac{1}{2} + \frac{1}{e^{\Theta_{v,i}/T} - 1} \right) \qquad \text{sum over all } n_v \text{ modes .} \tag{3.101}$$

The specific heat at constant volume can be obtained by differentiation of the energy with respect to temperature

$$c_v = \frac{d\varepsilon}{dT} . \tag{3.102}$$

The individual contributions of each mode to the specific heat are:

$$\text{translation} \quad c_{v,t} = \frac{3}{2} k_B ; \tag{3.103}$$

$$\text{rotation} \quad c_{v,r} = k_B \qquad \text{linear molecule } T \gg \Theta_r ; \tag{3.104}$$

$$\text{rotation} \quad c_{v,r} = \frac{3}{2} k_B \qquad \text{nonlinear molecule } T \gg \Theta_r ; \tag{3.105}$$

$$\text{vibration} \quad c_{v,v} = k_B \sum_{i=1}^{n_v} \left(\frac{\Theta_{v,i}}{T} \right)^2 \frac{e^{\Theta_{v,i}/T}}{(e^{\Theta_{v,i}/T} - 1)^2} \qquad \text{sum over all } n_v \text{ modes .} \tag{3.106}$$

High-Temperature Limit

In the limit as the temperature becomes sufficiently high, but not so high that electronic excitation is significant, the vibrational contribution to the energy is

$$\varepsilon \to n_v k_B T \quad \text{as} \quad T \to \infty , \tag{3.107}$$

and the contribution to the heat capacity is

$$c_{v,v} \to n_v k_B \quad \text{as} \quad T \to \infty . \tag{3.108}$$

In the high-temperature limit, the nuclear and rotational partition function are decoupled and the contribution of rotation motion to specific heat is a constant and only depends on the symmetry of the molecule.

Using the high-temperature limits of the partition function for the RRHO model, we obtain the contribution of each mode of molecular motion to the energy at high temperature to be $f_i \times 1/2 k_B T$ where f_i is the number of *degrees of freedom* for that mode.

$$f_i = \lim_{T \to \infty} 2 \frac{T}{q_i} \left(\frac{\partial q_i}{\partial T} \right)_V . \tag{3.109}$$

For each mode, we have:

$$\text{translation} \quad f_t = 3 ; \tag{3.110}$$
$$\text{rotation} \quad f_r = 2 \qquad \text{linear molecule } T \gg \Theta_r ; \tag{3.111}$$
$$\text{rotation} \quad f_r = 3 \qquad \text{nonlinear molecule } T \gg \Theta_r ; \tag{3.112}$$
$$\text{vibration} \quad f_v = 2 n_v . \tag{3.113}$$

As discussed in the previous section, the number of vibrational modes can be computed by subtracting the translation and rotational degrees of freedom from the total degrees of freedom $3 n_a$ of n_a atoms free to move in three dimensions

$$n_v = 3 n_a - 5 \qquad \text{linear molecule} , \tag{3.114}$$
$$n_v = 3 n_a - 6 \qquad \text{nonlinear molecule} . \tag{3.115}$$

The high-temperature limit value for total number of degrees of freedom for a molecule of n_a atoms is the sum of the values for all three modes:

$$f = 6 n_a - 5 \qquad \text{linear molecule} ; \tag{3.116}$$
$$f = 6 n_a - 6 \qquad \text{nonlinear molecule} ; \tag{3.117}$$

in agreement with the estimates given previously. Instead of using the degrees of freedom to characterize the specific heat, the *ratio of specific heats*

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{f} \tag{3.118}$$

is often employed. Note that the value of $\gamma = 1.4 = 7/5$ used for engineering computations with low-temperature air corresponds to $f = 5$ so that the vibration modes of N_2 and O_2 are not contributing to the heat capacity in this model, which is reasonable as long as T is sufficiently small compared to Θ_v (3393 K for N_2, 2273 K for O_2).

Low-Temperature Limit

At very low temperatures, $T \leq 5 \Theta_r$, the quantization of rotational levels and rotational-nuclear spin coupling requires a more sophisticated approach (Ch. 6 McQuarrie, 1976) to computing partition functions. This is not only relevant to spectroscopy of molecules in cold interstellar clouds or laboratory experiments at cryogenic conditions but also to the IR spectra as the nuclear symmetry of the molecule will determine the weighting factors of the populations of rotational levels (Ch 5 Hanson et al., 2016). Aside from the important implications for spectroscopy, the rotational contribution to thermodynamics is most important at temperatures comparable to the effective rotational energy level separation, for example hydrogen, with a value of $\Theta_r = 87.5$ K. We will only consider the computation of the rotational partition for diatomic molecules in the rigid rotator approximation. For linear heteronuclear molecules like NO, OH, CH, and CO, the nuclear-rotational partition function is just

