Chapter 30: Statistical Mechanics

Calculate K_p for ½ H_2 (g) + ½ Cl_2 (g) ⇄ HCl (g) at 25°C from spectroscopic data.

Statistical mechanics is the bridge between the world of single molecules and macroscopic thermodynamic systems. Statistical mechanics is one of the three major sub-disciplines within physical chemistry, which are quantum mechanics, statistical mechanics, and thermodynamics. The quantum structure of atoms and molecules directly determines thermodynamic properties. The molecular information necessary to determine thermodynamic potentials is derived from spectroscopy. The most important goal is to understand the molecular basis of chemical equilibrium. The equilibrium constant is the ratio of the number of accessible product states divided by the number of accessible reactant states. We need to build insight into how different aspects of molecular structure effect the position of equilibrium. We need to develop efficient working expressions to calculate reaction Gibbs energies and equilibrium constants of gas phase reactions. Statistical mechanics presents a richly meaningful perspective on chemical reactivity. The key underlying concept is that the available thermal kinetic energy is partitioned at random among the quantum states of the system. The equilibrium state is the most probable distribution. Fluctuations away from the most probable distribution are quite small. All the information necessary to characterize the thermodynamic properties of a system is contained in the molecular partition function.

30.1 Review of Statistical Mechanical Principles

The goal of statistical mechanics is to determine the equilibrium state of systems and the corresponding thermodynamic potential energy functions: U, H, A, and G. The flow of the concepts is summarized in Figure 12.2.6. The thermodynamic properties of a system are determined by time averages. Time averages are difficult to determine, so instead ensemble averages are used. The state of the ensemble is determined by the distribution of the energy states of the systems within the ensemble, Figure 30.1.1a. The most probable distribution is the overwhelmingly predominant distribution. As a result the ensemble average is given by the most probable distribution. The most probable distribution is the equilibrium state of the ensemble, which is given by the Boltzmann distribution.

(a). (b).

Figure 30.1.1: (a). A canonical ensemble with $\mathcal{N}$ identical systems with volume V and N molecules. (b). The statistical distribution of systems in the canonical ensemble at equilibrium is determined by the Boltzmann distribution with probability $p_i = n_i/\mathcal{N}$.

The Boltzmann distribution gives the probability of occurrence of a given system energy state within the ensemble, which is a function of the energy states of the system E_i and the temperature T, Figure 30.1.1b:

$$p_i = \frac{n_i}{\mathcal{N}} = \frac{e^{-E_i/kT}}{Q} \qquad (12.4.21) \qquad 30.1.1$$

with n_i the distribution number and $\mathcal{N}$ systems in the ensemble. The canonical ensemble partition function, Q, is the sum of the Boltzmann weighting factors over all system energy states:

$$Q = \sum_{i=0}^{\infty} e^{-E_i/kT} \qquad \text{(all energy states)} \quad (12.4.21) \qquad 30.1.2$$

If energy levels are degenerate, the sum over all <u>states</u> can be replaced with a sum over all energy <u>levels</u> by taking the degeneracy of level i, g_i, into account:

$$p_i = \frac{n_i}{\mathcal{N}} = \frac{g_i\, e^{-E_i/kT}}{Q} \qquad \text{with} \quad Q = \sum_{i=0}^{\infty} g_i\, e^{-E_i/kT} \qquad \text{(all energy levels)} \qquad 30.1.3$$

To provide for easier reading, we often omit the summation limits in formulas, with the understanding that the sums are over all possible energy states or levels. We will show that all thermodynamic properties of the system can be expressed in terms of the partition function. The partition function is central in determining the relationship between molecular and thermodynamic properties.

Constraining the Number of Systems and the Total Energy of the Ensemble: The canonical ensemble is constructed from $\mathcal{N}$ identical systems, each system with the same volume V and number of molecules N. The ensemble is isolated from the surroundings, constraining the number of systems and the total energy of the ensemble, $\mathcal{E}$. The systems are distinguished by their fixed position within the ensemble. The systems are placed in thermal contact so that the systems are all at the same temperature T. A state of the ensemble is a specific configuration of system energies, for example: system 1 in system energy state E_6, system 2 in state E_3, system 3 in E_8, and so on for each system, Figure 30.1.1a. The internal energy and entropy of the system are given by the ensemble averages:

$$U - U(0) = \frac{\mathcal{E}}{\mathcal{N}} = \sum_{i=0}^{\infty} p_i E_i \qquad \text{(ensemble,12.2.6)} \qquad 30.1.4$$

$$S = \frac{k}{\mathcal{N}} \ln \mathcal{W}_{max} = -k \sum_{i=0}^{\infty} p_i \ln p_i \qquad \text{(ensemble,12.2.1,12.4.9)} \qquad 30.1.5$$

where $\mathcal{W}_{max}$ is the maximum number of ways of arranging the energy states of the ensemble. Maximizing $\mathcal{W}$ gives the most probable distribution. A process that increases $\mathcal{W}_{max}$ increases energy dispersal. Because the systems are distinguished by their position in the ensemble, $\mathcal{W}_{max} = W_{max}^{\mathcal{N}}$, where W_{max} is the maximum number of ways of arranging the states of a single system. As a simple example, for a two-system ensemble if systems A and B each have three possible states, taken together there are 3^2 possible states. The entropy with an $\mathcal{N}$ system ensemble is then:

$$S = \frac{k}{\mathcal{N}} \ln W_{max}^{\mathcal{N}} = k \ln W_{max} = -k \sum_{i=0}^{\infty} p_i \ln p_i \qquad \text{(system,12.4.22)} \qquad 30.1.6$$

This relationship allows us to think in terms of the properties of a single system, instead of an ensemble. The probability of the system being in system energy state E_i is given by the Boltzmann distribution, Eqs. 30.1.1-30.1.3.

30.2 The Boltzmann Distribution is the Most-Probable Distribution

Canonical Ensemble Partition Functions and Molecular Partition Functions: The canonical ensemble partition function is the sum of the Boltzmann weighting factors over all states of the system. Thinking about states of the system is inconvenient. We prefer to think in terms of individual molecules. Can we write the canonical ensemble partition function in terms of states of individual molecules? We can in the case of an ideal gas.

No forces act between molecules in an ideal gas; the molecules are independent. Under the assumption of independent molecules, the energy of a system in state i is the sum of the molecular energies:

$$E_i = \varepsilon_{a,i} + \varepsilon_{b,i} + \varepsilon_{c,i} + \ldots \qquad \text{(system)} \qquad 30.2.1°$$

where $\varepsilon_{a,i}$ is the energy of molecule a in system state i, $\varepsilon_{b,i}$ is the energy of molecule b in the same system state i, and similarly for each of the N molecules in the system, Figure 30.2.1.

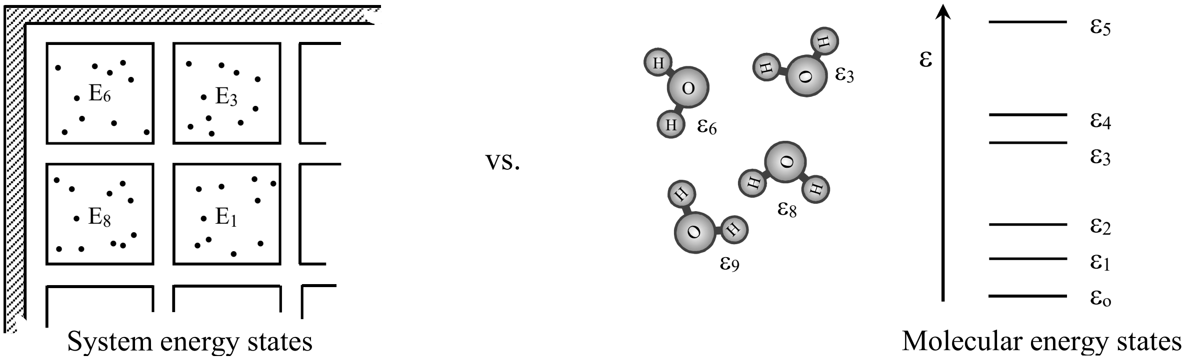


Figure 30.2.1: In the canonical ensemble, the ensemble partition function is replaced by the molecular partition function using $Q = q^N/N!$ for N identical molecules in the system.

The ensemble partition function is the sum over the Boltzmann weighting factors. Using Eq. 30.2.1° and noting that $e^{a+b} = e^a e^b$, the system weighting factor is the product of the weighting factors of each molecule:

$$Q = \sum_i e^{-E_i/kT} = \sum_i [e^{-\varepsilon_{a,i}/kT}\, e^{-\varepsilon_{b,i}/kT}\, e^{-\varepsilon_{c,i}/kT} \ldots] \qquad 30.2.2°$$

At this point it is tempting to ask if the sum of the products is the same as the product of the individual molecular sums:

$$Q \overset{?}{=} \sum_i e^{-\varepsilon_{a,i}/kT} \sum_i e^{-\varepsilon_{b,i}/kT} \sum_i e^{-\varepsilon_{c,i}/kT} \ldots \qquad 30.2.3°$$

The individual sums are over the energy states of a single molecule, for each molecule a, b, c, etc. The individual sums are the **molecular partition functions**:

$$q_a = \sum_i e^{-\varepsilon_{a,i}/kT}, \qquad q_b = \sum_i e^{-\varepsilon_{b,i}/kT}, \qquad \text{etc.} \tag{30.2.4°}$$

If Eq. 30.2.3° is true, the ensemble partition function is then simply the product of the individual molecular partition functions:

$$Q \overset{?}{=} q_a\, q_b\, q_c \ldots \tag{30.2.5°}$$

To explore if this relationship is correct, we consider an example of two identical molecules, a and b. Eq. 30.2.3° then reduces to just two multiplicative factors, one for molecule a and one for molecule b:

$$Q \overset{?}{=} (e^{-\varepsilon_{a,1}/kT} + e^{-\varepsilon_{a,2}/kT} + e^{-\varepsilon_{a,3}/kT} + \ldots)(e^{-\varepsilon_{b,1}/kT} + e^{-\varepsilon_{b,2}/kT} + e^{-\varepsilon_{b,3}/kT} + \ldots) \tag{30.2.6°}$$

Doing the multiplication gives cross terms of the form $e^{-\varepsilon_{a,1}/kT}\, e^{-\varepsilon_{b,2}/kT}$ and $e^{-\varepsilon_{a,2}/kT}\, e^{-\varepsilon_{b,1}/kT}$, which are diagrammed in Figure 30.2.2. The two different arrangements are indistinguishable because the two molecules are indistinguishable. The labels a and b are only used as conveniences to determine possible energy state assignments. We must not specify something that cannot be determined in the laboratory. One CO_2 molecule looks like any other CO_2 molecule. The requirement of experimental verification is also fundamental in establishing the Pauli Exclusion Principle, Sec. 25.4. For N molecules there are N! permutations of the labels among the indistinguishable molecules.

