Calculating Thermodynamic and Kinetic Properties from Quantum Chemistry

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1 THERMOCHEMICAL PROPERTIES

1.1 QUANTUM CHEMISTRY AND THE 0 K LIMIT

The energies obtained from quantum-chemical calculations almost universally correspond to the 0 K limit and represent the electronic energy of the system under investigation. Of course, the systems we wish to investigate in the laboratory setting are always at some finite temperature. If, for instance, one is interested in the relative stability of different materials or the thermodynamics of a given chemical reaction, the energetic properties at 0 K are only going to tell part of the story. The question, therefore, is how do we convert the computed 0 K properties to one at a given temperature? More specifically, how can we compute common thermodynamic properties, such as enthalpies, entropies, and Gibbs free energies, which are so crucial to understanding various chemical phenomena?

1.2 ZERO-POINT VIBRATIONAL ENERGY

Before we introduce temperature-based corrections to the computed 0 K electronic energy, we need to first acknowledge that there is another component to the total energy of a system in the 0 K limit – the zero-point vibrational energy (ZPVE). While it may seem paradoxical at first, the vibrational modes of a given system also contribute to the total energy in the 0 K limit. This purely quantum-mechanical phenomenon is due to the fact that the lowest vibrational energy state that the molecule retains even at 0 K is non-zero.

The ZPVE can be readily computed from a frequency analysis carried out on the system of interest, wherein the vibrational modes are computed. If these vibrational frequencies, denoted $\bar{\nu}_i$, have dimensions of 1/[length] (as is the case for the commonly used unit of wavenumbers, cm^{-1}), then these frequencies can be readily converted into vibrational energies, ε_i, via

$$\varepsilon_i = hc\bar{\nu}_i \tag{1}$$

where h and c are Planck's constant and the speed of light in a vacuum, respectively. Under the harmonic oscillator approximation (see Equation A11 in the Appendix), the energy due to vibrational motion at 0 K, E_{ZPVE}, can then quite simply be calculated as

$$E_{\text{ZPVE}} = \sum_i \frac{\varepsilon_i}{2} \tag{2}$$

This equation comes from the fact that the energy of the lowest vibrational level under the harmonic oscillator approximation is $\varepsilon_i/2$, and we are simply summing each one of these lowest-energy vibrational levels up throughout the system. While Equation (2) assumes that each vibrational mode is harmonic in character, this is typically a good approximation when it comes to calculating E_{ZPVE}. Adding this ZPVE correction to the 0 K electronic energy provides the true 0 K energy of the system, which is sometimes written as the 0 K internal energy

$$U_0 = E + E_{\text{ZPVE}} \tag{3}$$

where E is the 0 K electronic energy. With this, we can now consider thermodynamic corrections.

1.3 FROM PARTITION FUNCTIONS TO THERMOCHEMISTRY

The connection between the 0 K state of the system and the state at some finite temperature can be made through the use of the molecular partition functions, Q. This can be readily appreciated by recalling some fundamental thermodynamic definitions from statistical mechanics, namely that[1]

$$U = k_{\mathrm{B}} T^2 \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N,V} \tag{4}$$

and

$$A = -k_{\mathrm{B}} T \ln(Q) \tag{5}$$

where U is the internal energy, k_{B} is Boltzmann's constant, T is the absolute temperature, and A is the Helmholtz free energy. With Equations (4) and (5), we can compute the remaining thermochemical properties via simple thermodynamic relationships. Importantly, we can also state that the entropy, S, can be calculated via

$$S = \frac{U - A}{T} = k_{\mathrm{B}} \ln(Q) + k_{\mathrm{B}} T \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N,V} \tag{6}$$

1.4 FACTORIZING THE PARTITION FUNCTION

Before we calculate Q, we first need to ask ourselves: what is Q composed of? First, let's make a distinction. Typically, we are interested in the thermodynamic properties of an ensemble of N molecules. We will first tackle the partition function for one molecule, denoted Q_1. Since the total energy of a molecular system is the sum of translation (q_{trans}), vibrational (q_{vib}), rotational (q_{rot}), and electronic (q_{el}) components, we can say that the molecular partition function is the product of all its individual components, such that

$$Q_1 = q_{\mathrm{trans}} q_{\mathrm{vib}} q_{\mathrm{rot}} q_{\mathrm{el}} \tag{7}$$

The reason we multiply, rather than add, the different components of Q_1 together is because the thermodynamic properties of interest all involve taking the natural logarithms of the molecular partition function, such that the product of partition functions appropriately gives component-based sums of the thermodynamic properties of interest.