$$q_{n,r} = (2 I_1 + 1)(2 I_2 + 1) \sum_{j=0}^{\infty} (2 J + 1) e^{-J(J+1) \Theta_r / T} . \tag{3.119}$$
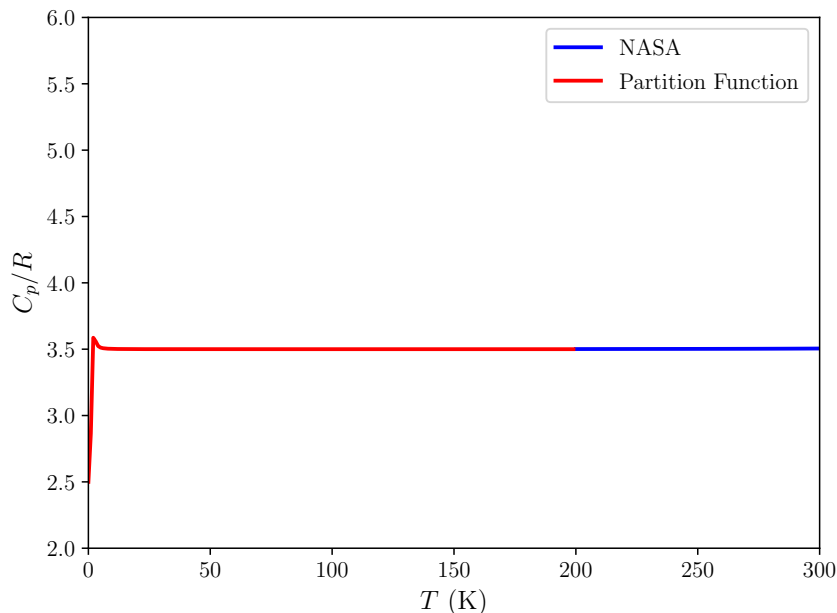
Figure 3.5: Low-temperature heat capacity of CO computed using the RRHO partition function (3.120) and compared to the standard NASA-9 fit.

where I_1 and and I_2 are the values of nuclei spins. The high temperature limit, $T \geq 5\Theta_r$, of the sum is just

$$q_{n,r} \approx (2I_1 + 1)(2I_2 + 1)\frac{T}{\Theta_r} \ . \tag{3.120}$$

This gives a contribution of precisely R to the specific heat capacity at high temperature, in agreement with the considerations about degrees of freedom of linear rotators. This is true for all of the diatomic rotors. An example of the low temperature specific heat capacity in CO is shown in Fig. 3.5. The script specificHeat.py implements the evaluation of the low temperature rotational partition function and specific heat calculation for several diatomic molecules. This was used to compute the examples shown in this section.

For homonuclear molecules like N_2, O_2, H_2, the rotational partition function depends on the symmetry characteristics of the nuclear wavefunction, which depends on the value of nuclear spin I. The total wavefunction of the molecule has to be symmetric under exchange of the identical nuclei for integer spin nuclei and antisymmetric for half-integer spin. The most common electronic ground state Σ_g^+, is symmetric and this means that the symmetry of the total wavefunction is controlled by the rotational component. For integral nuclear spin $(I = 0, 1, 2, \dots)$ the rotational-nuclear partition is

$$q_{n,r} = (I + 1)(2I + 1)\sum_{j=0,2,4,\dots}^{\infty}(2J + 1)e^{-J(J+1)\Theta_r/T} + I(2I + 1)\sum_{j=1,3,5,\dots}^{\infty}(2J + 1)e^{-J(J+1)\Theta_r/T} \ . \tag{3.121}$$

The high temperature limit of the sum is

$$q_{n,r} \approx \frac{(2I_1 + 1)^2}{2}\frac{T}{\Theta_r} \tag{3.122}$$

The factor of 2 in the denominator is due to the symmetry a the molecule with identical nuclei, otherwise the number of independent quantum states will be over counted. The approximate partition function (3.122) is valid for all of the homonuclear diatomic cases and as in the heteronuclear case, results in a contribution of R in the high temperature limit. The computation of specific heat with this model is illustrated for N_2, $I = 1$ for ^{14}N nuclei, in Fig. 3.6.
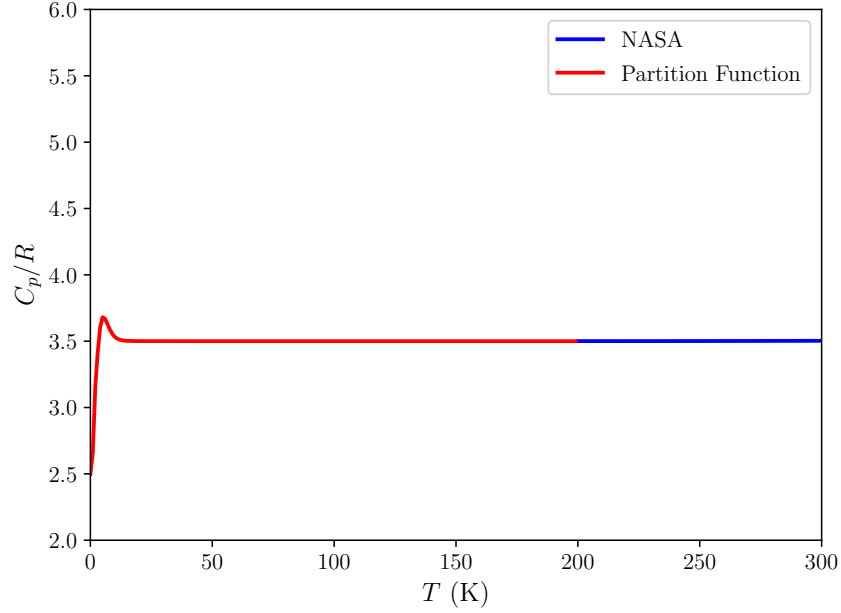
Figure 3.6: Low-temperature heat capacity of CO computed using the RRHO partition function (3.121) and compared to the standard NASA-9 fit.