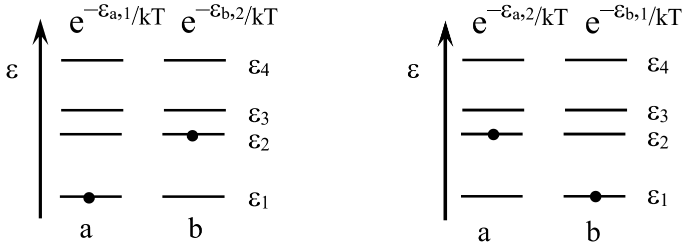


Figure 30.2.2: For indistinguishable molecules, the energy states ($\varepsilon_{a,1}$, ε_{b2}) and ($\varepsilon_{a,2}$, ε_{b1}) are indistinguishable and should not be counted separately. The molecule labels a and b cannot be determined experimentally.

To count only distinguishable states in a pure substance, the relationship in Eqs. 30.2.3° and 30.2.5° must be divided by N!. Since the molecules are identical, defining $q \equiv q_a = q_b = q_c$, gives the ensemble partition function in terms of the molecular partition function as:

$$Q = \frac{q^N}{N!} \qquad \text{indistinguishable molecules} \tag{30.2.7°}$$

On the other hand, if the molecules are of the same species, but are distinguishable by position, Eq. 30.2.5° is correct:

$$Q = q_a\, q_b\, q_c \ldots = q^N \qquad \text{distinguishable molecules} \tag{30.2.8°}$$

For example, in a solid, the molecules occupy fixed positions in a crystal lattice and may be distinguished by their positions in the lattice.

The validity of the factor of N! to account for indistinguishability depends on an additional approximation. The number of available quantum states must be much greater than the number of molecules. This approximation is called the **dilute limit** and is discussed in Sec. 30.6.

The Partition Function is the Number of Accessible States: The partition function can be interpreted in several important ways. The partition function is the normalization constant that ensures $\Sigma\ p_i = 1$. More importantly, the partition function is a measure of the **number of accessible states**. We consider three cases of a Boltzmann distribution over a set of equally spaced vibrational energy levels, Table 30.2.1. In the first case we assume that the spacing between the energy levels is much larger than the available thermal kinetic energy, $\Delta\varepsilon = 5$ kT. The probability of occupation of the $\upsilon = 1$ state is small. There is only one accessible state, q = 1.007. In the second case we assume that the energy level spacing is equal to the available thermal kinetic energy, $\Delta\varepsilon =$ kT. A broader distribution among the states results and the partition function increases to q = 1.582. In the third case we assume that the energy level spacing is smaller than the available thermal kinetic energy, $\Delta\varepsilon = 0.1$ kT. In this case there is sufficient energy to excite many molecules into higher energy states. A total of 114 states are necessary (not all shown in the table) to calculate the partition function, q = 10.508. We observe that q determines the average number of accessible states. This interpretation will be invaluable as we continue to relate thermodynamic variables to the partition function.

Table 30.2.1: Boltzmann Distribution of the Available Energy States. The partition function is the sum down the column of the Boltzmann weighting factors: $q = \Sigma\ e^{-\varepsilon_i/kT}$.

$\Delta\varepsilon$	= 5 kT		
υ	ε_i/kT	$e^{-\varepsilon i/kT}$	n_i/N
0	0	1	0.99
1	5	0.00674	0.01
2	10	0.00005	0.00
3	15		
4	20		
5	25		
6	30		
7	35		
8	40		
9	45		
10	50		
11	55		
12	60		
	q =	1.00678	

$\Delta\varepsilon$	= kT		
υ	ε_i/kT	$e^{-\varepsilon i/kT}$	n_i/N
0	0	1	0.63
1	1	0.3679	0.23
2	2	0.1353	0.09
3	3	0.0498	0.03
4	4	0.0183	0.01
5	5	0.0067	0.00
6	6	0.0025	
7	7	0.0009	
8	8	0.0003	
9	9	0.0001	
10	10		
11	11		
12	12		
	q =	1.5819	

$\Delta\varepsilon$	= 0.1	kT	
υ	ε_i/kT	$e^{-\varepsilon i/kT}$	n_i/N
0	0	1	0.10
1	0.1	0.90484	0.09
2	0.2	0.81873	0.08
3	0.3	0.74082	0.07
4	0.4	0.67032	0.06
5	0.5	0.60653	0.06
6	0.6	0.54881	0.05
7	0.7	0.49659	0.05
8	0.8	0.44933	0.04
9	0.9	0.40657	0.04
10	1	0.36788	0.04
↓	↓	↓	↓
114	11.4	0.00001	0.00
	q =	10.50823	

The Molecular Partition Function Factors into Translational, Rotational, Vibrational, and Electronic Partition Functions: The total energy of a molecule includes translational, vibrational, rotational, and electronic energies. Assuming ideal gas behavior and that translational, rotational, vibrational, and electronic energies are independent, the total molecular energy is the sum of each degree of freedom:

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e \qquad \text{(ideal gas, independent t,r,v,e)} \qquad 30.2.9°$$

Arguments parallel to Eqs. 30.2.2°-30.2.6° show that if the energy is a sum of independent terms, the corresponding partition function is the product of partition functions:

$$q = q_t\, q_r\, q_v\, q_e \qquad \text{(ideal gas, independent t,r,v,e)} \qquad 30.2.10°$$

where q_t, q_r, q_v, and q_e are the translational, rotational, vibrational, and electronic partition functions, respectively. The partition functions may then be considered separately. The individual partition functions are the number of accessible states occupied for the given degree of freedom. Taken together, rotation, vibration, and electronic degrees of freedom are called the **internal degrees of freedom**. The expression that we develop for the translational partition function is in the ideal gas limit and is based on the particle in a box model. The rotational partition function assumes a rigid-rotor. The vibrational partition function is in the harmonic approximation. The independence of the vibrational and electronic degrees of freedom is justified by the Born-Oppenheimer approximation. These approximations are usually sufficient to determine accurate values of the Gibbs energy and equilibrium constant of reactions of ideal gases near room temperature. By convention and for convenience, the correction for indistinguishability is grouped with the translational partition function, $Q = (q_t^N/N!)\,q_r^N\, q_v^N\, q_e^N$.

In the following discussions, the expressions for the molecular partition functions of translation, vibration, rotation, and electronic degrees of freedom are developed. In subsequent sections, these partition functions are used to determine the corresponding contributions to the internal energy, enthalpy, entropy, and Gibbs energy of a substance and to determine the Gibbs energy and equilibrium constants of chemical reactions.

The Translational Partition Function Depends on Volume: Translation of the center of mass of a molecule is independent of the internal degrees of freedom. The quantum mechanical model for translation of a molecule in an ideal gas is the particle in a box. Consider a rectangular box with side lengths a, b, and c. The volume of the container is then V = abc. The translational energy levels are given by Eq. 23.6.16. The x, y, and z components of the translation of the center of mass are independent with additive energies:

$$\varepsilon_t = \varepsilon_x + \varepsilon_y + \varepsilon_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad (23.6.16) \qquad 30.2.11°$$

where m is the molecule's mass and n_x, n_y, and n_z are the quantum numbers of the particle in the box energy levels, Figure 30.2.3.

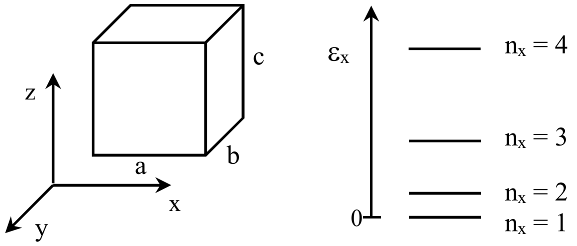


Figure 30.2.3: Molecular translation in an ideal gas is modeled by the particle in a box with volume V = abc. The energy levels for motion in the x-direction are illustrated.

