where μ_i is the *chemical potential* of the ith species. This equation and the analogs discussed below are often referred to as the *Fundamental Relations of Thermodynamics.*

This relationship can be used to define an *equation of state*

$$E = E(S, V, \mathbf{N}) \tag{2.7}$$

treating S, V and $\mathbf{N} = N_1, N_2, \ldots, N_K$ as the natural independent variables. The quantities temperature, pressure and chemical potential are then defined by the partial derivatives of E as follows:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,\mathbf{N}} \qquad P = -\left(\frac{\partial E}{\partial V}\right)_{S,\mathbf{N}} \qquad \mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}} . \tag{2.8}$$

Away from phase boundaries, the function E is continuous and has continuous first and second derivatives. The continuity of mixed second partials

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} \tag{2.9}$$

leads to a thermodynamic identity

$$\left(\frac{\partial T}{\partial V}\right)_{S,\mathbf{N}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\mathbf{N}} \tag{2.10}$$

which is one of four *Maxwell relations* that are often needed to transform thermodynamic expressions.

Extensive and Intensive Properties

The properties E, S, V, and N are *extensive* properties; for a given thermodynamic state, the magnitude of each property is linearly proportional to the amount of substance as measured by total mass M. The properties T, P and μ_i are *intensive* properties which are independent of the amount of substance.

An important consequence of the extensive nature of all properties in (2.7) is that if we increase the size of the system by a factor α, all properties increase in direct proportion.

$$\alpha E(S, V, N) = E(\alpha S, \alpha V, \alpha \mathbf{N}) . \tag{2.11}$$

Differentiating this equation with respect to α and setting $\alpha = 1$, we obtain

$$E = \left(\frac{\partial E}{\partial S}\right)_{V,\mathbf{N}} S + \left(\frac{\partial E}{\partial V}\right)_{S,\mathbf{N}} V + \sum_{i=1}^{K} \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}} N_i . \tag{2.12}$$

Using (2.8) to replace each of the partial derivatives with the associated thermodynamic property, we obtain

$$E = TS - PV + \sum_{i=1}^{K} \mu_i N_i \tag{2.13}$$

For fluid dynamics applications it is more convenient to work with mass specific quantities as the volume of a fluid element is a fictional notion which does not have a definitive value. These are

$$e = E/M \qquad s = S/M \qquad v = V/M \qquad n_i = N_i/M \tag{2.14}$$

where M is mass of substance. The equation of state terms of these variables is $e(s, v, \mathbf{n})$ and the fundamental relationship for a unit mass of substance in terms of specific properties is

$$\mathrm{d}e = T\mathrm{d}s - P\mathrm{d}v + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i \tag{2.15}$$

and energy can be defined as

$$e = Ts - Pv + \sum_{i=1}^{K} \mu_i n_i . \tag{2.16}$$

Thermodynamic Potentials

Internal energy $E(S, V, \mathbf{N})$ is an example of a *thermodynamic potential*. We can use *Legendre transformations* to transform the independent variables and create alternative versions of these potentials. The fundamental idea for a generic function F of two variables (x, y) is that to transform to a new function $C(x, z)$ where

$$z = \left(\frac{\partial B}{\partial y}\right)_x \tag{2.17}$$

we define C as follows

$$C(x, z) = B(x, y) - y\left(\frac{\partial B}{\partial y}\right)_x . \tag{2.18}$$

Applying this idea sucessively to the energy function, we can define three new functions.

$$\text{enthalpy} \quad H \equiv E + PV = TS + \sum_{i=1}^{K} \mu_i N_i \tag{2.19}$$

$$\text{Helmholtz} \quad A \equiv E - TS = -PV + \sum_{i=1}^{K} \mu_i N_i \tag{2.20}$$

$$\text{Gibbs} \quad G \equiv E - TS + PV = \sum_{i=1}^{K} \mu_i N_i \tag{2.21}$$

Each of these potentials has an associated differential form and a Maxwell relation as summarized in Table 2.1.

Table 2.1: Thermodynamic potentials and associated relationships.

energy:

$$E(S, V, \mathbf{N}) \quad = TS - PV + \sum_{i=1}^{K} \mu_i N_i \quad \mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{K} \mu_i \mathrm{d}N_i \quad \left(\frac{\partial T}{\partial V}\right)_{S,\mathbf{N}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\mathbf{N}} \tag{2.22}$$

enthalpy:

$$H(S, P, \mathbf{N}) \quad = TS + \sum_{i=1}^{K} \mu_i N_i \quad \mathrm{d}h = T\mathrm{d}S + V\mathrm{d}P + \sum_{i=1}^{K} \mu_i \mathrm{d}N_i \quad \left(\frac{\partial T}{\partial P}\right)_{S,\mathbf{N}} = \left(\frac{\partial V}{\partial S}\right)_{p,\mathbf{N}} \tag{2.23}$$

Helmholtz:

$$A(T, V, \mathbf{N}) \quad = -PV + \sum_{i=1}^{K} \mu_i N_i \quad \mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + \sum_{i=1}^{K} \mu_i \mathrm{d}N_i \quad \left(\frac{\partial S}{\partial V}\right)_{T,\mathbf{N}} = \left(\frac{\partial P}{\partial T}\right)_{V,\mathbf{N}} \tag{2.24}$$

Gibbs:

$$G(T, P, \mathbf{N}) \quad = \sum_{i=1}^{K} \mu_i \mathrm{d}N_i \quad \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_{i=1}^{K} \mu_i \mathrm{d}N_i \quad \left(\frac{\partial S}{\partial P}\right)_{T,\mathbf{N}} = -\left(\frac{\partial V}{\partial T}\right)_{P,\mathbf{N}} \tag{2.25}$$

Provide an example of how to use Cantera to evaluate the potentials.

Partial Molar Properties

For the thermodynamic treatment of mixtures, we need to consider how the properties depending on the amount of each species making up the substance.

For any property B, define the *partial molar property* as

$$\overline{B}_i \equiv \left.\frac{\partial B}{\partial N_i}\right|_{T,P,N_{k \neq i}} \tag{2.26}$$

The significance of this to computing mixture properties is due to *Euler's theorem for homogeneous functions*, which states that for a function $F(N_1, N_2, \ldots, N_k)$ which is homogeneous

$$F(\alpha N_1, \alpha N_2, \ldots, \alpha N_k) = \alpha F(N_1, N_2, \ldots, N_k) \tag{2.27}$$

then we can always write F as

$$F(N_1, N_2, \ldots, N_k) = \sum_{i=1}^{k} N_i \left(\frac{\partial F}{\partial N_i}\right)_{N_{k \neq i}} \tag{2.28}$$

This is a generalization of the idea used previously in discussing extensive properties and can be demonstrated by differentiating (2.27) with respect to α and set $\alpha = 1$ to obtain (2.28).