For half-integral values of the nuclear spin ($I = 1/2, 3/2, \dots$) the rotational partition function is

$$q_{n,r} = I(2I + 1) \sum_{j=0,2,4,\dots}^{\infty} (2J + 1)e^{-J(J+1)\Theta_r/T} + (I + 1)(2I + 1) \sum_{j=1,3,5,\dots}^{\infty} (2J + 1)e^{-J(J+1)\Theta_r/T} . \quad (3.123)$$

$$(3.124)$$

This case is appropriate for H_2 ($I = 1/2$) and the resulting specific heat capacity dependence on temperature is shown in Fig. 3.7. The pronounced peak and slow approach to the high temperature limit is a special feature of hydrogen that is a consequence of the large value of Θ_r and the two possible states of the alignment of the nuclei. Ortho-hydrogen has a symmetric nuclear state with parallel nuclei spins, para-hydrogen has an anti-symmetric nuclear state with opposite alignment nuclei spins. There are 3 possible para-states and only one possible ortho-state, the equilibrium between the states determines the average heat capacity, see the discussion in Ch. 6 of McQuarrie (1976).

The case of O_2 (^{16}O nuclei) is special, $I = 0$ but the ground electronic state $X^3\Sigma_g^-$ is antisymmetric. The rotational states have to be antiysmmetric for the total wavefunction to be symmetric so only the odd rotational states are allowed and the partition function is

$$q_{n,r} = (I + 1)(2I + 1) \sum_{j=1,3,\dots}^{\infty} (2J + 1)e^{-J(J+1)\Theta_r/T} . \quad (3.125)$$

The computation of specific heat capacity for O_2 with this model is illustrated in Fig. 3.8.