Arguments parallel to Eqs. 30.2.2°-30.1.6° show that if the energy is a sum of independent terms, the corresponding partition function is the product of partition functions:

$$q_t = q_x\, q_y\, q_z \qquad 30.2.12°$$

where q_x, q_y, and q_z are the one-dimensional translational partition functions taken separately in the x, y, and z directions, respectively. The motion in a gas is isotropic, so that the x, y, and z partition functions are equivalent, except for the box side length. Considering just the x-direction, the translational partition function is the sum of the Boltzmann weighting factors over the energy levels of one-dimensional translation with quantum number n_x:

$$q_x = \sum_{i=1}^{\infty} e^{-\varepsilon_{x,i}/kT} = \sum_{n_x=1}^{\infty} e^{-h^2 n_x^2/8ma^2kT} \qquad 30.2.13°$$

For ease of calculation, the lower limit of the summation is changed from $n_x = 1$ to zero. The error introduced by this approximation is small; the Boltzmann weighting factor for $n_x = 0$ is $e^0 = 1$. The value of q_x, the number of accessible translational states, will turn out to be greater than 10^{10}, so that $10^{10}+1$ is a negligible error. At all but the lowest temperatures, the energy level spacing is much less than kT so that the summation in the last equation may be replaced by an integral over the quantum number:

$$q_x = \int_0^{\infty} e^{-h^2 n_x^2/8ma^2kT}\, dn_x \qquad (h^2/8ma^2 << kT) \qquad 30.2.14°$$

The energy levels approach a continuum of available energy states, which gives the classical limit. We will also use this approximation, the **high temperature approximation**, for rotations and low frequency vibrations. To determine the integral, we define a change in variables replacing the exponent by:

$$x^2 = \frac{h^2 n_x^2}{8ma^2kT} \qquad x = \frac{h}{a}\left(\frac{1}{8mkT}\right)^{½} n_x \qquad \frac{dx}{dn_x} = \frac{h}{a}\left(\frac{1}{8mkT}\right)^{½} \qquad 30.2.15$$

where n_x and x^2 both range from zero to infinity. Substitution of the change of variables into Eq. 30.2.14° gives:

$$q_x = \frac{a}{h}(8mkT)^{½} \int_0^{\infty} e^{-x^2}\, dx \qquad 30.2.16°$$

The integral is in the standard form $\int_0^{\infty} e^{-x^2}\, dx = \sqrt{\pi}/2)$ giving the integral as:

$$q_x = (2\pi mkT)^{½}\, \frac{a}{h} \qquad 30.2.17°$$

In an isotropic ideal gas, the y and z partition functions have the same form, differing only by the corresponding box length:

$$q_y = (2\pi mkT)^{½}\, \frac{b}{h} \qquad q_z = (2\pi mkT)^{½}\, \frac{c}{h} \qquad 30.2.18°$$

The overall translational partition is the product of the three terms, Eq. 30.2.12°, with V = abc:

$$q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V \qquad 30.2.19°$$

The units for this expression are the molecule's mass, m, in kg and the volume in m^3.

Example 30.2.1: *Translational partition function*
Calculate the translational partition function for CO_2. Use the volume occupied by one mole of ideal gas at standard state conditions and at 298.15 K.

Answer: For CO_2 the molar mass is $\mathfrak{M} = 44.01$ g mol^{-1} giving m = 7.308×10^{-26} kg.
At T = 298.15 K and standard state, P° = 1 bar, the volume of the container is the molar volume: $V^{\circ}_m = RT/P° = 24.79$ L = 0.02479 m^3. Using Eq. 30.2.19°, the translational partition function is:

$$q_t = [2\pi(7.308\text{x}10^{-26}\text{ kg})(1.38065\text{x}10^{-23}\text{ J K}^{-1})(298.15\text{ K})]^{3/2} \frac{0.02479\text{ m}^3}{(6.6261\text{x}10^{-34})^3} = 7.002\text{x}10^{30}$$

This example shows that the number of accessible translational states has a large magnitude. How many vibrational states are typically accessible?

The Vibrational Partition Function is a Power Series: The vibrational partition function of a harmonic oscillator is the sum of the Boltzmann weighting factors over energy levels $\varepsilon_\upsilon = h\nu_o(\upsilon + ½)$, Eq. 24.2.15:

$$q_v = \sum_{\upsilon=0}^{\infty} e^{-h\nu_o(\upsilon + ½)/kT} = e^{-h\nu_o/2kT} \sum_{\upsilon=0}^{\infty} e^{-h\nu_o\upsilon/kT} \qquad \text{(harmonic)} \qquad 30.2.20$$

where ν_o is the observed fundamental vibration frequency and υ is the vibrational quantum number. The zero point energy state is the $\upsilon = 0$ state with energy $\varepsilon_o = ½h\nu_o$. The common term of $e^{-h\nu_o/2kT}$ factors out of the summation and is the Boltzmann weighting factor of the zero-point energy state. The sum in Eq. 30.2.20 is evaluated using the substitution:

$$a = e^{-h\nu_o/kT} \qquad \text{giving} \qquad e^{-h\nu_o\upsilon/kT} = a^\upsilon \qquad \text{(harmonic)} \qquad 30.2.21$$

The sum is then a power series in a, which for the sum from $\upsilon = 0$ to ∞ has the value:

$$1 + a + a^2 + a^3 + \ldots = \frac{1}{1-a} \qquad \text{(harmonic)} \qquad 30.2.22$$

Substitution of $a = e^{-h\nu_o/kT}$ into the Eq. 30.2.22 and the resulting expression back into Eq. 30.2.20 gives the vibrational partition function as:

$$q_v = \frac{e^{-h\nu_o/2kT}}{1 - e^{-h\nu_o/kT}} \qquad (\text{harmonic, } \varepsilon_o = ½h\nu_o) \qquad 30.2.23$$

This partition function is applicable to a diatomic molecule or a normal mode of a polyatomic. For polyatomics the overall vibrational partition function is the product of the partition functions of each of the 3N – 5 or 3N – 6 normal modes:

$$q_v = q_{mode1}\, q_{mode2}\, q_{mode3}\ldots \qquad \text{(harmonic)} \qquad 30.2.24$$

The energy zero for Eq. 30.2.23 is the bottom of the potential energy well, Figure 30.2.4a. For many purposes, the energy zero is shifted to coincide with the zero-point energy level, Figure 30.2.4b. Instead of $\varepsilon_o = \frac{1}{2}h\nu_o$, the more convenient energy zero is $\varepsilon_o = 0$, and then the minimum of the potential energy well is at $-\frac{1}{2}h\nu_o$. The corresponding vibrational partition function is:

$$q_v = \frac{1}{1 - e^{-h\nu_o/kT}} = \frac{1}{1 - e^{-hc\tilde{\nu}_o/kT}} \qquad (\text{harmonic}, \varepsilon_o = 0) \qquad 30.2.25$$

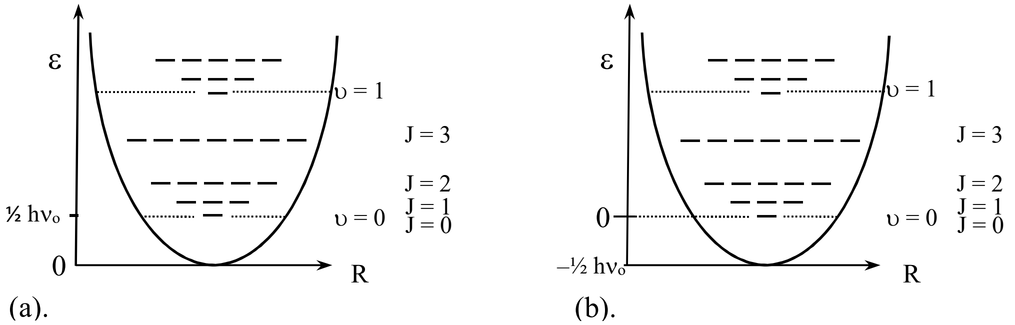


Figure 30.2.4: (a). Rotational and vibrational states for a diatomic molecule, referenced to the bottom of the potential energy well. (b). Reference to the lowest rotational and vibrational level, which is the zero-point energy, ZPE.

As a convenience in Eq. 30.2.25, the units of the fundamental vibration frequency are converted to wave numbers by $h\nu_o = hc\tilde{\nu}_o$. The observed fundamental vibration frequency provides the link between spectroscopy and molecular structure. This last expression can be cast into a convenient form for use at room temperature. At 25°C the constants can be combined to give the wave number equivalent of the temperature. At 298.15 K the wave number equivalent is:

$$\frac{kT}{hc} = 207.2244\ \text{cm}^{-1} \qquad 30.2.26$$

The available thermal kinetic energy at room temperature is 207.224 cm^{-1}. Substitution of this factor into Eq. 30.2.25 gives a particularly convenient form of the vibrational partition function:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}_o/207.224\ \text{cm}^{-1}}} \qquad (298.2\ \text{K, harmonic}, \varepsilon_o = 0) \qquad 30.2.27$$

The advantage of this expression is that the wave number of the transition can be read directly from the experimental spectrum, which highlights the close connection between the spectroscopic constants and the thermodynamic behavior. This expression is a direct and powerful instance of a **structure-function relationship**. Now, we can continue with a consideration of the effect of molecular rotation on the number of accessible states.

The Rotational Partition Function is Calculated in the High Temperature Approximation: As a rigid-rotor, the rotational energy of a linear molecule is given by $\varepsilon_J = \tilde{B}hc\ J(J + 1)$, Eq. 24.5.42, with degeneracy 2J + 1. The rotational partition function of a linear molecule is the sum of the Boltzmann weighting factors, accounting for the rotational degeneracy, Eq. 30.1.3:

$$q_r = \sum_{\upsilon=0}^{\infty} (2J + 1)\ e^{-\tilde{B}hc\ J(J+1)/kT} \qquad \tilde{B} = \frac{h}{8\pi^2 Ic} \qquad \text{(linear rigid rotor)} \qquad 30.2.28$$

The rotational constant provides the link between spectroscopy and molecular structure, since the moment of inertia is determined by the bond length. The moment of inertia of a diatomic is $I = \mu R^2$. This sum is easily calculated exactly by direct summation. However the rotational constant is usually smaller than the available thermal kinetic energy, $\tilde{B}hc << kT$, so that the summation can be approximated by an integral over all J values:

$$q_r = \int_0^{\infty} (2J+1)\ e^{-\tilde{B}hc\ J(J+1)/kT}\ dJ \qquad \text{(high T, rigid rotor)} \qquad 30.2.29$$

The relationship $\tilde{B}hc << kT$ is valid if the rotational constant is small or alternately if the temperature is high. This approximation is the **high temperature approximation**. The integral is simplified by noting that the derivative of the Boltzmann weighting factor gives:

$$\frac{d\left(e^{-\tilde{B}hc\ J(J+1)/kT}\right)}{dJ} = -\frac{\tilde{B}hc}{kT}(2J+1)\ e^{-\tilde{B}hc\ J(J+1)/kT} \qquad 30.2.30$$