Thermodynamic potentials as well as S and V are all extensive properties and therefore satisfy the conditions of (2.27) and can be written in the form of (2.28).

$$S = \sum_{i=1}^{k} N_i \overline{S}_i \qquad \overline{S}_i = \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.29}$$

$$V = \sum_{i=1}^{k} N_i \overline{V}_i \qquad \overline{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.30}$$

$$E = \sum_{i=1}^{k} N_i \overline{E}_i \qquad \overline{E}_i = \left(\frac{\partial E}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.31}$$

$$H = \sum_{i=1}^{k} N_i \overline{H}_i \qquad \overline{H}_i = \left(\frac{\partial H}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.32}$$

$$A = \sum_{i=1}^{k} N_i \overline{A}_i \qquad \overline{A}_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.33}$$

$$G = \sum_{i=1}^{k} N_i \overline{G}_i \qquad \overline{G}_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.34}$$

Partial molar properties play a particulary important role in the theory of solutions and multicomponent equilibria (Van Ness and Abbott, 1982, Smith et al., 1996). The definition of partial molar properties is motivated by the importance of the partial molar Gibbs energy to the computation of equilibrium at constant temperature and pressure.

$$\overline{G}_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.35}$$

The fundamental relation for Gibbs energy (2.25) identifies the partial molar Gibbs energy to be the chemical potential

$$\overline{G}_i = \mu_i(T, P, \mathbf{N})\,. \tag{2.36}$$

From the definition of the thermodynamic potentials and the corresponding fundamental relations we can also define the chemical potential as

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_{j\neq i}} = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}} . \tag{2.37}$$

Using the definition of G from (2.25), we obtain the *Gibbs-Duhem* relation

$$\sum_{i=1}^{K} N_i \mathrm{d}\mu_i = -S\mathrm{d}T + V\mathrm{d}P \tag{2.38}$$

Using the equality of mixed second partials we can compute the derivatives of $\overline{G}_i$ with respect to temperature and pressure to obtain

$$\left(\frac{\partial \overline{G}_i}{\partial T}\right)_{P,\mathbf{N}} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_{j\neq i}} = -\overline{S}_i \tag{2.39}$$

$$\left(\frac{\partial \overline{G}_i}{\partial P}\right)_{T,\mathbf{N}} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \overline{V}_i \tag{2.40}$$

which enables the determination of dependence of $\overline{G}_i$ on (T, P) at fixed composition

$$\mathrm{d}\overline{G}_i = -\overline{S}_i\mathrm{d}T + \overline{V}_i\mathrm{d}P \qquad \text{for fixed } \mathbf{N}. \tag{2.41}$$

The value of these relationships is that for fluids, the thermodynamic properties that can be determined most readily from experiments or theoretical considerations is a form of a $P(V, T, \mathbf{N})$ relationship. Analytical formulas fit to empirical data can be differentiated to obtain the partial molar properties and used to compute departures of the thermodynamic potentials from reference values. This is the strategy that is used to model chemical reactions in gases or fluids that have such significant molecular interactions that the ideal gas model is inappropriate (Melius et al., 1991, Schmitt and Butler, 1995a,b).

> Provide an example of how to use Cantera to evaluate partial molar properties using the Redlich-Kwong equation.

2.2 Ideal Gas

An ideal gas is a model of a gas in which the molecules[2] have negligible interactions aside from very brief collisions that serve to equilibrate the distribution of energy among the molecules and atoms. This is a useful approximation for real gases over a wide range of temperature and pressure; applying both to pure substances (a gas composed of a single species) and to homogeneous mixtures of multiple species. Collisions result in a common temperature for all species but otherwise there is no influence of one species on another. The size of the molecules or atoms is also small in comparison to the average distance between the molecules, so that the volume that the molecules occupy is negligible compared to the total volume occupied by the gas.

The mathematical basis of ideal gases can be expressed in terms of the following ideas which are often presented as physical laws or theorems. Although these are reliable guides to gas behavior under the conditions described in the previous paragraph, these ideas are not universal truths like the laws of thermodynamics.

1. **Ideal Gas Law** A quantity of N kmols of gas at pressure P and temperature T in volume V obeys the following relationship

$$PV = N\mathcal{R}T , \tag{2.42}$$

   where $\mathcal{R}$ is the *universal gas constant*, 8314.5 J·kmol^{-1}·K^{-1}. $\mathcal{R} = k_B N_A$ where k_B is the *Boltzmann constant* (1.381×10^{-23} J·K^{-1}) and N_A is *Avogadro's number* (6.022×10^{26} molecules·kmol^{-1}).

---

[2]We use the term molecules in this section but in general this can also include atoms, ions or even electrons as well as multi-atom molecules.

2. **Dalton Law of Partial Pressures** The total pressure P in a gas is the sum of the individual *partial pressures* P_i of each of the i components

$$P = \sum_{i=1}^{K} P_i \ , \tag{2.43}$$

and each component individually obeys the ideal gas law

$$P_i V = N_i \mathcal{R} T \ . \tag{2.44}$$

3. **Gibbs's Theorem** "A partial molar property (other than volume) of a constituent species in an ideal-gas mixture is equal to the corresponding molar property of the species as pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture. " (see Smith et al., 1996, p. 330)

$$\overline{B}_i^{i.g.} = B_i(T, P_i) \tag{2.45}$$

Where B is any thermodynamic property (other than volume) and B_i is the specific molar property of an ideal gas component i. For example, the specific thermodynamic potentials of a species i will have units J·kmol^{-1}.

Single Component Properties

This subsection needs to have some examples added of how to evaluate these quantities using Cantera.

According to Gibbs's Theorem the molar properties of a single component determines the partial molar properties of that component in an ideal gas mixture. In this section we begin by considering a gas composed of a single component and then subsequently extend the treatment to a mixture of ideal gases using Gibb's Theorem.

Internal energy

The Ideal Gas Law has significant implications for the dependence of molar internal energy E on the thermodynamic state. Consider $E(V,T)$ and use (2.10) and (2.6) to compute the dependence of E on volume

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \ . \tag{2.46}$$

Upon substituting (2.42) for the $P(V,T)$ relationship, the right-hand side is found to be identically zero, so we conclude that

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \qquad \text{for an ideal gas.} \tag{2.47}$$

Unlike real gases and liquids, the internal energy of an ideal gas does not depend on either pressure or volume but only temperature and the amount of substance. For pure substances, the dependence on the amount of substance can be eliminated for extensive properties by dividing by the amount of substance to define specific properties. In analogy to the definition of partial molar properties, the molar specific properties are defined by the overline notation, e.g., the molar specific internal energy is

$$\overline{E} = \frac{E}{N} \ . \tag{2.48}$$

and

$$\overline{E} = \overline{E}(T) \quad \text{only.} \tag{2.49}$$

Enthalpy

The specific enthalpy is also only a function of temperature since by definition

$$H \equiv E + PV \tag{2.50}$$

and using the Ideal Gas Law

$$H = E + N\mathcal{R}T \,, \tag{2.51}$$

we conclude

$$\overline{H} = \overline{H}(T) \,. \tag{2.52}$$

The specific enthalpy of an ideal gas does not depend on either pressure or volume but only temperature.