The partition function for N indistinguishable molecules can be written similarly:

$$Q = \frac{Q_1^N}{N!} = \frac{(q_{\mathrm{trans}})^N}{N!} q_{\mathrm{vib}}^N q_{\mathrm{rot}}^N q_{\mathrm{el}}^N \tag{8}$$

If we were to plug Q into a natural logarithm, as is often the case when computing thermodynamic properties, we would arrive at

$$\ln(Q) = \ln\left(\frac{(q_{\mathrm{trans}} q_{\mathrm{vib}} q_{\mathrm{rot}} q_{\mathrm{el}})^N}{N!} \right) = N(\ln(q_{\mathrm{trans}}) + \ln(q_{\mathrm{vib}}) + \ln(q_{\mathrm{rot}}) + \ln(q_{\mathrm{el}})) - \ln(N!) \tag{9}$$

which can be rewritten using Stirling's approximation to

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[1] Here, we are writing U such that it is the energy that needs to be added to U_0 in order to get the total internal energy of the system at a given temperature. In other words, we have written U using U_0 as the zero-energy reference point. This is a common convention in computational chemistry, where the expressions derived in this section are thought of as thermodynamic "corrections" that can be added the 0 K electronic energy and ZPVE.

$$\ln(Q) \approx N(\ln(q_\text{trans}) + \ln(q_\text{vib}) + \ln(q_\text{rot}) + \ln(q_\text{el})) - N\ln(N) + N \tag{10}$$

for large N, which is typically the case when attempting to model a real chemical system.

We have now clarified the individual components of Q, but this only changes the question: how do we calculate the translational, vibrational, rotational, and electronic components of Q? In principle, one must know all possible quantum states for the system, which is rarely practical. Instead, several assumptions and approximations can be made such that Q can be readily obtained.

1.5 TRANSLATIONAL PARTITION FUNCTION

If we assume the system is well-modeled under the quantum-mechanical particle-in-a-box approximation, the translational partition function is given by

$$q_\text{trans} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \tag{11}$$

where m is the mass of the molecule and V is the volume from the particle-in-a-box model. The above equation is only true for a 3D particle-in-a-box. If a molecule is constrained such that it can move in only two or one dimensions, the exponential term would be 1 or 1/2. The derivation for Equation (11) is given in the Appendix.

The volume term V is related to the choice of reference state for the system. For an ideal gas, the V term can be rewritten such that

$$q_\text{trans} = \frac{k_\text{B} T}{P^\circ}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \tag{12}$$

where P° is the reference state pressure, typically taken as 1 bar as convention (but should always be specified). Sometimes, the definition of q_trans in Equation (11) will be written such that it does not have the V term (i.e. such that it has units of inverse volume and is written out as q_trans/V). In this case, q_trans/V typically has a value of approximately 10^{24} cm^{-3}.

With this, we can compute the translational components of the thermodynamic properties of interest. Plugging Equation (12) into Equation (4) yields

$$U_\text{trans} = \frac{3}{2}k_\text{B} T \tag{13}$$

and Equation (12) into Equation (6) yields

$$S^\circ_\text{trans} = k_\text{B}\left(\ln\left(\frac{k_\text{B} T}{P^\circ}\left(\frac{2\pi m k_\text{B} T}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right) \tag{14}$$

In the calculation of S°_trans, we have tacitly assumed that the $-N\ln(N) + N$ component in Equation (10) is lumped in with the translational component, as is common convention. We have specified the $\circ$ superscript on the entropy to remind ourselves that it is dependent on the choice of reference state.

Fortunately, the translational components are quite simple to calculate, as they do not require any quantum-chemical calculations at all. All you need is the mass of the system and the specified temperature.