Solving for the integrand in Eq. 30.2.29 and substitution into the integral gives:

$$q_r = -\frac{kT}{\tilde{B}hc}\int_0^{\infty} \frac{d\left(e^{-\tilde{B}hc\ J(J+1)/kT}\right)}{dJ}\ dJ \qquad \text{(high T, rigid rotor)} \qquad 30.2.31$$

$$q_r = -\frac{kT}{\tilde{B}hc}\ e^{-\tilde{B}hc\ J(J+1)/kT}\Big|_0^{\infty} = \frac{kT}{\tilde{B}hc} \qquad \text{(high T, rigid rotor)} \qquad 30.2.32$$

For example, the rotational constant of $H^{35}Cl$ is 10.59 cm^{-1}, Table 27.6.1. At 25°C, $kT = 207.224$ cm^{-1}. The rotational partition function for $H^{35}Cl$ at room temperature is then $q_r = 207.224\ \text{cm}^{-1}/10.59\ \text{cm}^{-1} = 19.6$. The number of accessible rotational states is 19.6 at 25°C. However, for symmetrical linear molecules, such as N_2 and CO_2, the values calculated using the last equation are a factor of two high compared to experiment. The reason is that rotation about an axis perpendicular to the internuclear axis by 180° gives an orientation that is indistinguishable from the original molecule, Figure 30.2.5. We encountered issues with indistinguishability before, concerning the Pauli Exclusion Principle and relating the system and molecular partition functions. In quantum mechanics we discovered that we must not specify a result that cannot be verified in the laboratory. We can't count the two orientations of N_2 that differ by 180° as separate states. To prevent over-counting indistinguishable states, a **symmetry number** is introduced into the denominator of the last expression:

$$q_r = \frac{kT}{\sigma\tilde{B}hc} \qquad \text{(rigid rotor)} \qquad 30.2.33$$

The symmetry number, σ, is the number of indistinguishable orientations produced by rotations about the center of mass of the molecule. The symmetry number for HCl and other heteronuclear diatomics is $\sigma = 1$. The symmetry number for homonuclear diatomics and other symmetrical linear molecules is $\sigma = 2$, Figure 30.2.5. If you have covered the group theory section of the rotational vibrational spectroscopy chapter, you can conveniently determine the symmetry number as the order of the rotational sub-group of the point group of the molecule. The rotational sub-group is comprised of the proper rotations and the identity. For example, for H_2O in the $C_{2}v$ point group, the rotational subgroup is $\{E, C_2\}$. The H_2O symmetry number is then $\sigma = 2$. In general, for the C_{nv} point groups the symmetry number is $\sigma = n$. For BF_3 in the D_{3h} point group, the rotational subgroup is $\{E, 2C_3, 3C_2'\}$ giving $\sigma = 6$. For benzene in the D_{6h} point group, the rotational subgroup is $\{E, 2C_6, 2C_3, C_2, 3C_2', 3C_2''\}$ giving $\sigma = 12$.

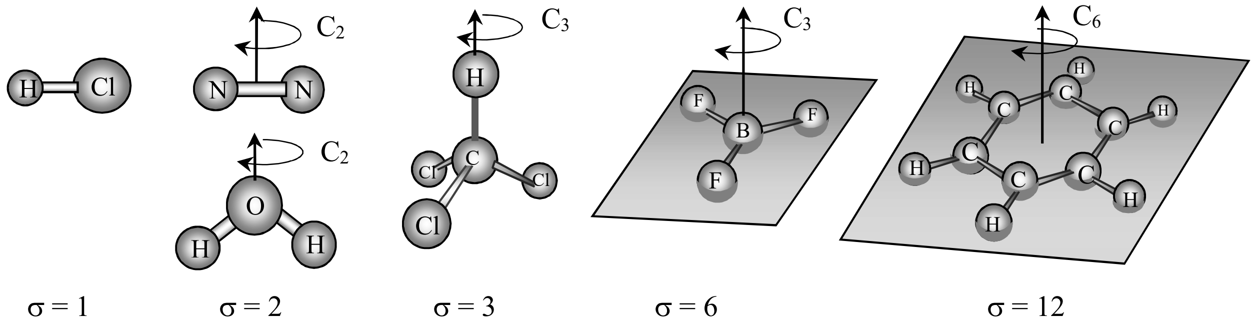


Figure 30.2.5: The symmetry number avoids over-counting indistinguishable states.

Specifically at 25°C the rotational partition function is easily calculated by:

$$q_r = \frac{207.224\ \text{cm}^{-1}}{\sigma\tilde{B}} \qquad \text{(298.2 K, rigid rotor)} \qquad 30.2.34$$

The available thermal kinetic energy at room temperature is a good point of comparison for which $\tilde{B}$ values are "large" or "small."

Non-linear molecules have three moments of inertia, Eq. 27.4.11, about three orthogonal axes, x, y, and z, Eq. 27.4.14. The rotational partition function of a non-linear molecule with the corresponding rotational constants, $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$, is:

$$q_r = \frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{\tilde{A}hc}\right)^{1/2}\left(\frac{kT}{\tilde{B}hc}\right)^{1/2}\left(\frac{kT}{\tilde{C}hc}\right)^{1/2} \quad \text{with} \quad \tilde{A} = \frac{\hbar}{4\pi I_{zz}c} \qquad \tilde{B} = \frac{\hbar}{4\pi I_{xx}c} \qquad \tilde{C} = \frac{\hbar}{4\pi I_{yy}c}$$

30.2.35

To complete the study of internal degrees of freedom, we still need to discuss the electronic degree of freedom, which is particularly important for atomic and reactive-molecular species.

Low Lying Electronic Degrees of Freedom Contribute to Internal Energy and Gibbs Energy: The electronic partition function is given by the sum of the Boltzmann weighting factors:

$$q_e = \sum_{\text{all energy levels}} g_i\, e^{-\varepsilon_i/kT} \qquad 30.2.36$$

where g_i are the electronic state degeneracies and ε_i are the electronic states energies, with the energy of the ground state as the reference energy, $\varepsilon_{gs} = 0$. The energies of the excited states of most molecules are significantly higher than the ground electronic state. As a consequence, under most circumstances the electronic partition function is simply the ground state degeneracy. Most stable molecules have ground singlet states giving $q_e = 1$. Diatomic O_2, however, has a ground state $^3\Sigma_g^-$ term. The lowest energy excited state has a $^1\Delta_g$ term, which lies at 7918.1 cm^{-1} above the ground state, which makes a negligible contribution to q_e. The electronic partition function for $^3\Sigma_g^-$ O_2 is the ground state degeneracy $q_e = 2$. Many atoms are also counter examples. The ground state configuration of oxygen is [He]$2s^22p^4$, giving three low lying terms ^3P_o, $^3P_1$, and $^3P_2$. The degeneracy of each term is determined by the total angular momentum, $g_J = 2J + 1$, Figure 30.2.6. The energy of these levels is on the order of kT above the ground state at room temperature, so they are partially populated.

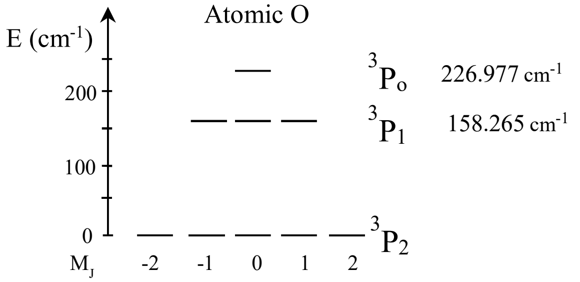
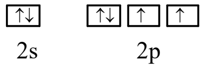


Figure 30.2.6: The ground state configuration of O-atoms is $2s^2$ $2p^4$, which results in low lying ^3P_o, $^3P_1$, and $^3P_2$ terms. The degeneracy of each electronic term is $g_e = 2J + 1$.

Example 30.2.2: *Electronic Partition Functions*
Calculate the electronic partition function of atomic oxygen at 298.2 K.

Answer: The ground state configuration of O-atoms is $2p^4$, giving low lying ^3P_o, $^3P_1$, and $^3P_2$ terms:

O: $2p^4$:



By Hund's third rule, Sec. 25.6, $^3P_2$ is the lowest energy term. The degeneracy of each term is $g_J = 2J + 1$. For example for the $^3P_3$ term:

$^3P_2$ $J = 2$ $M_J = -2,-1, 0, 1, 2$ $g_e = 5$

The explicit sum over the Boltzmann weighting factors, Eq. 30.2.36, using Figure 30.2.6 gives:

$$q_e = 5 + 3\ e^{-158.265/207.22} + 1\ e^{-226.977/207.22} = 5 + 1.39776 + 0.33443 = 6.7322$$

Additional atomic examples are given in Table 30.2.2.

Table 30.2.2: Ground State Atomic Terms, Low Lying Excited States, and Degeneracies (g_i).[1,2]

Element	H	B	C	N	O	F	P	S	Cl	Br
GS Term	$^2S_{½}$	$^2P_{½}$	^3P_o	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^2P_{3/2}$
g_{gs}	2	2	1	4	5	4	4	5	4	4
Excited states										
Term		$^2P_{3/2}$	$^3P_1$		$^3P_1$	$^2P_{½}$		$^3P_1$	$^2P_{½}$	
E (cm^{-1})		15.287	16.40		158.265	404.10		396.055	882.352	
g_{ex}		4	3		3	2		3	2	
Term			$^3P_2$		^3P_o			^3P_o		
E(cm^{-1})			43.40		226.977			573.640		
g_{ex}			5		1			1		
q_e at 298.2 K	2	5.7155	7.8269	4	6.7322	4.2845	4	5.5065	4.0283	4

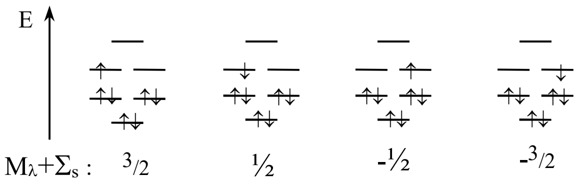
Example 30.2.3: *Electronic Partition Function for Molecules*
An important exception to the general expectation that most molecules have singlet ground states is NO. Determine the electronic partition function of NO. The ground state term is $^2\Pi_{½}$ and the first excited state term is $^2\Pi_{3/2,}$ which lies at 119.8 cm^{-1} above the ground state. The ground state configuration results in both terms: NO: $1\sigma^2\ 1\sigma^{*2}\ 2\sigma^2\ 3\sigma^{*2}\ 2\sigma^2\ 1\pi^4\ 1\pi^{*1}$.