Heat Capacity

The specific heat capacity at constant volume is defined as

$$\overline{C}_V = \left(\frac{\partial \overline{E}}{\partial T} \right)_V \,, \tag{2.53}$$

and from the previous considerations about energy, is a function of temperature only

$$\overline{C}_V = \overline{C}_V(T) \,. \tag{2.54}$$

The specific heat capacity at constant pressure is defined as

$$\overline{C}_P = \left(\frac{\partial \overline{H}}{\partial T} \right)_P \,, \tag{2.55}$$

and from the previous considerations about enthalpy, is a function of temperature only

$$\overline{C}_P = \overline{C}_P(T) \,. \tag{2.56}$$

The relationship between energy and enthalpy implies that these two heat capacities differ by the universal gas constant

$$\overline{C}_P = \overline{C}_V + \mathcal{R} \,. \tag{2.57}$$

The heat capacities can be integrated to give an alternate expression for internal energy and enthalpy

$$\overline{E} = \overline{E}^\circ + \int_{T^\circ}^{T} \overline{C}_V(T') \, dT' \,, \tag{2.58}$$

$$\overline{H} = \overline{H}^\circ + \int_{T^\circ}^{T} \overline{C}_P(T') \, dT' \,. \tag{2.59}$$

These expressions are employed to compute the realistic thermodynamic properties using specific heat capacities determined from statistical mechanics and thermochemical measurements to find the reference properties $\overline{E}^\circ = \overline{E}(T^\circ)$ and $\overline{H}^\circ = \overline{H}(T^\circ)$. Only one of the reference properties needs to be specified, usually H°, as they are related by

$$\overline{E}^\circ = \overline{H}^\circ - \mathcal{R}T^\circ \,. \tag{2.60}$$

Entropy

The molar entropy of an ideal gas component can be computed from the fundamental relation for energy

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V \tag{2.61}$$

from the definition of specific heat capacity and the Ideal Gas Law

$$\overline{C}_V\,\mathrm{d}T = T\mathrm{d}\overline{S} - \frac{\mathcal{R}T}{\overline{V}}\,\mathrm{d}\overline{V}\ , \tag{2.62}$$

which we can rearrange to obtain

$$\mathrm{d}\overline{S} = \overline{C}_V(T)\,\frac{\mathrm{d}T}{T} + \mathcal{R}\,\frac{\mathrm{d}\overline{V}}{\overline{V}}\ . \tag{2.63}$$

Integrating both sides of this equation

$$\overline{S} = \overline{S}^{\circ} + \int_{T^{\circ}}^{T} \overline{C}_V(T')\,\frac{\mathrm{d}T'}{T'} + \mathcal{R}\ln(\overline{V}/\overline{V}^{\circ})\ , \tag{2.64}$$

where $(T^{\circ}, \overline{V}^{\circ})$ are reference states and $\overline{S}^{\circ} = \overline{S}(T^{\circ}, \overline{V}^{\circ})$ is the entropy evaluated at the reference state. Alternatively, we can start from the fundamental relation for enthalpy and definition of specific heat at constant pressure to obtain the equivalent expression

$$\overline{S} = \overline{S}^{\circ} + \int_{T^{\circ}}^{T} \overline{C}_P(T')\,\frac{\mathrm{d}T'}{T'} - \mathcal{R}\ln(P/P^{\circ})\ . \tag{2.65}$$

We can separate the temperature and pressure dependence and defining the terms with temperature dependence as $\overline{S}^{\circ}(T)$ we obtain

$$\overline{S} = \overline{S}^{\circ}(T) - \mathcal{R}\ln(P/P^{\circ})\ , \tag{2.66}$$

where

$$\overline{S}^{\circ}(T) = \overline{S}^{\circ} + \int_{T^{\circ}}^{T} \overline{C}_P(T')\,\frac{\mathrm{d}T'}{T'}\ . \tag{2.67}$$

The constant $\overline{S}^{\circ}$ has to be determined from thermodynamic and statistical mechanical considerations.

Helmholtz energy

The Helmholtz energy A can be computed from the energy and entropy

$$A = E - TS\ , \tag{2.68}$$

and the specific molar value is given by

$$\overline{A}(T, P) = \overline{E}(T) - T\overline{S}^{\circ}(T) + \mathcal{R}T\ln(P/P^{\circ}) \tag{2.69}$$

Gibbs Energy and Chemical Potential

The Gibbs energy can be computed from enthalpy and entropy

$$G = H - TS\ . \tag{2.70}$$

Substituting the expressions for specific enthalpy and entropy, we obtain

$$\overline{G} = \underbrace{\overline{H}^\circ + \int_{T^\circ}^T \overline{C}_P(T') - T\left(\overline{S}^\circ + \int_{T^\circ}^T \overline{C}_P(T')\frac{\mathrm{d}T'}{T'}\right)}_{\text{temperature dependence}} + \underbrace{\mathcal{R}T\ln(P/P^\circ)}_{\text{pressure dependence}} . \tag{2.71}$$

We can separate the temperature and pressure dependence and defining the terms with temperature dependence as $\overline{G}^\circ(T)$ we obtain

$$\overline{G} = \overline{G}^\circ(T) + \mathcal{R}T\ln(P/P^\circ) , \tag{2.72}$$

where the temperature dependence is all contained in

$$\overline{G}^\circ(T) = \overline{H}(T) - T\overline{S}^\circ(T) . \tag{2.73}$$

The chemical potential of an ideal gas is the molar Gibbs energy G

$$\mu(T, P) \equiv \overline{G}(T, P) , \tag{2.74}$$
$$\mu = \mu^\circ(T) + \mathcal{R}T\ln(P/P^\circ) , \tag{2.75}$$

where $\mu^\circ(T) = \overline{G}^\circ(T)$ and it is common to simplify this relationship by measuring P in units of P°

$$\mu(T, P) = \mu^\circ(T) + \mathcal{R}T\ln P . \tag{2.76}$$

This relationship is fundamental to the computation of chemical equilibrium in gases and through the principle of detailed balance, is used in computing consistent forward and reverse reaction rates.

> Provide examples of evaluating the properties of individual species using Cantera.