1.6 VIBRATIONAL PARTITION FUNCTION

If we assume the system is well-modeled by the harmonic oscillator quantum-mechanical model, the vibrational partition function can be written as

$$q_{\text{vib}} = \prod_i \frac{1}{1 - e^{-\frac{\varepsilon_i}{k_{\text{B}}T}}} \tag{15}$$

where the product is carried out over all vibrational energies ε_i. For a linear molecule, there will be $3N - 5$ vibrational modes, whereas there will be $3N - 6$ vibrational modes for a nonlinear molecule. The derivation of Equation (15) can be found in the Appendix. For reference, the value of q_{vib} is unitless and is approximately a value of 1 in terms of order of magnitude.

By plugging in Equation (15) into Equation (4), we can state

$$U_{\text{vib}} = \sum_i \frac{\varepsilon_i}{e^{\frac{\varepsilon_i}{k_{\text{B}}T}} - 1} \tag{16}$$

and by plugging in Equation (15) into Equation (6), we get

$$S_{\text{vib}} = k_{\text{B}} \sum_i \left(\frac{\varepsilon_i}{k_{\text{B}}T \left(e^{\frac{\varepsilon_i}{k_{\text{B}}T}} - 1 \right)} - \ln \left(1 - e^{-\frac{\varepsilon_i}{k_{\text{B}}T}} \right) \right) \tag{17}$$

It is clear from the above expressions that the vibrational energies (and thereby frequencies) are needed. These can be obtained a frequency analysis of the optimized structure. Note that monatomic species will not have any vibrational frequencies, in which case all the vibrational contributions to the thermodynamic functions are non-existent.

1.7 ROTATIONAL PARTITION FUNCTION

If we assume the system is well-modeled by the rigid-rotor quantum-mechanical model, the rotational partition function for a linear molecule can be written as

$$q_{\text{rot linear}} = \frac{k_{\text{B}}T}{\sigma\Theta} \tag{18}$$

where σ is the symmetry number (i.e. the number of ways a molecule can be oriented in indistinguishable ways) and Θ is the rotational temperature (here in units of J) defined by

$$\Theta \equiv \frac{h^2}{8\pi^2 I} \tag{19}$$

where I is the (degenerate) moment of inertia. The symmetry number of a monatomic species or one without any symmetry is given by 1. Note that sometimes the rotational temperature is given in units of K (as the name suggests), in which case a factor of k_{B} can be used to interconvert between the two. Sometimes it is given in units of inverse length (e.g. wavenumbers), in which case it is simply called the rotational constant and can be interconverted using a factor of hc.

Equation (18) is only true for linear molecules with a single, well-defined moment of inertia. For nonlinear molecules, the analogue of Equation (18) is given by

$$q_{\text{rot nonlinear}} = \frac{1}{\sigma}\left(\frac{\pi(k_\text{B}T)^3}{\Theta_\text{A}\Theta_\text{B}\Theta_\text{C}}\right)^{\frac{1}{2}} \tag{20}$$

where there is a given rotational constant corresponding to each principle axis of rotation in three dimensions. The rotational temperatures in Equation (20) are defined the same way as in Equation (19) except that the moment of degenerate moment of inertia I is now the principle moment of inertia (i.e. Θ_A uses I_A, Θ_B uses I_B, and Θ_C uses I_C).

The rotational constants are computed based on the definition of the moment of inertia, which is

$$I = \sum_i m_i r_i^2 \tag{21}$$

where m_i is the mass of atom i and r_i is the perpendicular distance of atom i to the axis of rotation. For a simple diatomic molecule, the moment of inertia is quite easy to compute and is given by μd^2, where μ is the reduced mass given by

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \tag{22}$$

and d is the bond length. Since one is rarely just dealing with diatomic molecules and the principle axes of rotation can be difficult to determine, most computational chemistry codes will provide the rotational constants of the structure upon performing a frequency analysis. The symmetry number can be determined based on the point group of the molecule, which can be automatically determined using various symmetry-detection algorithms. For reference, the value of q_{rot} is unitless and is approximately $10^2 - 10^4$ for linear molecules and $10^3 - 10^6$ for nonlinear molecules.