Answer: The degeneracies of $^2\Pi_{½}$ and $^2\Pi_{3/2}$ are both $g_e = 2$. The sum of the Boltzmann weighting factors, Eq. 30.2.36, for NO is:

$$q_e = 2 + 2\ e^{-119.8/207.22} = 3.156$$

Why are the degeneracies of both terms $g_e = 2$? In Sec. 28.1 we defined the projection of the total angular momentum as: $\Omega = |\Lambda + \Sigma_s|$, where the projection of the electron spin angular momentum varies as Σ_s: -S, …, +S. For NO, $\Lambda = 1$ and S = ½, giving the projection of the spin angular momentum as $\Sigma_s = +½, -½$. The result is $\Omega = 3/2$ and ½, giving two terms: $^2\Pi_{3/2}$ and $^2\Pi_{½}$. The explicit enumeration of the possible values for the orbital and spin angular momenta are given below.

M_λ	Σ_s	$M_\lambda+\Sigma_s$		
1	½	3/2		$^2\Pi_{3/2}$
1	-½	½	$^2\Pi_{½}$	
-1	½	-½		
-1	-½	-3/2		



The $M_\lambda+\Sigma_s = \pm 3/2$ states are the two degenerate states for $^2\Pi_{3/2}$. The $M_\lambda+\Sigma_s = \pm½$ states are the components of the two degenerate states for $^2\Pi_{½}$. For another example, a $^1\Delta_g$ term is for $\Lambda = 2$ and has two degenerate projections of the orbital angular momenta, $M_\lambda = \pm 2$, while S = 0, which also gives $g_e = 2$.

30.3 Thermodynamic Properties are Determined by the Partition Function

The fundamental properties of thermodynamics are internal energy and entropy. By the First Law, the internal energy of a process is conserved. By the Second Law, the entropy of an isolated system always increases for a spontaneous process in an isolated system. The internal energy and entropy can be expressed directly in terms of the canonical ensemble and molecular partition functions.

Internal Energy and Entropy: For the internal energy, substitution of Eq. 30.1.1 into Eq. 30.1.4 for the energy average over all states gives the internal energy as:

$$U - U(0) = \Sigma p_i E_i = \frac{\Sigma E_i e^{-E_i/kT}}{Q} \qquad 30.3.1$$

In some cases, the algebra of statistical mechanics is easier if we return to using β = 1/kT, where β is the Lagrange multiplier that we used in deriving the Boltzmann equation, Section 12.5:

$$U - U(0) = \Sigma p_i E_i = \frac{\Sigma E_i e^{-\beta E_i}}{Q} \qquad 30.3.2$$

We then notice that the sum in the numerator of this last equation can be obtained as a derivative of the partition function with respect to β:

$$\left(\frac{\partial Q}{\partial \beta}\right)_V = \left(\frac{\partial[\Sigma e^{-\beta E_i}]}{\partial \beta}\right)_V = -\Sigma E_i e^{-\beta E_i} \qquad 30.3.3$$

Substitution of this last equation into Eq. 30.3.2 gives the internal energy entirely in terms of the partition function:

$$U - U(0) = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V \qquad 30.3.4$$

Thinking in terms of the energies of a system as a whole is awkward. The internal energy of a system can be written directly in terms of the molecular partition function. Substituting Eq. 30.2.7° into $(\partial Q/\partial \beta)_V$ and using the chain rule to complete the derivative gives:

$$\left(\frac{\partial Q}{\partial \beta}\right)_V = \left(\frac{\partial q^N/N!}{\partial \beta}\right)_V = \frac{1}{N!}\left(\frac{\partial q^N}{\partial \beta}\right)_V = \frac{N\, q^{N-1}}{N!}\left(\frac{\partial q}{\partial \beta}\right)_V \qquad \text{(ideal gas)} \qquad 30.3.5°$$

Substituting the derivative into the expression for the internal energy, Eq. 30.3.4 simplifies to:

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V \qquad \text{(ideal gas)} \qquad 30.3.6°$$

The derivative with respect to β is often computationally convenient. However, to obtain better insight into the meaning of the internal energy, it is useful to switch to the derivative in terms of temperature. We can find the relationship to the derivative with respect to T by using the chain rule. For the ensemble partition function, from Eq. 30.3.4:

$$U - U(0) = -\frac{1}{Q}\left(\frac{\partial Q}{\partial T}\right)_V\left(\frac{\partial T}{\partial \beta}\right) \qquad 30.3.7$$

with $\left(\frac{\partial\beta}{\partial T}\right) = \frac{1}{k}\left(\frac{\partial(^1/T)}{\partial T}\right) = -\frac{1}{kT^2}$ 30.3.8

Inverting the last derivative and substitution back into Eq. 30.3.7 gives:

$$U - U(0) = \frac{kT^2}{Q}\left(\frac{\partial Q}{\partial T}\right)_V \qquad 30.3.9$$

Similarly, for the molecular partition function, from Eq. 30.3.6°:

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -\frac{N}{q}\left(\frac{\partial q}{\partial T}\right)_V \frac{\partial T}{\partial \beta} \qquad \text{(ideal gas)} \quad 30.3.10°$$

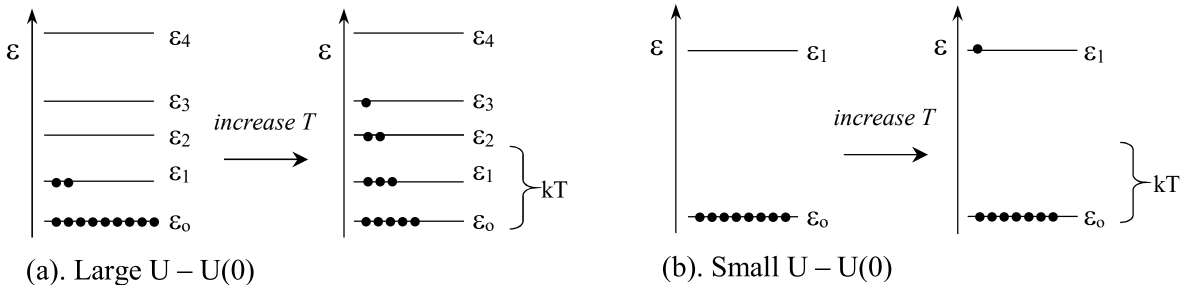
The $\partial T/\partial\beta$ derivative is given by Eq. 30.3.8, which upon substitution into Eq. 30.3.10° shows that the internal energy is proportional to the change in the number of accessible states with small changes in temperature:

$$U - U(0) = \frac{NkT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V \qquad \text{(ideal gas)} \quad 30.3.11°$$

Given that Boltzmann's constant is the gas constant per molecule gives Nk = nR with the result:

$$U - U(0) = \frac{nRT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V \qquad \text{(ideal gas)} \quad 30.3.12°$$

What exactly does the internal energy of a system mean? Eq. 30.3.12° has a useful interpretation, Figure 30.3.1. The fractional increase of the number of accessible states is given by $^{\partial q}/_{q}$. The internal energy is proportional to the fractional increase of the number of accessible states with a small increase in temperature, ∂T. If the energy states are closely spaced compared to kT, a small change in temperature excites many molecules from low lying to higher energy states. This promotion requires the absorption of energy, resulting in a large internal energy. If the energy states are widely spaced, a small change in temperature promotes few molecules into higher energy states, which requires little or no absorption of energy.



(a). Large U – U(0) (b). Small U – U(0)

Figure 30.3.1: Internal energy is proportional to the fractional change of accessible states caused by a small change in temperature. (a). For small quantum spacing, a small change in temperature causes energy transfer into the system, giving a large internal energy. (b). For large quantum spacing, a small change in temperature excites few molecules into higher energy states, requiring little transfer of energy, giving a small internal energy.

Example 30.3.1: *Estimation of the Internal Energy*
For one mole of an ideal gas at 25°C and constant volume, the number of accessible states increases by 10% with a temperature increase of 5°C. Estimate to a single significant figure (don't use a calculator) the internal energy of the substance.

Answer: We can develop an approximate formula based on the fractional change $\partial q/q$ and Eq. 30.3.12°. Note that at room temperature $RT^2 = 739.1$ kJ K mol^{-1}, and using finite differences:

$$U_m - U_m(0) = RT^2\left(\frac{\partial q/q}{\partial T}\right)_V \approx 1000 \text{ kJ K mol}^{-1}\left(\frac{\delta q/q}{\delta T}\right)_V \qquad 30.3.13°$$

For a 10% increase in the partition function, $\delta q/q = 0.10$. For the change in temperature of 5°C:

$$U_m - U_m(0) \approx 1000 \text{ kJ K mol}^{-1}\left(\frac{0.10}{5\text{ K}}\right) \approx 20 \text{ kJ mol}^{-1}$$

We will have many opportunities to calculate accurate values of thermodynamic parameters, but intuition is often aided by approximate calculations without the use of a calculator.

The molecular partition function, q, is for a single molecule. The ensemble partition function is for a system of N molecules. The internal energy written in terms of the molecular partition function, Eq. 30.3.11°, is in exactly the same form as of the ensemble partition function, Eq. 30.3.9, except that the molecular result is multiplied by the number of molecules in the system. Comparing the relationships that are written in terms of q and Q, the advantage of using the molecular partition function is in ease of interpretation. However, the versions that we derive using the molecular partition function require independent molecules, in other words an ideal gas. The advantage of the relationship written in terms of the ensemble partition function is that the equations are general for any system, real or ideal.