Ideal Gas Mixtures

The composition of a mixture has so far been specified by the amounts of each species $i = 1, 2, \ldots K$. These amounts can be specified as masses M_i of each species or moles N_i of each species. An alternative, non-dimensional method to specify composition is by mole or mass fraction. The mole fraction $X_i = N_i/N$ where N is the total number of moles of gas

$$N = \sum_{i=1}^K N_i . \tag{2.77}$$

The mass fraction $Y_i = M_i/M$ where M is the total mass of gas

$$M = \sum_{i=1}^K M_i , \tag{2.78}$$

where $M_i = \mathcal{W}_i N_i$ where $\mathcal{W}_i$ is the molar mass of species i. The partial pressures can be expressed in terms of total pressure and mole fractions.

$$P_i = X_i P . \tag{2.79}$$

The average molar mass of a mixture is

$$\mathcal{W} = \frac{M}{N} = \sum_{i=1}^K X_i \mathcal{W}_i . \tag{2.80}$$

The gas constant for a mixture can be written as

$$R = \frac{\mathcal{R}}{\mathcal{W}} . \tag{2.81}$$

The ideal gas law can then be written in terms of the average mass density.

$$\rho = \frac{M}{V} \qquad P = \rho R T . \tag{2.82}$$

Note that the average molar mass can also be written as

$$\frac{1}{\mathcal{W}} = \sum_{i=1}^{K} \frac{Y_i}{\mathcal{W}_i} , \tag{2.83}$$

and the mole (X_i) and mass (Y_i) fractions are related by

$$X_i = \frac{\mathcal{W}}{\mathcal{W}_i} Y_i . \tag{2.84}$$

When considering a unit mass or mol of material, it is most convenient to define the thermodynamic state of a mixture by two thermodynamic properties, e.g. (T, P), and the gas composition, which can be either the array of mass fractions $\mathbf{Y} = (Y_1, Y_2, \ldots, Y_k)$ or mole fractions $\mathbf{X} = (X_1, X_2, \ldots, X_k)$.

Partial Molar Properties

From the properties of the single component ideal gas and Gibbs's Theorem, we can define the partial molar properties of each component i in a mixture in terms of the thermochemical constants $\overline{H}_i^\circ$ and $\overline{S}_i^\circ$ for each species and the molar specific heat capacity $\overline{C}_{P,i}$. Representation of these three quantities for each species is the basis for realistic computations of thermochemistry and is discussed at length in Sections 3.3 and 5. When referring to the specific properties of the individual species in a mixture, it is conventional to drop the overline notation to simplify the presentation as follows:

$$\overline{E}_i = E_i(T) = E_i^\circ + \int_{T^\circ}^{T} C_{V,i}(T')\mathrm{d}T' . \tag{2.85}$$

$$\overline{H}_i = H_i(T) = H_i^\circ + \int_{T^\circ}^{T} C_{P,i}(T')\mathrm{d}T' , \tag{2.86}$$

where individual species specific heat capacities are related by

$$\overline{C}_{P,i} = C_{P,i} = C_{V,i} + \mathcal{R} . \tag{2.87}$$

The enthalpy and energy reference values are related by

$$H_i^\circ = E_i^\circ + \mathcal{R}T^\circ . \tag{2.88}$$

The specific molar entropy is

$$\overline{S}_i = S_i(T, P_i) = S_i^\circ(T) - \mathcal{R}\ln(P_i/P^\circ) , \tag{2.89}$$

$$S_i^\circ(T) = S_i^\circ + \int_{T^\circ}^{T} C_{P,i}(T') \frac{\mathrm{d}T'}{T'} . \tag{2.90}$$

$$S_i^\circ = S_i(T^\circ, P^\circ) \tag{2.91}$$

The specifc molar Helmholtz energy is

$$\overline{A}_i = A_i(T, P_i) = A_i^\circ(T) + \mathcal{R}T\ln(P_i/P^\circ) , \tag{2.92}$$

$$A_i^\circ(T) = E_i^\circ - TS_i^\circ(T) , \tag{2.93}$$

The specific molar Gibbs energy is

$$\overline{G}_i = G_i(T, P_i) = \mu_i(T, P) = \mu_i^\circ(T) + \mathcal{R}T\ln(P_i/P^\circ) , \tag{2.94}$$
$$\mu_i^\circ(T) = H_i(T) - TS_i^\circ(T) . \tag{2.95}$$

The partial molar volumes of an ideal gas are all identical and from the Ideal Gas Law can be computed to be

$$\overline{V}_i = \frac{\mathcal{R}T}{P} = \frac{V}{N} = \overline{V} \tag{2.96}$$

The specific properties of a species can also be expressed on a mass basis using the molar mass $\mathcal{W}_i$ for that species. Mass specific properties are used in formulating the equations of motion and are indicated by lower case letters and related to the molar specific properties as follows:

$$e_i = \frac{E_i}{\mathcal{W}_i} , \quad c_{v,i} = \frac{C_{V,i}}{\mathcal{W}_i} , \quad s_i = \frac{S_i}{\mathcal{W}_i} , \ \ldots \tag{2.97}$$

Mixture Average Properties

The total value of property can be computed from the definition of partial molar properties and Euler's theorem. For example

$$E = \sum_{i=1}^{K} M_i e_i(T) = \sum_{i=1}^{K} N_i E_i(T) \tag{2.98}$$

The mixture average mass specific properties are obtained by dividing by the total mass, e.g.

$$e = \frac{E}{M} , \tag{2.99}$$

and can be most conveniently written in term of the mass fractions, e.g.,

$$e = \sum_{i=1}^{K} Y_i e_i(T) \tag{2.100}$$

$$h = \sum_{i=1}^{K} Y_i h_i(T) \tag{2.101}$$

$$s = \sum_{i=1}^{K} Y_i s_i(T, P_i) \tag{2.102}$$

$$c_v = \sum_{i=1}^{K} Y_i c_{v,i}(T) \tag{2.103}$$

$$c_p = \sum_{i=1}^{K} Y_i c_{p,i}(T) \tag{2.104}$$

$$c_p = c_v + R \tag{2.105}$$

The Gibbs energy is most conveniently written in terms of the composition in specific moles, $n_i = N_i/M$ and the chemical potential.

$$g = \sum_{i=1}^{K} n_i \mu_i(T, P_i) \tag{2.106}$$

Provide examples of evaluating the properties of mixtures for ideal and real gases using Cantera.

2.3 Perfect Gases

A *perfect gas* has a heat capacity that is constant (independent of temperature). In mass units, the key properties of a single component perfect gas are

$$\frac{\mathrm{d}e}{\mathrm{d}T} = c_v \, , \tag{2.107}$$

$$e = e_\circ + c_v(T - T^\circ) \, , \tag{2.108}$$

$$\frac{\mathrm{d}h}{\mathrm{d}T} = c_p \, , \tag{2.109}$$

$$h = h_\circ + c_p(T - T^\circ) \, , \tag{2.110}$$

$$s = s_\circ + c_v \ln\left(\frac{T}{T^\circ}\right) + R\ln\left(\frac{v}{v_\circ}\right) \, , \tag{2.111}$$

$$s = s_\circ + c_p \ln\left(\frac{T}{T^\circ}\right) - R\ln\left(\frac{P}{P^\circ}\right) \, , \tag{2.112}$$

$$\tag{2.113}$$

The ratio of constant pressure to constant volume heat capacity of a perfect gas is a constant known as the *ratio of specific heats*

$$\gamma = \frac{c_p}{c_v} \, . \tag{2.114}$$

In terms of γ, the specific heat capacities are

$$c_v = \frac{R}{\gamma - 1} \qquad c_p = \frac{\gamma R}{\gamma - 1} \, . \tag{2.115}$$

2.4 Thermochemistry

> This section needs to have some examples added of how to evaluate these quantities using Cantera using specific examples of mixtures, discuss how heats of reaction depend on temperature.