With this, we can get the rotational contribution to the internal energy by plugging in Equations (18) and (20) into (4) to yield

$$U = \begin{cases} k_\text{B}T, & \text{linear} \\ \dfrac{3}{2}k_\text{B}T, & \text{nonlinear} \end{cases} \tag{23}$$

Similarly, by plugging in Equations (18) and (20) into (6), the vibrational component of the entropy can be calculated as

$$S_{\text{rot}} = \begin{cases} k_\text{B}\left(\ln\left(\dfrac{k_\text{B}T}{\sigma\Theta}\right) + 1\right), & \text{linear} \\ k_\text{B}\left(\ln\left(\dfrac{1}{\sigma}\left(\dfrac{\pi(k_\text{B}T)^3}{\Theta_\text{A}\Theta_\text{B}\Theta_\text{C}}\right)^{\frac{1}{2}}\right) + \dfrac{3}{2}\right), & \text{nonlinear} \end{cases} \tag{24}$$

As with the vibrational degrees of freedom, a monatomic species has no contribution to the rotational thermodynamic properties.

1.8 ELECTRONIC PARTITION FUNCTION

The electronic partition function is related to the number of available electronic states. The electronic partition function is given by

$$q_{el} = \sum_i g_i e^{-\frac{E_i}{k_B T}} \tag{25}$$

where the sum is carried out over all electronic states i, g_i is the degeneracy of state i, and E_i is the electronic energy of state i with respect to the ground state. In other words, E_i is defined as 0 for the ground state. If the excited states are high in energy relative to the ground state and cannot be readily accessed then for a molecule, the electronic partition function simply becomes $q_{el} = g_0$ where g_0 is the degeneracy of the ground state. If the system of interest has no unpaired electrons, then the ground state energy occurs only once and $g_0 = 1$. If the system has unpaired electrons, then the degeneracy is given by $g_0 = n_{\text{unpaired e}^-} + 1$ such that

$$q_{el} = n_{\text{unpaired e}^-} + 1 \tag{26}$$

where $n_{\text{unpaired e}^-}$ is the number of unpaired electrons in the system (also written as $2S$ where S here is the spin quantum number and each electron is spin one-half). The value $n_{\text{unpaired e}^-} + 1$ is referred to as the spin multiplicity of the system. While many molecules as so-called "closed-shell" (i.e. have no unpaired electrons), there are many cases where unpaired electrons must be considered. For instance, a radical (e.g. Cl ·) by definition has one unpaired electron and therefore has a spin multiplicity of 2. Similarly, many transition metal complexes can exist in one of many different possible spin states, which must be considered. Another important molecule with unpaired electrons is gas-phase O_2, which (unlike most gases) has a ground state with two unpaired electrons (i.e. it has spin multiplicity of 3).

By plugging in Equation (26) into (4), we find that

$$U_{el} = 0 \tag{27}$$

and Equation (26) into (6), we find that

$$S_{el} = k_B \ln(n_{\text{unpaired e}^-} + 1) \tag{28}$$

for the situation where excited states are not readily accessible.

1.9   THERMOCHEMICAL PROPERTIES OF AN IDEAL GAS

For an ideal gas, the enthalpy is not a function of pressure. Therefore, we can state that

$$H(T) = E + E_{\text{ZPVE}} + \int_0^T C_P(T)\, dT \tag{29}$$

where E is the 0 K electronic energy, C_P is the constant-pressure heat capacity, and T is the absolute temperature. For an ideal gas, we know that

$$C_P(T) = k_B + C_V(T) \tag{30}$$

We also know that the definition of the constant-volume heat capacity is

$$C_V(T) \equiv \left(\frac{\partial U(T)}{\partial T}\right)_V \tag{31}$$

Therefore, we can rewrite the expression for $H(T)$ as

$$H(T) = E + E_{\text{ZPVE}} + U(T) + k_B T \tag{32}$$

for an ideal gas. Here, we can split $U(T)$ into its various components such that

$$U(T) = U_{\text{trans}}(T) + U_{\text{vib}}(T) + U_{\text{rot}}(T) + U_{\text{el}}(T) \tag{33}$$

The ideal gas entropy is calculated with respect to a reference pressure, as will be discussed in greater detail below. The ideal gas entropy, $S(T, P)$, is calculated as

$$S(T, P) = S(T, P°) - k_{\text{B}} \ln\left(\frac{P}{P°}\right) = S_{\text{trans}}° + S_{\text{vib}} + S_{\text{rot}} + S_{\text{el}} - k_{\text{B}} \ln\left(\frac{P}{P°}\right) \tag{34}$$

The Gibbs free energy is most often computed simply by its definition of

$$G(T, P) \equiv H(T) - TS(T, P) \tag{35}$$

With this, if the reaction Gibbs free energy ΔG were of interest, one would compute G for the product(s), G for the reactant(s), and subtract the two quantities. In this way, the thermodynamics of chemical reactions can be readily determined from quantum-chemical calculations.