The NASA9 fits could be extended to low temperatures using the RRHO partition function and adding additional polynomial segments. The temperature ranges will need to be carefully chosen to properly represent the rapid variation of specific heat near the characteristic rotational temperature Θ_r. The values of Θ_r (Table F.2) are much lower than the temperatures at which condensation occurs for most diatomic molecules (H_2 is an exception) so that for most purposes the high-temperature limit of the classical approximation to rotation is a reasonable approximation even at quite low temperatures.
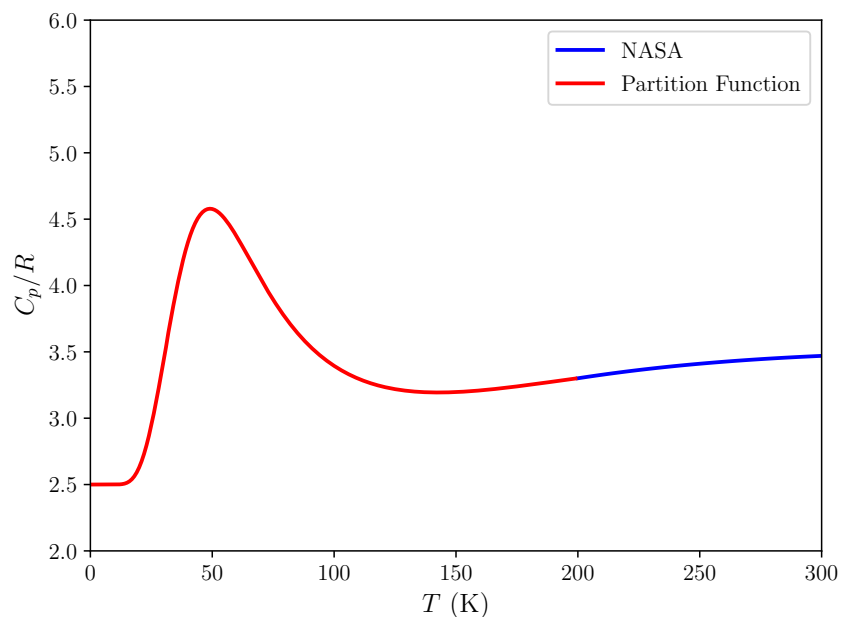
Figure 3.7: Low-temperature heat capacity of H_2 computed using the RRHO partition function (3.123) assuming equilibrium between ortho and para states with comparison to the standard NASA-9 fit.
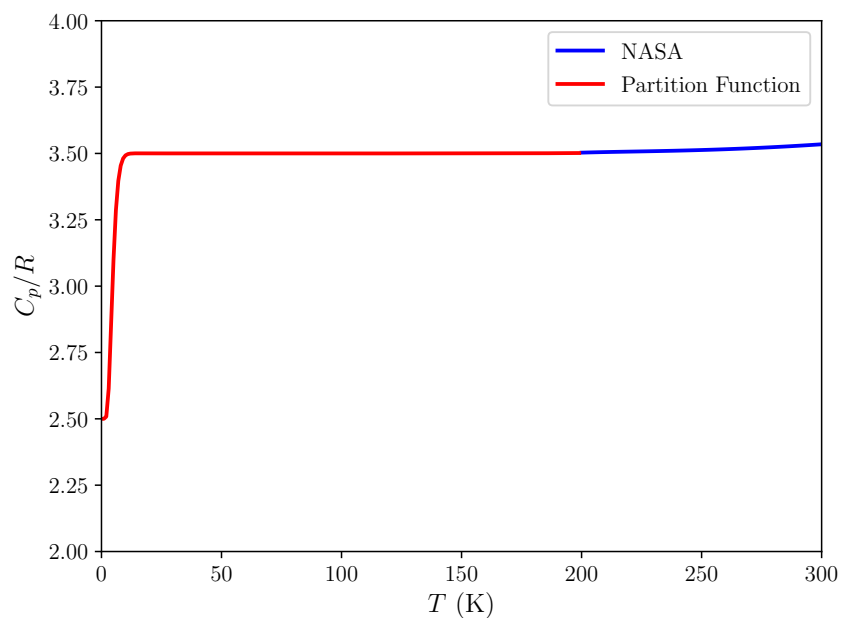

Figure 3.8: Low-temperature heat capacity of O_2 computed using the RRHO partition function (3.125) and compared to the standard NASA-9 fit.

Chapter 4

Equilibrium

This chapter describes the fundamental basis of chemical equilibrium and outlines methods for computing equilibrium composition. All discussions of equilibrium are based on the First and Second Law of thermodynamics. The Second Law can be interpreted as an optimization problem which can be solved numerically to determine the thermodynamic state. The optimization is constrained by both the physical and thermal conditions under which equilibrium is achieved and for chemical equilibrium, the conservation of atoms. The thermodynamic and chemical considerations underlying chemical equilibrium are presented with examples of how these are implemented in Cantera.

The fundamentals principles of chemical equilibrium analysis, applications to gaseous combustion, and numerical methods are discussed in depth in a number of monographs (Denbigh, 1981, van Zeggeren and Storey, 1970, Smith and Missen, 1991, Powers, 2016), reports (Huff et al., 1951, Gordon and McBride, 1976, Reynolds, 1981, 1986, McBride and Gordon, 1996) and journal papers (Brinkley, 1946, 1947, White et al., 1958, Zeleznik and Gordon, 1960) as well as textbooks on thermodynamics and combustion. Chemical equilibrium computations are also discussed in monographs on detonation (Fickett and Davis, 1979, Mader, 1979) that have an emphasis on high explosives, a specialized topic that requires considerable extension of gas phase methods to treat non-ideal multi-phase mixtures at high pressure using complex equations of state. Computation of gaseous chemical equilibrium at high temperature remains an important topic in planetary re-entry (Bottin, 2000), chemical engineering (Smith et al., 1996), geologic and environmental applications (Fegley, 2013) motivate explorations of new formulations and numerical methods, particularly for multi-component, multi-phase mixtures (Tsanas et al., 2017) that contain solids, gaseous or liquids or involve supercritical fluids.

4.1 Second Law of Thermodynamics

The basis of chemical equilibrium is the Second Law of Thermodynamics. For a fixed mass of material (considered as a thermodynamic system) which can exchange work and heat with its surroundings but is otherwise isolated, the Second Law is:

> The total entropy of the universe consisting of a system and its surroundings either remains constant or increases.

In mathematical terms, this is an extremum principle:

$$\mathrm{d}S_{universe} = \mathrm{d}S_{system} + \mathrm{d}S_{surroundings} \geq 0 \ . \tag{4.1}$$

The inequality holds for all irreversible processes, at equilibrium, this is an equality.