The determination of the thermochemical properties relies on a combination of laboratory measurements, thermodynamics and statistical mechanical computations.

Heat of Reaction

A key thermodynamic concept in determining thermochemical properties is enthalpy change associated with a constant pressure reaction

$$\text{Reactants} \xrightarrow{P=const} \text{Products}$$
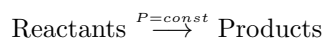
The First Law of Thermodynamics for a reaction process at constant pressure is

$$Q = \sum_{Products} N_i H_i(T_P) - \sum_{Reactants} N_j H_j(T_R) \, , \tag{2.116}$$

where Q is the thermal energy added ($Q > 0$) or removed ($Q < 0$) during the reaction process. If reactants and products are at the same temperature $T_R = T_P = T$, the thermal energy added or removed to maintain the reactor at a constant temperature is defined as the heat of reaction

$$\Delta_r H(T) = \sum_{Products} N_i H_i(T) - \sum_{Reactants} N_j H_j(T) \, . \tag{2.117}$$

For exothermic reactions $\Delta_r H < 0$, for endothermic reactions $\Delta_r H > 0$.

Standard heat of formation

The standard heat of formation $\Delta_f H^\circ$ is the heat of reaction for the formation of one mole of the species of interest from the elements in their most stable state at standard thermodynamic conditions, 298.15 K and either 1 atm (101.325 kPa) for older tabulations or 1 bar (100 kPa) for new tabulations

$$\Delta_f H_i^\circ = \Delta_r H(T^\circ) = H_i(T^\circ) - \sum_{Reactants} N_j H_j(T^\circ) \,. \tag{2.118}$$

where the reactants are the elements in the most stable state at T°, P°. For example, the heat of formation of gaseous water can determined to be -241.81 MJ·kmol^{-1} from the reaction

$$H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(g)$$
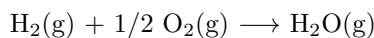
using calorimetry McGlashan (1979) and combusting hydrogen with oxygen.

The standard heat of formation is by definition, the enthalpy at the standard state $T = T^\circ = 298.15$ K.

$$\Delta_f H_i^o \equiv H_i(T^\circ) = H_i^\circ \tag{2.119}$$

because for the elements in their most stable state, the standard heat of formation is, *by definition*, zero.

$$\Delta_f H_i^o(\text{stable elements}) \quad \equiv 0 \tag{2.120}$$

Thermodynamic properties of various species have to be defined in a self-consistent fashion to reproduce the known experimental relationships for enthalpy and chemical equilibrium; see Chase et al. (1998) for a complete exposition of the methods used to do this. For example, suppose we need the enthalpy of formation of a species A and no measurement is available. The heat of formation can be computed using Hess's law which is simply a form of the conservation of energy. Given the heat of formation values for the compounds B-C and A-B-C and the heat of reaction for

$$A + B\text{-}C \longrightarrow A\text{-}B\text{-}C$$
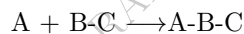
at standard conditions, then the enthalpy of formation of A can be determined using conservation of energy

$$\Delta_r H = \Delta_f H_A^\circ + \Delta_f H_{BC}^\circ - \Delta_f H_{ABC}^\circ \tag{2.121}$$

Therefore, solving for the heat of formation of species A yields

$$\Delta_f H_A^\circ = \Delta_r H - \Delta_f H_{BC}^\circ + \Delta_f H_{ABC}^\circ \tag{2.122}$$

Note that we have carried out the computation using the *molar enthalpy* which is consistent with the standard chemical practice and can be simply related to the stoichiometry of the reaction. The relationship to mass-specific enthalpy is simply $h_i = H_i/\mathcal{W}_i$. Consistent values for the standard state enthalpy and entropy have been evaluated from experimental data for a number of substances and are available in the JANAF compilation (Chase et al., 1998). However, in some cases experimentally-based values are not available, and the standard state enthalpy and entropy must be estimated using theoretical or empirical methods. The most common empirical method is known as the group additivity method, which is discussed in detail by Benson (1976).

A section on equilibrium constants for ideal and real gas mixtures is needed here.

Chapter 3

Statistical Mechanics and Thermodynamics

The thermodynamic data provided with Cantera and used in the Shock and Detonation Toolbox come from many sources. As discussed above, the standard state enthalpy and entropy are determined from experimental data or semi-empirical data. However, the temperature dependence of the specific heat (and by implication, the enthalpy and entropy) are usually based on statistical mechanics. A sketch of the methodology is given below and the full details are found in numerous textbooks, a simple one is Maczek (2004), and detailed presentations are given in McQuarrie (1976) and specifically for combustion in Chapter 8 of Kee et al. (2003).

The key concept in statistical mechanics is that there exists a *partition function* that contains all the information needed to determine the properties of a system consisting of a large number of molecules in thermodynamic equilibrium. The thermodynamic properties of the system, such as the internal energy, pressure, entropy, and enthalpy, can all be expressed in terms of functions of the partition function or its derivatives. The partition function can be constructed by finding the quantum states and energy levels for the system of molecules.

The fundamental relation between thermodynamics and statistical mechanics connects the Helmholtz energy A and the *system partition function*, $\mathcal{Q}$.

$$A - A_0 = -k_B T \ln \mathcal{Q} \tag{3.1}$$

The constant A_0 and similar constants for the other thermodynamic potentials are introduced to make the statistical mechanics results consistent with the thermodynamic standard state. Statistical mechanics and the computational methods of quantum mechanics used to estimate energy levels in molecules consider the zero energy state to be nuclei and electrons separated by an infinite distance (Irikura and Frurip, 1998). However, the ground state (lowest energy) of the molecules where the electrons are bound most tightly to the nuclei corresponds to the thermodynamically stable state. The zero level of the heat of formation is chosen (arbitrarily) to be that of the reference elements at the standard state. In order to obtain the constants A_0 for each species that will agree with the thermochemical convention for heat of formation, a formation reaction has to be selected and the heat of reaction determined with ab initio computations of electronic structure of the other species and Hess' Law. Using the experimental standard state enthalpies of the other species in the reaction, Hess' Law and the ab initio heat of reaction can be used to define the standard state heat of formation of the species of interest and by further computation, the constant A_0. Entropy is computed in a different fashion, using the Third Law of Thermodynamics to define the entropy at absolute zero and integrating all contributions from $T = 0$ to T° as described in Irikura and Frurip (1998).