As can be seen from the above equations, for an ideal gas, if we calculate E (obtained from the output of a quantum-chemical calculation), E_{ZPVE}, $U(T)$ and $S(T, P)$, then we can also get $H(T)$ and $G(T, P)$. Since vibrational frequencies are needed for calculating E_{ZPVE}, U_{vib}, and S_{vib}, many computational chemistry codes will compute various thermodynamic properties automatically after a vibrational frequency analysis has been performed.

2 KINETIC PROPERTIES

2.1 EYRING EQUATION FROM TRANSITION STATE THEORY

Transition state theory (TST) treats the activated intermediate as a real (but transient) species, which means that we can use thermodynamics to estimate its properties. Let us consider the unimolecular reaction given by

$$\text{A} \overset{K^{\ddagger}}{\leftrightarrow} \text{A}^{\ddagger} \rightarrow \text{P} \tag{36}$$

where the activated complex is in quasi-equilibrium with the reactant and has an equilibrium constant given by $K^{\ddagger}$. The equilibrium constant for this example reaction is given by

$$K^{\ddagger} = \frac{[\text{A}]^{\ddagger}}{[\text{A}]} \tag{37}$$

The rate of reaction, r, can be taken as simply

$$r = v^{\ddagger}\left[\text{A}^{\ddagger}\right] \tag{38}$$

where $v^{\ddagger}$ is the frequency of passage over the energy barrier and $\left[\text{A}^{\ddagger}\right]$ is the concentration of the activated complex. Using the definition of the equilibrium constant, we can rewrite the rate expression in terms of measurable concentrations as

$$r = v^{\ddagger} K^{\ddagger}[\text{A}] \tag{39}$$

We can define the frequency $v^{\ddagger}$ as the provided thermal energy such that

$$v^{\ddagger} = \frac{k_B T}{h} \tag{40}$$

Therefore,

$$r = \frac{k_B T}{h} K^{\ddagger} [A] \tag{41}$$

Recall that we can relate the equilibrium constant to the Gibbs free energy change such that

$$\Delta G^{\ddagger} = -RT \ln(K^{\ddagger}) \tag{42}$$

We can then use the fact that

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger} \tag{43}$$

to say

$$K^{\ddagger} = \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \tag{44}$$

We can then write the rate expression as

$$r = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) [A] \tag{45}$$

The above expression is the Eyring equation from TST. We can immediately see that it takes the form of

$$r = k[A] \tag{46}$$

if we define

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \tag{47}$$

However, there is a big problem. The units of k are always in s^{-1} in this equation, regardless of the molecularity of the reaction. As a result, Eyring's TST equation only has the correct units for unimolecular reactions and does not work as-written for higher molecularities, such as the bimolecular reaction $A + B \rightarrow P$.

Strictly speaking, Eyring's TST equation is only applicable for first order reactions of the type $A \rightarrow P$. The more accurate equation for the rate constant, accounting for different molecularities, should be

$$k = C^{\circ(1-n)} \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \tag{48}$$

where C° is a reference concentration and n is the molecularity. The reference concentration is typically given by $P^{\circ}/k_B T$ where the reference pressure P° is typically 1 bar when dealing with ideal gases. The more rigorous derivation of this reference concentration factor can be found in the following subsection and uses the partition functions directly in the calculation of the rate constant. Here, the need for C° comes from the reference state used in calculating $\Delta S^{\ddagger}$. Therefore, the choice of P° must be identical both in the use of C° (if applying the ideal gas law) and in calculating $\Delta S^{\ddagger}$. As-written in Equation (48), k is on a molecule basis and can be converted to a mol basis using P°/RT instead of $P^{\circ}/k_B T$.