The changes in entropy of the surroundings is determined by the thermal interactions with the surroundings. An isolated system has no heat or work interactions with the surroundings, therefore from the First

Law of Thermodynamics, we conclude that the internal energy E is a constant and for a P-V-T system, if there is no work interaction, the volume V of the system is constant. We conclude that at constant energy and volume, the extremum principle implied by the Second Law of Thermodynamics is that entropy tends towards a maximum as the system approaches equilibrium.

$$\mathrm{d}S_{system} \geq 0 \text{ for } (E, V) \text{ constant} \tag{4.2}$$

If the surroundings are considered as a *thermal bath* with a fixed temperature $T_\circ$, the change in entropy of the surroundings is equal in magnitude and opposite in sign to the thermal energy Q transferred into the system.

$$\mathrm{d}S_{surroundings} = -\frac{\mathrm{d}Q}{T} \tag{4.3}$$

The work $\mathrm{d}W$ done on the system by expansion into an atmosphere of constant pressure $P_\circ$ is

$$\mathrm{d}W = -P_\circ \mathrm{d}V \tag{4.4}$$

The Second Law of Thermodynamics implies that

$$\mathrm{d}S_{system} = \mathrm{d}S \geq \frac{\mathrm{d}Q}{T_\circ} \tag{4.5}$$

The First Law of Thermodynamics can be used to write this as a inequality

$$\mathrm{d}Q = \mathrm{d}E - \mathrm{d}W \leq T_\circ \mathrm{d}S \tag{4.6}$$

or

$$0 \geq \mathrm{d}E + P_\circ \mathrm{d}V - T_\circ \mathrm{d}S \tag{4.7}$$

This is the key extremum principle for equilibrium and by making different choices for the constraints on heat and work interactions, the principle can be interpreted in terms of the thermodynamic potentials as shown in Table 4.1.

Table 4.1: Optimization problems for equilibrium processes Kondepudi and Prigogine (1998).

Constraints	Optimization
E, V constant	S maximum
S, V constant	E minimum
S, P constant	H minimum
H, P constant	S maximum
T, V constant	A minimum
T, P constant	G minimum

4.2 Equilibrium at Constant Temperature and Pressure

The most common approach to computing chemical and phase equilibrium is to consider a constant temperature and pressure equilibrium process. This is particularly convenient for ideal gases due to the separation of temperature and pressure dependence of the chemical potential.

The total Gibbs energy of a single-phase mixture of K species is

$$G(T, P, \mathbf{N}) = \sum_{k=1}^{K} N_k \mu_k(T, P, \mathbf{N}) \,, \tag{4.8}$$

The use of this relationship requires a expression for the chemical potential $\mu_i(T, P, \mathbf{N})$, which depends on the mixture equation of state for the phase, see Section 9.8. The ideal gas is the simplext model and applicable to many combustion problems, the chemical potential of species k in an ideal gas mixture is

$$\mu_k(T, P_k) = \mu_k^o(T) + \mathcal{R}T \ln(P_k/P^\circ) \,, \tag{4.9}$$
$$= \mu_k^o(T) + \mathcal{R}T \ln(P/P^\circ) + \mathcal{R}T \ln(N_k/N) \,, \tag{4.10}$$

and the total number of moles N is

$$N = \sum_{k=1}^{K} N_k \,. \tag{4.11}$$

For a closed system of fixed mass M, we will specify the composition by K composition variables $n_k = N_k/M$. Chemical equilibrium is defined by the set of values $\mathbf{n}^* = (n_1^*, n_2^*, \ldots, n_K^*)$ that minimize $g = G/M$ at constant (T, P) subject to the constraints of conservation of atoms. This is valid for any single phase mixture and the ideal gas is just a special case. From the fundamental relation for Gibbs energy, a necessary condition is that g is stationary for variations in composition about the equilibrium value

$$\delta g = \sum_{k=1}^{K} \mu_k(T, P, \mathbf{n}^*) \, \delta n_k = 0 \,. \tag{4.12}$$

The variations in composition δn_k are constrained by the conservation of atomic composition for a closed system. The Gibbs-Duhem relation (2.38) constrains the variations in μ_k at constant (T, P)

$$0 = \sum_{k=1}^{K} \delta \mu_k \, n_k \,. \tag{4.13}$$

These results are useful in simplifying the equations used for numerical simulation of chemical equilibrium at constant pressure and temperature.