For combustion and high-temperature gas dynamics applications, additional simplifications are possible. For a system consisting of N independent and indistinguishable molecules (Maxwell-Boltzmann statistics) at high temperatures, the partition function can be defined in terms of the products of the partition function q for each molecule

$$\mathcal{Q} = \frac{q^N}{N!} \tag{3.2}$$

and is a function of the independent variables (N, V, T). The *molecular partition function* q is determined from the geometry and fundamental properties of a molecule, such as the geometrical configuration (bond

length and angles), mass of the atoms, moments of inertia, vibrational modes and frequencies, and electronic energy levels. Atoms are just a special case of molecules and the partition function for an atom is constructed in a similar fashion to that of a molecule but only translation and electronic energy states are considered.

These molecular partition functions are computed as the sum over the Boltzmann factors for all possible quantum states of the molecule.

$$q = \sum_{states\ j} \exp\left(-\frac{\epsilon_j}{k_B T}\right) \tag{3.3}$$

where ϵ_j is the energy of state j relative to the energy of the ground state of the molecule. If the sum is done in terms of energy levels instead of quantum states then the sum is written in terms of g_i, the degeneracy (multiplicity) of each molecular energy level

$$q = \sum_{energies\ j} g_j \exp\left(-\frac{\epsilon_j}{k_B T}\right) . \tag{3.4}$$

The simplifying assumption usually made in computing the energies is to assume that interactions between translational (t), rotational (r), vibrational (v), electronic (e), and nuclear (n) motions can be neglected and the total energy computed as the sum of indepedently computed energy levels for each type of motion

$$\epsilon = \epsilon_\mathrm{t} + \epsilon_\mathrm{r} + \epsilon_\mathrm{v} + \epsilon_\mathrm{e} + \epsilon_\mathrm{n} . \tag{3.5}$$

In that case the molecular partition function will be composed of a product of partition functions corresponding to each separable (independent) motions and the net molecular partition function can be expressed as the product

$$q = q_t q_r q_v q_e q_n . \tag{3.6}$$

The conventional assumption is that $q_n = $ constant and for most purposes can be taken to be one. A less restrictive assumption that enables accounting for the known coupling between the internal modes (rotation, vibration, electronic, and nuclear) is to only separate the motion into external (translation) and internal models

$$q = q_t q_i . \tag{3.7}$$

This assumption (known as the *Born-Oppenheimer* approximation) is justified by the vastly different time scales for the motion of the molecules relative to each other as compared to the motions of the electrons and the nuclei within a molecule. The relative molecular motion is mediated by the relatively weak *intermolecular* potential as compared to the strong electrostatic forces and quantum exchange effects that determine the *intramolecular* potentials. The most common example of the intramolecular coupling is between vibration and rotation. The higher the vibration or rotational state, the larger the mean separation of the nuclei which increases the rotational moment of inertia and decreases the vibrational frequency. The nuclear spin also has to be accounted for when computing the finer details of the rotational energy levels and the partition functions, and is particularly important at low temperature or for high accuracy computations. For homonuclear molecules such as N_2, O_2 or H_2, considerations about nuclear spin and the symmetric properties of the wavefunction place additional restrictions on the rotational states in comparison to heteronuclear molecules like NO, CH, or OH; see McQuarrie (1976, Ch. 6.5).

3.1   Molecular Partition Functions and RRHO model

The computation of the individual partition functions relies on solving for the quantum energy levels based on models of the molecular structure and dynamics (McQuarrie, 1976). The translational partition function is a special case and the sum can be converted to an integral since there are such large number of states

available in typical macroscopic volumes and the energy levels are closely spaced together. After carrying out the integration, the result can be simply expressed as

$$q_t = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V \tag{3.8}$$

where V is the system volume, m is the atom or molecule mass in kg, and h is Planck's constant.

For the rotational modes, the basic model is that of the rigid rotator in each independent axis of rotation. The energy levels are quantized and there are multiple quantum states for each energy level with the details depending on the shape of the molecule and symmetry properties. The fundamental idea is that rotation is quantized and the total angular momentum can only have discrete values that are multiples of $\hbar = h/2\pi$. For a linear molecule, there is an infinite set of angular momentum energy levels labeled by the index J, each with energy

$$\epsilon_J = J(J+1)\frac{\hbar^2}{2\mathcal{I}} \quad J = 0, 1, 2, \dots \tag{3.9}$$

where $\mathcal{I}$ is the moment of inertia. A diatomic molecule with masses m_1 and m_2 and internuclear spacing r_e has $\mathcal{I} = \mu r_e^2$, $\mu = m_1 m_2/(m_1+m_2)$. The rotational energy levels are often expressed in terms of spectroscopic constant B

$$\epsilon_J = J(J+1)hcB , \qquad B = \frac{h}{8\pi^2 \mathcal{I}c} \quad . \tag{3.10}$$

For simple heteronuclear molecules, each rotational energy level is *degenerate* with $g_J = 2J+1$ quantum states with energy ϵ_J and the allowed radiative transitions (emission or absorption of photons) between energy levels are $\Delta J = \pm 1$. This is only true for diatomic molecules with distinct nuclei, molecules with multiple indistinguishable nuclei have more complex degeneracy and radiative transition rules. The spacing between energy levels is

$$\Delta\epsilon = \epsilon_{J+1} - \epsilon_J \tag{3.11}$$

$$= (J+1)\frac{\hbar^2}{\mathcal{I}} \tag{3.12}$$

Defining the characteristic rotational temperature as

$$\Theta_r = \frac{\hbar^2}{2\mathcal{I}k_B} \tag{3.13}$$

and evaluating this numerically we find that $\Theta_r \leq 10$ K except for molecules that contain light atoms, especially hydrogen. For cases where $T > 10\Theta_r$, the partition function sum can be approximated as an integral

$$q_r = \frac{T}{\sigma\Theta_r} \tag{3.14}$$

where the symmetry factor $\sigma = 1$ for unsymmetrical molecules like CO, NO and OH, and $\sigma = 2$ for symmetrical molecules like O_2, N_2, and CO_2. In general, the symmetry factor is equal to the number of indistinguishable configurations that can be generated by rotation. The case of nonlinear molecules is more complex and depends on the rotational symmetry class (Ch. 8 McQuarrie, 1976) of the molecule. For a nonlinear molecule that is asymmetric, there will be three principal moments of inertia $\mathcal{I}_1$, $\mathcal{I}_2$, $\mathcal{I}_3$ and three corresponding characteristic rotational temperatures Θ_{r1}, Θ_{r2}, Θ_{r3}. The high-temperature limit of the partition function is

$$q_r = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_{r1}\Theta_{r2}\Theta_{r3}}\right)^{1/2} \tag{3.15}$$