The ratio $\partial q/q$ is the fractional change of accessible molecular states. Another way of looking at this relationship takes advantage of the useful property of logarithms:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_V = \frac{1}{q}\left(\frac{\partial Q}{\partial \beta}\right)_V \qquad \text{or} \qquad \left(\frac{\partial \ln q}{\partial \beta}\right)_V = \frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V \qquad 30.3.14$$

Combining these relationships with Eqs. 30.3.4, 30.3.6°, 30.3.9, and 30.3.12° gives:

$$U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V \qquad \text{or} \qquad U - U(0) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V \qquad 30.3.15°$$

$$U - U(0) = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V \qquad \text{or} \qquad U - U(0) = nRT^2\left(\frac{\partial \ln q}{\partial T}\right)_V \qquad 30.3.16°$$

The logarithm of the partition function is proportional to the order of magnitude of the number of accessible states, since ln x = 2.303 log x. For example, a factor of 10 increase in accessible states gives a factor of 2.303 larger internal energy.

We have shown that the internal energy can be expressed entirely in terms of the partition function. Next we show that the entropy can also be related to the partition function.

Entropy is Determined from the Partition Function: The statistical definition of entropy is based on the number of ways of arranging the energy states of the ensemble at equilibrium, $\mathcal{W}_{\max}$:

$$S = \frac{k}{\mathcal{N}} \ln \mathcal{W}_{\max} \qquad \text{(Canonical ensemble) (12.2.1)} \qquad 30.3.17$$

where the number of ways of arranging the energy states of the ensemble is given by the distribution numbers, n_i, Figure 30.2.1b:

$$\mathcal{W} = \frac{\mathcal{N}!}{n_o!n_1!n_2!\ldots} \qquad \text{(Canonical ensemble) (12.2.8)} \qquad 30.3.18$$

Defining the probability of occurrence of state i as $p_i = n_i/\mathcal{N}$ and using Sterling's approximation for the factorials gives the entropy of a substance as the sum over all energy states:

$$S = -k \sum_{i=0}^{\infty} p_i \ln p_i \qquad (12.4.9) \qquad 30.3.19$$

The probabilities at equilibrium, which maximize $\mathcal{W}$, are given by the Boltzmann distribution over the energy states of the ensemble, E_i:

$$p_i = \frac{e^{-E_i/kT}}{Q} \qquad \ln p_i = -\ln Q - E_i/kT \qquad (12.5.14) \qquad 30.3.20$$

Substitution of $\ln p_i$ from the last expression into Eq. 30.3.19 gives:

$$S = -k \sum_{i=0}^{\infty} p_i \ln p_i = k\, \Sigma\, p_i \ln Q + \frac{\Sigma\, p_i E_i}{T} \qquad 30.3.21$$

The Boltzmann distribution is normalized giving $\Sigma\, p_i = 1$. The averaged quantum mechanical energy is $\langle E\rangle = \Sigma\, p_i E_i$, summed over all states of the ensemble. Eq. 30.3.21 then reduces to:

$$S = k \ln Q + \frac{\langle E\rangle}{T} \qquad 30.3.22$$

The fundamental postulate of statistical mechanics is that the average quantum mechanical energy is equal to the internal energy of the system above the reference point, $\langle E\rangle = U - U(0)$, with U(0) the internal energy of the system at a temperature of absolute zero:

$$S = k \ln Q + \frac{U - U(0)}{T} \qquad 30.3.23$$

The entropy is also directly related to the molecular partition function. For N identical molecules in the system, the ensemble partition function is given in terms of the molecular partition function by Eq. 30.2.7°. For very large numbers of systems, the factor of N! can be expressed using Sterling's approximation, Eq. 12.4.2:

$$Q = \frac{q^N}{N!} \qquad \text{with} \quad N! \cong (N/e)^N \qquad \text{gives} \quad Q \cong \left(\frac{qe}{N}\right)^N \qquad 30.3.24°$$

Substitution of the last relationship into Eq. 30.3.23 gives the absolute entropy of an ideal gas as:

$$S = Nk \ln\left(\frac{qe}{N}\right) + \frac{U - U(0)}{T} = nR \ln\left(\frac{qe}{N}\right) + \frac{U - U(0)}{T} \qquad 30.3.25°$$

The importance of these expressions is that the absolute entropy of a substance is expressed entirely in terms of the partition function. The partition function gives the number of accessible states. As the number of accessible states increases the entropy increases; the available energy is more dispersed over multiple energy states.

We often consider the separate contributions of translation and internal degrees of freedom. By convention and for convenience, the factor that accounts for indistinguishability in Eq. 30.3.25°, e/N, is combined with the translational partition function:

$$S = \underbrace{\left[nR \ln\left(\frac{q_t e}{N}\right) + \frac{U_t - U_t(0)}{T}\right]}_{\substack{\textit{center of mass translation} \\ \textit{Sackur-Tetrode equation}}} + \underbrace{\left[nR \ln q_{int} + \frac{U_{int} - U_{int}(0)}{T}\right]}_{\textit{internal: } q_{int} = q_r q_v q_e} \qquad 30.3.26°$$

where U_t and U_{int} are the contributions to the internal energy of translations and of internal degrees of freedom, respectively.

Entropy of a Monatomic Gas: An important test case of the validity of the statistical mechanical definition of entropy is to evaluate the absolute molar entropy of an ideal monatomic gas. In other words, we start with something simple and experimentally well characterized. We assume no low-lying electronic excited states. A monatomic gas then has only translational degrees of freedom. The internal energy of an ideal monatomic gas is well known from experiment and Equipartition, $U - U(0) = {}^3\!/_2\, nRT = {}^3\!/_2\, NkT$, giving Eq. 30.3.25° as:

$$S = nR \ln\left(\frac{qe}{N}\right) + {}^3\!/_2\, nR \qquad \text{(monatomic ideal)} \quad 30.3.27°$$

Substitution of the translational partition function, Eq. 30.2.19°, gives the entropy of an ideal monatomic gas as:

$$S = nR \ln\left[\frac{(2\pi mkT)^{3/2} e}{Nh^3} V\right] + {}^3\!/_2\, nR \qquad \text{(monatomic ideal)} \quad 30.3.28°$$

The molar entropy is for $N = N_A$ and $n = 1$ mol and the molar volume, V_m.
Eq. 30.3.28° can be condensed by noting that ${}^3\!/_2 = \ln e^{3/2}$. Combining the logarithmic terms:

$$S_m = R \ln\left[\frac{(2\pi mkT)^{3/2} e^{5/2}}{N_A h^3} V_m\right] \qquad \text{(monatomic ideal)} \quad 30.3.29°$$

This historically important relationship is called the **Sackur-Tetrode equation**. In this expression the mass, m, is in kg molecule^{-1} and the volume V is in m^3. Converting to more commonly used units of g mol^{-1} for the molecular mass and liters for the volume gives:

$$S_m = R \ln V_m + {}^3\!/_2\, R \ln T + {}^3\!/_2\, R \ln \mathcal{M} + R \ln\left[\frac{(2\pi k(1\text{ kg}/1000\text{ g})/N_A)^{3/2} e^{5/2} (1\text{ m}^3/1000\text{ L})}{N_A h^3}\right]$$

$$S_m = R \ln(V_{m/L}) + {}^3\!/_2\, R \ln T + {}^3\!/_2\, R \ln(\mathcal{M}_{/\text{g mol}^{-1}}) + 11.1037\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\text{(monatomic ideal)} \quad 30.3.30°$$

The change in entropy of various processes in a monatomic ideal gas can now be determined and compared to purely thermodynamic results. For specific processes constant terms in Eq. 30.3.30° cancel between the initial and final states giving familiar results. For an isothermal expansion of one mole of ideal gas from volume V_1 to V_2, the change in entropy using Eq. 30.3.30° is:

$$\Delta S_m = R \ln\left({}^{V_2}/_{V_1}\right) \qquad \text{(ideal gas, cst. T)} \quad 30.3.31°$$

At constant volume from temperature T_1 to T_2 the change in entropy using Eq. 30.3.30° is:

$$\Delta S_m = {}^3/_2\, R \ln\left({}^{T_2}/_{T_1}\right) = C_{v,m} \ln\left({}^{T_2}/_{T_1}\right) \qquad \text{(monatomic, cst. V\&}C_v\text{)} \quad 30.3.32$$

where $C_{v,m} = {}^3/_2\, R$ for an ideal monatomic gas. These results reproduce the results we obtained using purely thermodynamic considerations, Eqs. 13.2.4° and 13.2.29.

Absolute entropies are normally tabulated in the standard state, which fixes the molar volume at $V = V_m^\circ$. At standard state, P° = 1 bar, the corresponding standard state volume at 298.15 K is:

$$V_m^\circ = RT/P^\circ = 0.0247890\ \text{m}^3 = 24.7890\ \text{L} \qquad \text{(298.2 K)} \quad 30.3.33$$

Using the standard state molar volume and $R = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}$ in Eq. 30.3.30° gives the standard state molar entropy of an ideal monatomic gas as:

$$S^\circ_{m,298.15\,\text{K}} = 26.6929 + 71.0587 + {}^3/_2\, R \ln\left(\mathcal{M}/_{\text{g mol}^{-1}}\right) + 11.1037\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$\text{(monatomic ideal, P°, 298 K)} \quad 30.3.34°$$

Comparison between theory and experiment requires only the molar mass of the substance. For example, the theoretical prediction using Eq. 30.3.34° of the absolute entropy of argon, with the isotope averaged molar mass from the Periodic Table, gives 154.85 J K^{-1} mol^{-1}. The experimental value is 154.7335 J K^{-1} mol^{-1}, showing excellent agreement. An important milestone in the acceptance of the principles of statistical mechanics was the accurate theoretical prediction of the absolute entropy of monatomic gases.