4.3   Composition Constraints

At the outset of any chemical equilibrium problem, the researcher has to choose an appropriate set of K distinct chemical species $\{C_1, C_2, \ldots, C_K\}$ which are made up of J distinct atomic elements $\{E_1, E_2, \ldots, E_J\}$, $K \geq J$. For a given set of species, the researcher also needs to choose a reference composition $\mathbf{n}^\circ$ that can be used to fix the elemental (atomic) composition. While the composition of the species can change substantially in the course of the chemical reaction, the number of atoms of each element cannot change as long as we are considering ordinary combustion conditions and an isolated mass of material, e.g., a closed system. Mathematically, the conservation of atoms can be expressed as a set of linear equations

$$b_j = \sum_{k=1}^{K} a_{jk} n_k \quad j = 1, 2, \ldots, J \,, \tag{4.14}$$

where a_{jk} is the number of atoms of type j in species k and b_j is the total number (moles) of elements of type j. The total number of elements is determined by the composition n_k° used to initialize the equilibrium computation

$$b_j = \sum_{k=1}^{K} a_{jk} n_k^\circ \,. \tag{4.15}$$

In addition, the amount of each species has to be nonnegative,

$$n_k \geq 0 \quad i = 1, 2, \ldots, K \,. \tag{4.16}$$

For a given mixture, the b_j are constants and the variations $\delta \mathbf{n}$ in the species composition are constrained by the linear equations

$$0 = \sum_{k=1}^{K} a_{jk} \delta n_k \quad j = 1, 2, \ldots, J \tag{4.17}$$

The set of coefficients $\{a_{ij}\}$ are positive integers that depend only on the elemental composition of each species in the mixture. The set of values can be represented by a $J \times K$ matrix A with components $(\mathsf{A})_{ji} = a_{ji}$ and the contraint on composition variations can be expressed as the matrix relation

$$0 = \mathsf{A}\, \delta \mathbf{n} \tag{4.18}$$

The number M of independent constraints is given by the rank of the constraint matrix

$$M = \operatorname{rank}(\mathsf{A}) . \tag{4.19}$$

Usually, but not always $M = J$; in certain cases (e.g., when one or more of the elements is also a species that is nonreactive or inert), $M < J$. The constraints on composition for a closed system means that the number of independent composition variables or *reaction coordinates* will be less than the number of species

$$\text{Number of independent reaction coordinates} = K - M \geq 1 \tag{4.20}$$

for a nontrivial solution to the equilibrium composition.

4.4   Equilibrium as Constrained Minimization

The equilibrium solution at constant temperature and pressure for a closed system can be concisely formulated as finding the solution to the minimum of g subject to constraints.

$$\text{Minimize } g = \sum_{k=1}^{K} \mu_k n_k \tag{4.21}$$

subject to

$$b_j = \sum_{k=1}^{K} a_{jk} n_k \quad j = 1, 2, \ldots, J . \tag{4.22}$$

$$\tag{4.23}$$

where we have implicitly assumed that $\operatorname{rank}(\mathsf{A}) = J$ and also require $n_k \geq 0$ for all k. A subtle point in formulating equilibrium algorithms is that we only need consider the chemically active species and species that are chemically inert (e.g., argon and other rare gases) are not included in the Gibbs energy or constraint equations. This reduces the total species count and in some cases, the number of constraint equations.

The classical method of solving constrained minimization problems is the method of *Lagrange multipliers* which enforces the J constraints by introducing J additional variables (multipliers) λ_j to create an unconstrained optimization problem for the objective function $\mathcal{L}$.

$$\mathcal{L} = \sum_{k=1}^{K} \mu_k n_k + \sum_{j=1}^{J} \lambda_j \left(b_j - \sum_{k=1}^{K} a_{jk} n_k \right) . \tag{4.24}$$

This function has been constructed so that $\delta \mathcal{L} = 0$ at equilibrium for arbitrary variations δN_k and $\delta \lambda_k$. The solution to the unconstrained optimization problem must therefore satisfy the following condition at equilbrium

$$\delta \mathcal{L} = \sum_{k=1}^{K} \left(\frac{\partial \mathcal{L}}{\partial n_k} \right)_{n_{i \neq k}, \lambda} \delta n_k + \sum_{j=1}^{J} \left(\frac{\partial \mathcal{L}}{\partial \lambda_j} \right)_{\mathbf{n}, \lambda_{i \neq j}} \delta \lambda_j = 0 \tag{4.25}$$

Because the variations δn_k and $\delta \lambda_j$ are arbitrary (but bounded), this can only be satisfied if each of the partial derivatives of $\mathcal{L}$ must individually vanish at equilibrium. Carrying out the differentiation, we obtain the following $K + J$ equations in $K + J$ unknowns $(\mathbf{n}, \lambda)$

$$\left(\frac{\partial \mathcal{L}}{\partial n_k}\right)_{n_{i \neq k}, \lambda} = \mu_k - \sum_{j=1}^{J} a_{jk} \lambda_j = 0 \qquad i = 1, 2, \ldots, K \ , \tag{4.26}$$

requiring that $n_k \geq 0$ for all k and

$$\left(\frac{\partial \mathcal{L}}{\partial \lambda_j}\right)_{\mathbf{n}, \lambda_{i \neq j}} = b_j - \sum_{k=1}^{K} a_{jk} n_k = 0 \qquad j = 1, 2, \ldots, J \ . \tag{4.27}$$