2.2 GENERALIZED RATE EXPRESSION

A more rigorous way of approaching the expression for the rate constant is by using the partition functions directly. For any equilibrium process, we can write the equilibrium constant as

$$K = \exp\left(-\frac{\Delta U_0}{RT}\right) \prod_i \left(\frac{Q_i}{V}\right)^{\nu_i} \tag{49}$$

where ΔU_0 is the 0 K change in internal energy (i.e. $E + E_{\text{ZPVE}}$). For the bimolecular reaction $A + B \rightarrow P$, we can say

$$K^{\ddagger} = \frac{\frac{Q^{\ddagger}}{V}}{\frac{Q_A}{V}\frac{Q_B}{V}} \exp\left(-\frac{\Delta U_0^{\ddagger}}{RT}\right) \tag{50}$$

Therefore, the rate expression can be given by

$$r = \frac{k_B T}{h} \frac{\frac{Q^{\ddagger}}{V}}{\frac{Q_A}{V}\frac{Q_B}{V}} \exp\left(-\frac{\Delta U_0^{\ddagger}}{RT}\right)[A][B] \tag{51}$$

This is reminiscent of the Arrhenius equation. We can say that the pre-exponential factor, A, is

$$A = \frac{k_B T}{h} \frac{\frac{Q^{\ddagger}}{V}}{\frac{Q_A}{V}\frac{Q_B}{V}} \tag{52}$$

such that the rate constant k is given by

$$k = A \exp\left(-\frac{\Delta U_0^{\ddagger}}{RT}\right) \tag{53}$$

and then we get the functional form of

$$r = k[A][B] \tag{54}$$

like we would expect. Unlike with the derivation of the Eyring equation, here the units are appropriate because they rely on the number of reactant molecular partition functions (and q_{trans}/V has units of inverse volume). Therefore, the generalized rate constant expression can be correctly written in its general form as

$$k = \frac{k_B T}{h} \frac{\frac{Q^{\ddagger}}{V}}{\prod_i^{\text{reactants}}\left(\frac{Q_i}{V}\right)} \exp\left(-\frac{\Delta U_0^{\ddagger}}{RT}\right) \tag{55}$$

As-written in Equation (55), k is on a molecule basis and can be converted to a mol basis using Avogadro's constant, N_A, via

$$k = N_A^{n-1} \frac{k_B T}{h} \frac{\frac{Q^{\ddagger}}{V}}{\prod_i^{\text{reactants}}\left(\frac{Q_i}{V}\right)} \exp\left(-\frac{\Delta U_0^{\ddagger}}{RT}\right) \tag{56}$$

While both Equation (48) and (56) are fundamentally identical, Equation (56) is the rigorous way to show that k has the appropriate units regardless of the dimensionality. Nonetheless, in practice, Equation (48) is more commonly used in the area of computational chemistry given that most quantum chemistry packages automatically compute H and S when a frequency analysis is performed.

3 APPENDIX

3.1 DERIVATION OF THE TRANSLATIONAL PARTITION FUNCTION

Recall from quantum mechanics that the one-dimensional particle-in-a-box solution to the Schrodinger wave equation is given by

$$E_{n,1D} = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \tag{A1}$$

where E_n is the energy of quantum number n, m is the mass of the system, and L is the length of the box. Note that $\hbar$ is the reduced Planck constant, given by $h/2\pi$. We can write the partition function for a one-dimensional, single particle-in-a box as the following

$$q_{\text{trans 1D}} = \sum_{n=1}^{\infty} e^{-\frac{E_n}{k_B T}} = \sum_{n=1}^{\infty} e^{-\gamma n^2} \approx \int_0^{\infty} e^{-\gamma n^2} \, \mathrm{d}n = \frac{L}{\lambda_D} \tag{A2}$$

where

$$\gamma \equiv \frac{1}{k_B T} \frac{\hbar^2 \pi^2}{2mL^2} \tag{A3}$$

and

$$\lambda_D = \left(\frac{2\pi \hbar^2}{m k_B T} \right)^{\frac{1}{2}} \tag{A4}$$

This only applies for sufficiently small γ for the summation to be computed as an integral. The λ_D term is known as the thermal de Broglie wavelength. To scale this up to a 3D particle-in-a-box, the energy term must be modified to become