Eq. 30.3.30° also holds for the translational contribution to the molar entropy of any ideal gas. The translational kinetic energy of the center of mass of any polyatomic molecule is in the identical form as a monatomic substance. As a consequence, the Sackur-Tetrode equation is generally useful. However for polyatomics, the additional contributions of rotation, vibration, and electronic degrees of freedom are also required. Specification of standard state conditions only applies to the translational component, because internal degrees of freedom don't depend on volume. The Sackur-Tetrode equation also shows an important attribute of statistical mechanics. The goal is to provide easily implemented working equations for the rapid prediction of thermodynamic properties. Statistical mechanics has a practical bent. Now that we have a better idea of the molecular basis of internal energy and entropy, we can proceed to calculate the reaction enthalpy, Helmholtz energy, and Gibbs energy of chemical process.

All Thermodynamic Parameters can be Calculated from Partition Functions: In this section we show that all thermodynamics functions can be expressed in terms of the partition function. The partition function gives the number of accessible states. The relationship between the number of accessible states and the thermodynamic functions provides an intuitive interpretation of the fundamental aspects of thermodynamic processes. The internal energy is directly accessible from the ensemble partition function using Eq. 30.3.4. However, for constant pressure processes, enthalpy is more useful. Enthalpy is defined using Eq. 7.8.14:

$$H \equiv U + PV \qquad 30.3.35$$

However, in relating molecular properties to thermodynamic properties we need to be careful about the reference points. Thermodynamics does not provide a unique choice for a reference point. A useful reference point that is applicable in quantum mechanics and thermodynamics is the internal energy of the system at absolute zero. The PV product is zero at absolute zero; at absolute zero the enthalpy and internal energy of a system are identical. Subtracting $H(0) = U(0)$ from both sides of Eq. 30.3.35 gives the enthalpy referenced to the enthalpy at absolute zero:

$$H - H(0) = U - U(0) + PV \qquad 30.3.36$$

Internal energy and enthalpy at absolute zero correspond to each molecule occupying the zero-point vibrational level, $\upsilon = 0$, and the lowest rotational state, $J = 0$. The differences, $U - U(0)$ and $H - H(0)$, are the contributions of thermally excited motions. For an ideal gas, $PV = nRT$ giving the enthalpy as:

$$H - H(0) = U - U(0) + nRT \qquad \text{(ideal gas)} \qquad 30.3.37°$$

Helmholtz energy is defined as, Eq. 15.2.4:

$$A \equiv U - TS \qquad 30.3.38$$

At absolute zero $A(0) = U(0)$. Subtracting $A(0) = U(0)$ from both sides of Eq. 30.3.38 gives the Helmholtz energy referenced to the Helmholtz energy at absolute zero:

$$A - A(0) = U - U(0) - TS \qquad 30.3.39$$

Using Eq. 30.3.23 relates entropy to the partition function. Then cancelling terms gives:

$$A - A(0) = U - U(0) - kT \ln Q - (U - U(0))$$
$$A - A(0) = -kT \ln Q \qquad 30.3.40$$

This equation has a particularly useful interpretation. The contribution of thermally excited motions to the Helmholtz energy is given by the number of accessible states of the systems in the ensemble. The natural flow of a process is from fewer accessible states to more accessible states, which lowers the Helmholtz energy. For example consider translational energy in an isothermal expansion as modeled by the particle in a box. An increase in the volume of a system decreases the spacing between the translational energy levels, which increases the number of accessible states. From a purely thermodynamic perspective, Helmholtz energy is the total work available from a process. An isothermal expansion does work and decreases the Helmholtz energy, which is consistent with the statistical mechanical perspective. The spontaneous direction of a process at constant temperature is a decrease in Helmholtz energy. Greater stability results from increases in the number of accessible states.

The Helmholtz energy also provides a method for finding the pressure of a system using the thermodynamic force in Eq. 16.3.7:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \qquad 30.3.41$$

Substituting into this equation the Helmholtz energy from Eq. 30.3.40 gives:

$$P = -\left(\frac{\partial(A(0) - kT \ln Q)}{\partial V}\right)_T = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T \qquad 30.3.42$$

The pressure is a measure of the change in number of accessible states as the volume changes. Given the pressure and Helmholtz energy, the Gibbs energy follows directly from the definition, Eq. 15.2.15:

$$G \equiv A + PV \qquad 30.3.43$$

At absolute zero G(0) = A(0), given the PV product is zero at absolute zero. Subtracting G(0) = A(0) from both sides of the definition, Eq. 30.3.43, gives the Gibbs energy referenced to the Gibbs energy at absolute zero as:

$$G - G(0) = A - A(0) + PV \qquad 30.3.44$$

Using the pressure from Eq. 30.3.42 gives the complete expression for the Gibbs energy:

$$G - G(0) = A - A(0) + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T \qquad 30.3.45$$

For an ideal gas, however, PV = nRT giving Eq. 30.3.44 as:

$$G - G(0) = A - A(0) + nRT \qquad \text{(ideal gas)} \qquad 30.3.46°$$

Our focus of the remainder of this chapter is on ideal gases, so this last equation is the central relationship of our treatment of chemical reactions. Substituting Eq. 30.3.40 for the Helmhotlz energy into this last equation gives the Gibbs energy in terms of the ensemble partition function:

$$G - G(0) = -kT \ln Q + nRT \qquad \text{(ideal gas)} \qquad 30.3.47°$$

The interpretation of the Gibbs energy in terms of the number of accessible states is parallel to that for the Helmholtz energy, except that the Gibbs energy is particularly useful for constant temperature and constant pressure processes. In particular the Gibbs energy is the non-PV work available from a process, which is often our particular interest. Chemical work is non-PV work. The natural flow of a process is from fewer accessible states to more accessible states, which then lowers the Gibbs energy at constant temperature and pressure.

These thermodynamic expressions are more useful when recast into terms of the molecular partition function. Using Eq. 30.2.7° the ensemble partition function is given by $Q = q^N/N!$, which when substituted into Eq. 30.3.47° gives:

$$G - G(0) = -kT \ln q^N + kT \ln N! + nRT \qquad \text{(ideal gas)} \qquad 30.3.48°$$

In the first term, we can rewrite $\ln q^N$ as N ln q. Then using Sterling's approximation, Eqs. 12.4.2 and 12.9.12, in the form ln N! = N ln N – N gives:

$$G - G(0) = -NkT \ln q + NkT \ln N - NkT + nRT \qquad \text{(ideal gas)} \qquad 30.3.49°$$

Remembering that Boltzmann's constant is just the gas constant per molecule with Nk = nR, the last two terms cancel to give:

$$G - G(0) = -nRT \ln q + nRT \ln N \qquad \text{(ideal gas)} \qquad 30.3.50°$$

Combining the logarithmic terms then gives the final particularly useful expression:

$$G - G(0) = -nRT \ln\left(\frac{q}{N}\right) \qquad \text{(ideal gas)} \qquad 30.3.51°$$

The partition function gives the number of accessible molecular states and the factor of N avoids counting indistinguishable states. The molecular partition function can be split into a term for the translation of the molecules and the remaining internal degrees of freedom, $q = q_t\, q_{int}$. The internal partition function includes rotation, vibration, and electronic degrees of freedom, $q_{int} = q_r\, q_v\, q_e$, Eq. 30.2.10°. The influence of the internal degrees of freedom on the Gibbs energy can be seen by substituting q_{int} into Eq. 30.3.51°:

$$\begin{aligned} G - G(0) &= -nRT \ln\left(\frac{q_t}{N}\right) - nRT \ln q_{int} \\ &= -nRT \ln\left(\frac{q_t}{N}\right) - nRT \ln(q_r\, q_v\, q_e) \qquad \text{(ideal gas)} \qquad 30.3.52° \end{aligned}$$

By convention and for convenience, the factor of N is always combined with the translational partition function. This final expression allows us to determine the influence of rotation, vibration, and electronic terms separately on the Gibbs energy. Doing so is a great aid to building our intuition about structure-function relationships.

On first introduction, thermodynamics can seem mysterious. The preceding relationships show that all thermodynamics can be derived from a few simple expressions. The understanding that random chance controls the partitioning of the available energy among the energy states of the system completely determines thermodynamic behavior. We are now in the position of being able to accurately calculate the thermodynamic properties of ideal gases directly from spectroscopic constants.

30.4 Statistical Mechanics and the Ideal Gas

Units, Units, Units: For the translational partition function, Eq. 30.2.19°, the molecular mass is in kg and the volume is in m^3. These units are not the most convenient. In addition, the translational contribution is often required under standard state conditions, giving $V^{\circ}_m = RT/P°$ with $R = 8.3145$ J K^{-1} mol and $P° = 1x10^5$ N m^{-2}, Eq. 30.3.33. With the molecular mass converted to the more conventional molar mass, in g mol^{-1}, the translational partition function is:

$$\frac{q^{\circ}_{t,m}}{N_A} = \frac{(2\pi m k T)^{3/2}}{h^3} RT/P° = \Gamma\, (\mathcal{M}/\text{g mol}^{-1})^{3/2}\, (T/K)^{5/2} \qquad (P°=1 \text{ bar}) \qquad 30.4.1°$$

with the units conversion factor Γ defined as:

$$\Gamma = \left(\frac{2\pi k}{N_A\, 1000 \text{ g kg}^{-1}}\right)^{3/2} \frac{R}{N_A P°\, h^3} = 0.0259467 \qquad (P°=1 \text{ bar}) \qquad 30.4.2°$$

For rotation and vibration, Eqs. 30.2.34 and 30.2.27, we converted the energy units to wave numbers, using $kT/hc = 207.224$ cm^{-1} at room temperature. Wave number units allow the use of spectroscopic constants directly from spectra. Equivalent temperatures in eV can also be used, with $kT/e = 0.025693$ eV at 298.15 K. However, at other temperatures, we need to recalculate the equivalent kT/hc and kT/e, Table 30.4.1.