This is a set of $K + J$ *nonlinear* equations in $K + J$ unknowns. The nonlinearity arises because of the dependence of chemical potential on composition. For an ideal gas

$$\mu_i = \mu_i^\circ(T) + \mathcal{R}T \left[\ln(P/P^\circ) + \ln(n_i/n)\right] \ , \tag{4.28}$$

where the total number of moles (kmol/kg) are

$$n = \sum_{k=1}^{K} n_k \ . \tag{4.29}$$

For a nonideal gas, one typical approach is to modify this by including an *activity coefficient* $\phi_i(T, P, \mathbf{n})$ that must be computed from the $P(V, T, \mathbf{n})$ equation of state,

$$\mu_i = \mu_i^\circ(T) + \mathcal{R}T \left[\ln(P/P^\circ) + \ln(n_i/n) + \ln \phi_i\right] \ . \tag{4.30}$$

The numerical solution of these equations requires the development of a robust algorithm to perform an iterative procedure to deal with the nonlinearity. An algorithm developed for an ideal mixture can be adopted for this purpose by method of successive approximation assuming $\phi = $ constant at each step m with $\phi^{m+1} = \phi(P, T, \mathbf{n}^m)$, $\phi^1 = 1$.

The Lagrange multiplier method is one of many techniques for solving chemical equilibrium problems. Thorough expositions of this and the other solution techniques (with extensions to multi-phase systems) are given in van Zeggeren and Storey (1970), Smith and Missen (1991). Cantera has several methods that can be invoked for equilibrium solutions using the Cantera `equilibrate` function. The documentation at the Cantera website describes the three solvers that this implements. Solver 0 is based on the element potential method (Reynolds, 1981, 1986)- fast but not robust; Solver 1 is based on Gibbs energy minimization (described above), slower than element potentials but very robust; Solver 2 is based on the VCS algorithm described in Smith and Missen (1991) and is based on transformation to reaction coordinates that is discussed in the next section.

Numerical Solution of Equilibrium   One approach (other than the approaches available in Cantera) to numerical solution is to use a generic optimization method to minimize the Gibbs energy applying the element and positivity constraints. For example this can be implemented through sequential quadratic programming using a package such as `sqp` in MATLAB. This works acceptably when there are a small number of components and the mole amounts are not too disparate in size.

At high pressures or low temperature, the solution by `sqp` requires very small step sizes and even then, will have difficulty getting accurate results for minor species. There will be large differences between the magnitude of the constraint coefficients λ_i in comparison to the mole numbers n_i of minor species. This will cause significant convergence issues and the minor species present in less than some minimum amount will not be converged to equilibrium values.

For a modest number of species it is possible to refine an `sqp` solution by performing a Newton-Raphson iteration starting from preliminary result $\mathbf{n}_{sqp}$. One way to resolve the issues of difference in magnitude in the variables is to eliminate the constraints by switching to reaction coordinates ξ and carry out unconstrained minimization.

4.5   Reaction Coordinates

An alternative to the method of Lagrange multipliers, which increases the dimensionality of the system of equations to be solved, is to use reaction coordinates, which decreases the dimensionality. The number of independent reaction coordinates is $R = K - J$ in the most straightforward situations and the reaction coordinates ξ_i, $i = (1, 2, \ldots, R)$ are bounded but otherwise independent, i.e., unconstrained. If for some reason the matrix is rank deficient, that is, if $\text{rank}(\mathsf{A}) < \min(J, K)$, then R can be less than $K - J$.

The key idea is that there is a set of linearly independent R vectors $\boldsymbol{\nu}^i$ that span the subspace of solutions that satisfy the element constraints. Possible compositions can be specified by forming linear combinations of these vectors in the proportion ξ_i.

$$\mathbf{n} = \mathbf{n}^\circ + \sum_i^R \boldsymbol{\nu}^i \xi_i \ . \tag{4.31}$$

Applying the element constraint equations and simplifying, we obtain

$$\mathsf{A}\boldsymbol{\nu}^i = 0 \quad \text{for} \quad i = 1, 2, \ldots R \tag{4.32}$$

which can be written in matrix form

$$\mathsf{A}\mathsf{N} = 0 \tag{4.33}$$

where the columns of the *stoichmetric matrix* N are the vectors $\boldsymbol{\nu}^i$

$$\mathsf{N} = \begin{bmatrix} \boldsymbol{\nu}^1 \ \boldsymbol{\nu}^2 \ \ldots \ \boldsymbol{\nu}^R \end{bmatrix} \tag{4.34}$$

The procedure for computing the elements of N is described in (Smith and Missen, 1991, pp. 23-25). In MATLAB, this can be accomplished by determining the basis that spans the null space of the matrix A, $\mathsf{N} = \texttt{null(A)}$.