For the vibrational modes, the simplest model is that each mode is represented as a simple harmonic oscillator with a single vibrational frequency ω_i and there is one quantum state per energy level. The harmonic oscillator model has quantized energy levels labeled by index n

$$\epsilon_n = (n + \tfrac{1}{2})\hbar\omega \quad n = 0, 1, 2, \ldots \tag{3.16}$$

with allowed radiative transitions $\Delta n = \pm 1$. For a diatomic molecule, ω corresponds to the classical frequency of the harmonic motion in a potential

$$V(r) = \tfrac{1}{2}k(r - r_e)^2 \tag{3.17}$$

where r_e is the equilibrium distance between the nuclei and the characteristic oscillator frequency is

$$\omega = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} . \tag{3.18}$$

The partition function can be computed exactly for this model

$$q_v = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \tag{3.19}$$

where the characteristic vibrational temperature is

$$\Theta_v = \frac{\hbar\omega}{k_B} . \tag{3.20}$$

For multi-atom (greater than two) molecules, the characteristics frequencies and modes of oscillations have to be determined by finding the normal modes that correspond to small oscillations of the nuclei about equilibrium positions in a specified molecular electronic state. If there are n_a atoms in the molecule, there are $n_v = 3n_a - 5$ vibrational modes for linear molecules and $n_v = 3n_a - 6$ modes for nonlinear molecules, each mode has a characteristic vibrational frequency ω_i and corresponding temperature Θ_{vi}. The vibrational partition function is the product

$$q_v = q_{v1}q_{v2} \ldots q_{vn_v} \tag{3.21}$$

$$= \prod_{i=1}^{n_v} \frac{e^{-\Theta_{vi}/2T}}{1 - e^{-\Theta_{vi}/T}} \tag{3.22}$$

The electronic contributions are represented by q_e and for most combustion problems it is usually possible to consider only the ground or first excited state but multiple electronic states are needed to model the thermodynamics of high-temperature gas dynamics, plasma physics or astrophysical situations. The electronic quantum states consist of a set of discrete levels with energy ϵ_{ek} with degeneracy g_{ek}. The partition function is

$$q_e = g_{e1}e^{-\varepsilon_{e1}/k_BT} + g_{e2}e^{-\varepsilon_{e2}/k_BT} + \ldots . \tag{3.23}$$

The electronic energy levels depend on the choice of a reference state for zero energy datum. For atoms, the reference state is chosen as the neutral atom ground state at zero temperature, i.e., no electronic excitation and $\varepsilon_{e1} = 0$ and the higher energy levels are measured as differences from the ground state $\varepsilon_{ek} = \Delta\varepsilon_{k-1}$. For ionized atoms, the energy levels are all higher than the neutral species by an amount equal to the *ionization energy* ε_I and the partition function for the ionized atom is

$$q_{e,I} = e^{-\varepsilon_I/k_BT} \left(g_{e1,I} + g_{e2,I}e^{-\Delta\varepsilon_{e2,I}/k_BT} + \ldots \right) . \tag{3.24}$$

For molecules, the ground state energy is less than the separated atoms due to the energy of bonds between the constituents as discussed in the next section.

Energy Level Conventions

The datum from which energy is measured is a matter of convenience and consistency with thermodynamic convention. The convention in molecular modeling is to take the zero of energy corresponding to the configuration of widely separated atoms in their ground state. For that convention, $\epsilon_1 = -D_e$, the minimum of the potential energy function relative to the separated atoms, $D_e = V(r \to \infty) - V_{min}$. The energy D_e is slightly larger than the energy D_0 that is needed to dissociate the molecule starting from the lowest vibrational state due to the *zero-point energy* $\frac{1}{2}\hbar\omega$ of the lowest vibrational state. For a multi-vibrational mode molecule, there are zero-point energies associated with each mode so that

$$D_0 = D_e - \sum_{i=1}^{n_v} \tfrac{1}{2}\hbar\omega_i \tag{3.25}$$

The convention in spectroscopy is to measure the minimum of the potential energy for each electronic state from the minimum of the ground state, which corresponds to $\epsilon_{e1} = 0$. To make computed energies consistent with the conventions of chemical thermodynamics (discussed in the previous section), an additive constant E_0 has to be determined and used to adjust the statistical mechanical result for energy as described below. The linkage between dissociation energy and thermodynamic values of enthalpy is that the heat of reaction for dissociation computed from the enthalpies of formation extrapolated to absolute zero (McBride et al., 2002) is equal to the dissociation energy. For example, consider the dissociation of N_2

$$N_2 \longrightarrow N + N \quad . \tag{R1}$$

At $T = 0$ K, the heat of reaction is identical the energy of reaction because $H = E + \mathcal{R}T$ implies $H(0) = E(0)$. The heat of reaction for dissociation is

$$\Delta_R H = H_N(0 \text{ K}) + H_N(0 \text{ K}) - H_{N_2}(0 \text{ K}) \tag{3.26}$$

using the values in Table B1 of McBride et al. (2002), we find that

$$\Delta_R H = 466.483 + 466.483 - (-8.670) \tag{3.27}$$
$$= 941.636 \text{ kJ} \cdot \text{mol}^{-1} \tag{3.28}$$

The energy of dissociation determined from spectroscopic measurements (see Barklem and Collet, 2016, Table 2) is $D_0 = 9.75394$ eV or 941.112 kJ·mol^{-1}, which is very reasonable agreement. In general, evaluating the internal energy with (3.57) and extrapolating to $T = 0$ K, we find that

$$E(0 \text{ K}) = E_o + N_a \left(\sum_{i=1}^{n_v} \tfrac{1}{2}\hbar\omega_i + \epsilon_{e1} \right) \quad . \tag{3.29}$$

This relationship and the thermodynamic value of the $E(0 \text{ K})$ will determine the constant E_0 for a particular choice of electronic energy reference state that determines ϵ_{e1}.

The energy difference between isolated atoms and a molecule with energy $-D_e$ relative to the isolated atoms can be accounted for by multiplying the vibrational partition by the factor

$$\exp^{\dfrac{D_e}{k_B T}} \tag{3.30}$$

With this convention, the vibrational energies are measured relative to the potential energy minimum which can be computed from the dissociation energy $D_\circ$ using (3.25). Molecules with multiple excited electronic states will have distinct sets of vibrational-rotational modes for each electronic level that have to be accounted for in constructing the internal partition function. For thermodynamic conditions where these excited states make a significant contribution to the partition functions, the sum over quantum states must correctly account for the electronic levels. If the electronic energy levels are widely spaced, each electronic state can be considered individually and the internal partition function will be the product of factors corresponding to each electronic level. At typical combustion temperatures, it is typical to only consider the ground electronic state when computing the thermodynamic properties although the first electronic state is important spectroscopic applications.