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right) \tag{A5}$$

such that the partition function for a single particle in the 3D box becomes

$$q_{\text{trans}} = L^3 \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} = \frac{L^3}{\lambda_D^3} \tag{A6}$$

Substituting V for L^3 (and using h instead of $\hbar$ for simplicity) then yields

$$q_{\text{trans}} = V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} = \frac{V}{\lambda_D^3} \tag{A7}$$

3.2 DERIVATION OF THE VIBRATIONAL PARTITION FUNCTION

Under the harmonic oscillator quantum-mechanical model, the vibrational energy for a single vibrational mode is given by

$$E_{n,1 \text{ mode}} = h\nu \left(n + \frac{1}{2} \right) \tag{A9}$$

where ν is the vibrational frequency and n is the vibrational quantum number. The partition function for this single vibrational mode is then

$$q_{\text{vib,1 mode}} = \sum_{n=0}^{\infty} e^{-\frac{h\nu\left(n+\frac{1}{2}\right)}{k_B T}} = \frac{e^{-\frac{h\nu}{2k_B T}}}{1 - e^{-\frac{h\nu}{k_B T}}} \tag{A10}$$

To scale this up to multiple vibrational modes, we must rewrite Equation (A9) as

$$E_n = \sum_{i=1} h\nu_i \left(n_i + \frac{1}{2}\right) \tag{A11}$$

where the sum is carried out for all relevant vibrational modes. In analogy to Equation (A10), the vibrational partition function is then

$$q_{\text{vib}} = \prod_i \frac{e^{-\frac{h\nu_i}{2k_B T}}}{1 - e^{-\frac{h\nu_i}{k_B T}}} \tag{A12}$$

Oftentimes, it is standard convention to rewrite Equation (A11) such that the $n_i = 0$ states yield an energy of zero since this is the ZPVE and is typically separated out from the vibrational partition function, as shown in Equation (2). In this case, we can rewrite Equation (A12) as

$$q_{\text{vib}} = \prod_i \frac{1}{1 - e^{-\frac{h\nu_i}{k_B T}}} \tag{A13}$$

3.3 DERIVATION OF THE ROTATIONAL PARTITION FUNCTION

Under the rigid-rotor quantum-mechanical model, the energy of a single rotational degree of freedom for a specified quantum number ℓ is given by

$$E_\ell = \frac{\hbar^2 \ell(\ell + 1)}{2I} \tag{A14}$$

where I is the moment of inertia and $\hbar$ is the reduced Planck constant given by $h/2\pi$. With this definition, the rotational partition function is

$$q_{\text{rot}} = \sum_{\ell=0}^{\infty} (2\ell + 1)e^{-\frac{\hbar^2\ell(\ell+1)}{2Ik_B T}} = \sum_{\ell=0}^{\infty} (2\ell + 1)e^{-\frac{\Theta\ell(\ell+1)}{k_B T}} \tag{A15}$$

where Θ is the rotational constant defined as

$$\Theta \equiv \frac{\hbar^2}{2I} \tag{A16}$$

For $\Theta \ll k_B T$, which is often the case except at temperatures close to absolute zero, we can approximate the summation as an integral to get

$$q_{\text{rot}} \approx \int_0^{\infty} (2\ell + 1)e^{-\frac{\Theta\ell(\ell+1)}{k_B T}} \, d\ell = \frac{k_B T}{\Theta} \tag{A17}$$

Strictly speaking, this formula also needs to take into account the symmetry of the molecule and therefore

$$q_{\text{rot}} = \frac{k_{\text{B}}T}{\sigma\Theta} \tag{A18}$$

where σ is the symmetry number (i.e. the number of ways a molecule can be oriented in indistinguishable ways) and is related to the point group of the molecule. The above expression is only true for linear molecules with a single, well-defined moment of inertia. For nonlinear molecules,

$$q_{\text{rot}} = \frac{1}{\sigma}\left(\frac{\pi(k_{\text{B}}T)^3}{\Theta_{\text{A}}\Theta_{\text{B}}\Theta_{\text{C}}}\right)^{\frac{1}{2}} \tag{A19}$$

where Θ_{A}, Θ_{B}, and Θ_{C} are the three rotational constants (one for each spatial dimension, resulting from the different moments of inertia that exist in each dimension).