4.6   Equilibrium as Unconstrained Minimization

The reaction coordinates provide a different route to computing chemical equilibrium. The variation in species can be related to the (independent) variations in reaction coordinates by the stoichiometric coefficients

$$\delta\mathbf{n} = \mathsf{N}\delta\boldsymbol{\xi} = \sum_{i=1}^R \boldsymbol{\nu}^i \delta\xi_i \ , \quad \text{or} \quad \delta n_k = \sum_{i=1}^R \nu_{ki}\delta\xi_i \qquad k = 1, 2, \ldots, K \qquad \nu_{ki} = (\mathsf{N})_{k,i} \ . \tag{4.35}$$

Substituting this into the differential for the Gibbs energy

$$\delta g = \sum_{i=1}^R \left(\sum_{k=1}^K \mu_k \nu_{ki} \right) \delta\xi_i \ . \tag{4.36}$$

Because the variations $\delta\xi_k$ in reaction coordinates are independent and arbitrary, the minimization condition $\delta g = 0$ implies the terms in parentheses must all vanish identically.

$$\frac{\partial g}{\partial \boldsymbol{\xi}} = 0 \qquad \text{or} \qquad \frac{\partial g}{\partial \xi_i} = 0 \qquad i = 1, 2, \ldots, R \ . \tag{4.37}$$

One possible numerical solution strategy is to apply the Newton-Raphson method to compute updates $\delta\boldsymbol{\xi}$ to a trial solution for $\boldsymbol{\xi}$. The algorithm to advance from trial m to $m + 1$ is

$$\boldsymbol{\xi}^{m+1} = \boldsymbol{\xi}^m + \delta\boldsymbol{\xi}^m \tag{4.38}$$

$$\delta\boldsymbol{\xi}^m = - \left(\frac{\partial^2 g}{\partial \xi^2} \right)_{\mathbf{n}^m}^{-1} \left(\frac{\partial g}{\partial \boldsymbol{\xi}} \right)_{\mathbf{n}^m} \tag{4.39}$$

where

$$\mathbf{n}^m = \mathbf{n}^\circ + \mathsf{N}\boldsymbol{\xi}^m \; . \tag{4.40}$$

To carry out this computation, we will need to compute the *Hessian* matrix of g

$$\left(\frac{\partial^2 g}{\partial \boldsymbol{\xi}^2}\right)_{i,j} = \frac{\partial^2 g}{\partial \xi_i \xi_j} \; , \tag{4.41}$$

and the *gradient* of g w.r.t. reaction coordinates

$$\left(\frac{\partial g}{\partial \boldsymbol{\xi}}\right)_i = \frac{\partial g}{\partial \xi_i} \; . \tag{4.42}$$

From the definition of $\boldsymbol{\xi}$, μ_i and g, these can be computed explicitly for an ideal solution. An ideal solution is defined by having a chemical potential with the form

$$\mu_k = \mu_k^*(T,P) + \mathcal{R}T \ln(n_k/n) \tag{4.43}$$

An ideal gas is particular case of an ideal solution. The derivatives of the chemical potential needed for the Hessian and gradient can be computed analytically by first carrying out the differentiation w.r.t. n_k

$$\frac{\partial g}{\partial n_k} = \mu_k^* + \mathcal{R}T \ln(n_k/n) \tag{4.44}$$

$$\frac{\partial^2 g}{\partial n_i \partial n_k} = \frac{\delta_{ik}}{n_k} - \frac{1}{n} \tag{4.45}$$

and then transform to the reaction coordinates

$$\frac{\partial}{\partial \xi_i} = \sum_k \frac{\partial n_k}{\partial \xi_i} \frac{\partial}{\partial n_k} \tag{4.46}$$

$$= \sum_k \nu_{ki} \frac{\partial}{\partial n_k} \tag{4.47}$$

$$\frac{\partial g}{\partial \xi_i} = \sum_k \nu_{ki} \frac{\partial g}{\partial n_k} \tag{4.48}$$

$$= \sum_{k=1}^{K} \nu_{ki} \mu_k \tag{4.49}$$

$$\frac{\partial^2 g}{\partial \xi_i \xi_j} = \mathcal{R}T \sum_{k=1}^{K} \sum_{l=1}^{K} \nu_{ki} \nu_{lj} \left(\frac{\delta_{kl}}{n_k} - \frac{1}{n}\right) \; , \tag{4.50}$$

$$\tag{4.51}$$

where $\delta_{kl} = 1$ if $k = l$ and $= 0$ for $k \neq l$. The Hessian is a symmetric, square (dimension $R \times R$) matrix

$$\frac{\partial^2 g}{\partial \xi_i \xi_j} = \frac{\partial^2 g}{\partial \xi_j \xi_i} \tag{4.52}$$

with rank R and it can be shown (see Smith and Missen (1991) and the discussion and references in Powers and Paolucci (2008)) that it has the property of being *positive definite* which is defined by

$$\sum_i \sum_j \frac{\partial^2 g}{\partial \xi_i \xi_j} x_i x_j \geq 0 \tag{4.53}$$