3.2   Spectroscopic Approach for Diatomic Molecules

The rigid-rotator harmonic oscillator model with decoupling of all internal states is often a useful approximation. However, for some cases, and to have the highest accuracy, it is essential to include coupling between the states. There are a number of physical processes that can be significant in computing energy levels and partition functions including rotational stretching, low-temperature rigid rotation, Fermi resonance, anharmonicity, vibration-rotation interactions and coupling of spin (electronic and nuclear) with orbital angular momentum as well as symmetry considerations that restrict the admissible quantum states. Including these effects requires numerical solution of the quantum molecular structure at the appropriate level of approximation to treat these processes or by semi-empirical methods based on corrections to the RRHO model and precision spectroscopic data. The methodology for computing partition functions is described in McBride and Gordon (1992), Gordon and McBride (1999).

The spectroscopy and statistical mechanics of diatomic molecules and atoms has been extensively studied and there is a substantial literature on computing partition functions using spectroscopic data. The molecular electronic, vibrational and rotational states for many diatomic molecules are tabulated in two NIST data bases: diatomic spectra and chemistry webbook. See p. 73-83 and Eq. 2.97 of Boyd and Schwartzentruber (2017) to translate the spectroscopic symbols for molecular states into degeneracy factors. States for all of these atoms and molecules (including NO and NO+) are tabulated in Park (1990), at the end of Chapter 1. Chapter 9 and 10 of Hanson et al. (2016) and Bernath (2016) give a more in depth discussion of the fundamentals of electronic structure of atoms and molecules. Another source of data is the astrophysics community, Barklem and Collet (2016) have critically evaluated and made available for download data on a large number of diatomic molecules.

The energy levels derived from spectroscopic measurement for diatomic molecules are given in term of expansions in integer powers of the vibrational and rotational quantum numbers (n, J). One way of doing this is to use the *Dunham* coefficients $Y_{k,l}$ and the formula

$$E(n, J) = \sum_{k,l} Y_{k,l}(n + \tfrac{1}{2})^k [J(J + 1)]^l . \tag{3.31}$$

Many papers and some databases, particularly the multivolume compilations of Herzberg and Huber **Molecular Spectra and Molecular Structure**, use a different nomenclature and a translational table between conventional and Dunham notation is given below.

$k \setminus l$	0	1	2	3	4
0		B_e	$-D_e$	H_e	L_e
1	ω_e	$-\alpha_e$	$-\beta_e$		
2	$-\omega_e x_e$	γ_e			
3	$\omega_e y_e$				
4	$\omega_e z_e$				

The spectroscopically determined energy levels or *terms* are fit to empirical functions of the quantum levels in order to account for anharmonicity and vibrational-rotational coupling. The spectroscopic levels are conventionally given in terms of wavenumber units (cm^{-1}) and have to be converted to standard energy units (J). In the following formulas for the rotational and vibrational term functions F and G, the coefficients are specific to the particular electronic state k being considered but have not been explicitly labeled as such. The total energy for a state labeled with electronic, vibrational and rotational quantum levels (k, n, J) is

$$E(k, n, J) = E_\mathrm{r}(k, n, J) + E_\mathrm{v}(k, n) + E_\mathrm{e}(k) . \tag{3.32}$$

The rotational contribution to the energy is

$$E_\mathrm{r} = hcF_n(J) , \tag{3.33}$$

$$F_n(J) = B_n J(J + 1) - D_n J^2 (J + 1)^2 , \tag{3.34}$$

where the first term represents the rigid rotor contribution to the energy with corrections for the effect of vibration on the mean distance between atoms in the molecule

$$B_n = B_e - \alpha_e(n + \tfrac{1}{2}) + \gamma_e(n + \tfrac{1}{2})^2 \ , \tag{3.35}$$

and the second term represents the effect of the rotation on increasing the mean distance between atoms in the molecule. The term D_n is the *centrifugal distortion constant* and contains a small correction associated with the effect of vibration on the mean distance between atoms

$$D_n = D_e + \beta_e(n + \tfrac{1}{2}) \ . \tag{3.36}$$

The vibrational contribution is

$$E_{\rm v} = hcG(n) \tag{3.37}$$

and contains a series of terms, the first of which can be associated with the simple harmonic motion and the higher powers represent the corrections for the anharmonic nature of realistic potential energy interactions between the atoms in the molecule

$$G(n) = \omega_e(n + \tfrac{1}{2}) - \omega_e x_e(n + \tfrac{1}{2})^2 + \omega_e y_e(n + \tfrac{1}{2})^3 + +\omega_e z_e(n + \tfrac{1}{2})^4 \ . \tag{3.38}$$

The electronic contribution is

$$E_{\rm e} = hcT_{e,k} \ . \tag{3.39}$$

The internal energy partition function is computed with a triple sum over the states

$$q_i = \sum_{k=1}^{k_{max}} \sum_{n=0}^{n_{max}} \sum_{J=\Lambda}^{J_{max}} g_\Lambda(2S + 1)(2J + 1)\exp\left(-\frac{E(k, n, J)}{k_B T}\right) \tag{3.40}$$

The factor $2S + 1$ accounts for the degeneracy associated with the electron spin, $2J + 1$ is the degeneracy associated with rotation of the nuclei about the center of mass, Λ is the total orbital angular momentum of the electronic state ($\Lambda = 0, 1, 2$ for Σ, Π and Δ states). The factor g_Λ represents the effects of Λ-doubling and nuclear hyperfine structure. Π and Δ states have degeneracy of 2 and Σ is nondegenerate. For a heteronuclear molecule, i.e., two distinct nuclei, the $g_\Lambda = 1$ for a Σ electronic state or $g_\Lambda = 2$ for any other state (Π, Δ, etc). For a homonuclear molecule, i.e., two indistinguishable nuclei, the value of g_Λ depends on the value of J, the nuclear spin I, and the symmetry properties of the electronic wavefunction as shown in Table 3 of Irwin (1987).

The upper limits n_{max} and J_{max} on the sums for vibrational and rotational states are determined by requiring that the combined effects of vibration and rotation do not cause dissociation of the molecule. One simple way of implementing this is to find the largest values of (n, J) for each electronic state k such that the combined vibrational and rotational energy do not exceed the dissociation energy of the molecule.

$$E_{\rm v}(k, n, J) + E_{\rm r}(k, n, J) \le D_e(k) \ . \tag{3.41}$$

The highest vibration state possible n_{max} is the vibration level ($J = 0$) which has the highest energy but does not exceed the potential well depth D_e.

$$G(n_{max} + 1) > D_e \quad \text{and} \quad G(n_{max}) < D_e \ . \tag{3.42}$$

For a given vibrational level n, the highest value of $J = J_{max}(n)$ that is possible is bounded by same considerations. Other bounds can be generated by considering the dependence of the functions $G(n)$ and $F_n(J)$ on the states Irwin (1987). Physically reasonable energy levels should be non-decreasing with quantum