Table 30.4.1: Equivalent Temperature in Wave numbers and eV.

T (K)	50.00	100.00	298.15	500.00	1000.0	1500.0	2000.0
kT/hc (cm^{-1})	34.752	69.503	207.224	347.52	695.03	1042.6	1390.1
kT/e (eV)	0.00431	0.008617	0.025693	0.04309	0.08617	0.12926	0.17235

Another useful method of handling the unit conversions is to define the **spectroscopic temperature** of the transition. The partition function for rotation is Eq. 30.2.33. For rotation, the spectroscopic temperature is defined as:

$$\Theta_r = \frac{\tilde{B}hc}{k} \qquad \text{giving} \qquad q_r = \frac{T}{\sigma\Theta_r} \qquad \text{(linear)} \qquad 30.4.3$$

The partition function for a vibration is Eq. 30.2.25. The vibrational temperature is defined as

$$\Theta_v = \frac{\tilde{\nu}_o hc}{k} \qquad \text{giving} \qquad q_v = \frac{1}{1 - e^{-\Theta_v/T}} \qquad \text{(each mode)} \qquad 30.4.4$$

Example 30.4.1: *Accessible States in Translation, Rotation, and Vibration*

For one mole of CO_2 at 298.2 K, calculate (a) the standard state translational partition function, as $q^\circ_{t,m}/N_A$, (b) the rotational partition function given the rotational constant $\tilde{B}_o = 0.379\ cm^{-1}$, and (c) the vibrational partition function of the bending mode with frequency $\tilde{\nu}_o = 526.\ cm^{-1}$. (d). For comparison also calculate the vibrational partition function of a mode with $\tilde{\nu}_o = 150.\ cm^{-1}$.

Answer: (a). For one mole at P°=1 bar, T=298.2 K, and $\mathfrak{M} = 43.99\ g\ mol^{-1}$:

with Eq. 30.4.1°: $$\frac{q^\circ_{t,m}}{N_A} = \Gamma\,(43.99)^{3/2}\,(298.15)^{5/2} = 0.0259467\,(43.99)^{3/2}(298.15)^{5/2} = 1.16\text{x}10^7$$

(b). We use two equivalent methods to find the partition functions, the first in wave number units and the second using spectroscopic temperatures. A useful conversion constant to obtain spectroscopic temperatures is:

$$\frac{hc}{k} = 1.438778\ cm\ K \qquad \text{giving} \quad \Theta_r = \frac{\tilde{B}hc}{k} = 0.379\ cm^{-1}(1.438778\ cm\ K) = 0.545\ K$$

The symmetry number of CO_2 is $\sigma = 2$. The rotational partition function using Eq. 30.2.34 is:

$$q_r = \frac{207.22\ cm^{-1}}{\sigma\tilde{B}} = \frac{207.22\ cm^{-1}}{\sigma(0.379\ cm^{-1})} = \frac{547}{\sigma}$$

Equivalently using Eq. 30.4.3: $$q_r = \frac{T}{\sigma\Theta_r} = \frac{298.2\ K}{\sigma(0.545\ K)} = \frac{547}{\sigma}$$

(c). For the bending vibration with $\tilde{\nu}_o = 526.\ cm^{-1}$, the vibrational temperature is:

$$\Theta_v = \frac{\tilde{\nu}_o hc}{k} = 526.\ cm^{-1}(1.438778\ cm\ K) = 756.8\ K$$

The vibrational partition function using Eq. 30.4.33 is:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}_o/207.22\ cm^{-1}}} = \frac{1}{1 - e^{-526./207.22}} = 1.086$$

Equivalently using Eq. 30.4.4: $$q_v = \frac{1}{1 - e^{-\Theta_v/T}} = \frac{1}{1 - e^{-756.8/298.2}} = 1.086$$

(d). For comparison, given $\tilde{\nu}_o = 150.\ cm^{-1}$, the vibrational temperature is:

$$\Theta_v = \frac{\tilde{\nu}_o hc}{k} = 150.\ \text{cm}^{-1}(1.438778\ \text{cm K}) = 215.8\ \text{K}$$

Using Eq. 30.4.33: $$q_v = \frac{1}{1 - e^{-\tilde{\nu}_o/207.22\ \text{cm}^{-1}}} = \frac{1}{1 - e^{-150./207.22}} = 1.941$$

Equivalently, using Eq. 30.4.4: $$q_v = \frac{1}{1 - e^{-\Theta_v/T}} = \frac{1}{1 - e^{-215.8/298.2}} = 1.941$$

Additional comparisons are listed in Table 30.4.2. The choice of method, wave number or spectroscopic temperature, is a matter of convenience and personal preference.

Table 30.4.2: Vibrational Wave Number, Spectroscopic Temperature, and Gibbs Energy at 298.2 K.

$\tilde{\nu}_o$ (cm^{-1})	50	69.50	100	104.26	150	207.224	300	500	1000
Θ_v (K)	71.94	100	143.88	150	215.82	298.15	431.63	719.39	1438.78
q_v	4.665	3.509	2.612	2.529	1.941	1.582	1.307	1.098	1.008
G-G(0) (kJ mol^{-1})	-3.82	-3.11	-2.38	-2.30	-1.64	-1.14	-0.66	-0.23	-0.02

Order of magnitude estimates of the number of accessible states in translation, rotation, and vibration are helpful in assessing thermodynamic contributions to the Gibbs energy of a substance. In summary for small molecules, the typical sizes of partition functions of the different degrees of freedom are:

$$q_t \cong 10^{28} - 10^{29}\ \text{V/L} \qquad q_t^\circ/N_A \cong 10^6 - 10^7 \qquad q_r \cong 10 - 100 \qquad q_v \cong 1 - 10 \qquad 30.4.5^\circ$$

We next consider the contributions of translation, rotation, and vibration to internal energy, entropy, and Gibbs energy. The molar contribution of translation to the internal energy is $^3/_2$RT and the enthalpy is $^5/_2$RT. The contribution of translation to the entropy is given by the Sackur-Tetrode equation. Rotations and low energy vibrations also make significant contributions to the internal energy, enthalpy, entropy, and Gibbs energy of an ideal gas.

Rotational Contribution to Internal Energy and Gibbs Energy: The rotational partition function of a linear molecule, modeled as a rigid-rotor in the high temperature approximation, is given by Eq. 30.2.33. Substitution into Eq. 30.3.10° gives the contribution of molecular rotation to the internal energy of a diatomic molecule or a linear polyatomic as:

$$U_r - U_r(0) = \frac{nRT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V = \frac{nRT^2}{\left(\frac{kT}{\sigma\tilde{B}hc}\right)}\left(\frac{k}{\sigma\tilde{B}hc}\right) = nRT \qquad \text{(linear rigid-rotor)} \qquad 30.4.6$$

The contribution of nRT of rotation corresponds to the Equipartition prediction, Sec. 8.9. Finding agreement with Equipartition isn't surprising since we invoked the high temperature approximation in calculating the rotational partition function. In this limit the spacing between energy levels is much less than kT and the energy levels effectively approach a continuum. A continuum of energy levels gives the classical limit, which gives the maximum value of the partition function and the maximum contribution to the corresponding thermodynamic function. At temperatures near absolute zero, Eq. 30.4.6 fails and the explicit summation must be used.

The contribution of rotation of a linear molecule to the entropy is obtained by substituting the rotational partition function into Eq. 30.3.26°, assuming a rigid rotor at high temperature:

$$S_r = nR \ln q_r + \frac{U_r - U_r(0)}{T} = nR \ln\left(\frac{kT}{\sigma\tilde{B}hc}\right) + nR \qquad \text{(linear rigid-rotor)} \qquad 30.4.7$$

The contribution of rotation of a linear molecule to the Gibbs energy is obtained by substituting the rotational partition function into Eq. 30.3.52°:

$$G_r - G_r(0) = -nRT \ln q_r = -nRT \ln\left(\frac{kT}{\sigma\tilde{B}hc}\right) \qquad \text{(linear rigid-rotor)} \qquad 30.4.8$$

The connection between the Gibbs energy and molecular structure is through the spectroscopic determination of the rotational constant, $\tilde{B} = \hbar/(4\pi Ic)$. For a diatomic molecule, as the bond length increases, the moment of inertia increases, the rotational constant decreases, the spacing between rotational levels decreases, the rotational partition function increases, and the absolute value of the contribution to the Gibbs energy is increased. The Gibbs energy of a molecule is stabilized, made more negative, by an increase in bond length. The insight into the thermodynamic effects of molecular structure that is enabled by statistical mechanics is invaluable. Statistical principles place thermodynamic properties on a firm molecular foundation.

At 298 K, the available thermal connect energy is $kT/hc = 207.224\ \text{cm}^{-1}$, which when substituted into Eq. 30.4.8 gives:

$$G_v - G_v(0) = -nRT \ln\left(\frac{207.224\ \text{cm}^{-1}}{\sigma\tilde{B}}\right) \qquad \text{(298.2 K, linear rigid-rotor)} \qquad 30.4.9$$

The rotational constant can then be read directly from the microwave or rotational Raman spectrum or from the rotational fine-structure in the infrared or vibrational Raman spectrum. The corresponding relationship at other temperatures is given by the values of kT/hc in Table 30.4.1.

Example 30.4.2: *Rotational Contribution to Internal Energy and Gibbs Energy*
The rotational constant for CO_2 is $0.379\ \text{cm}^{-1}$. Calculate the contribution of rotations to the molar internal energy and Gibbs energy at 25.0°C.

Answer: At 298 K, the rotational contribution of a linear molecule to the internal energy is $RT = 2.479\ \text{kJ mol}^{-1}$, in the high temperature approximation. The symmetry number of CO_2 is $\sigma = 2$, since CO_2 gives indistinguishable states under rotation of 180°. The contribution of rotation to the Gibbs energy is, Eq. 30.4.9:

$$G_m - G_m(0) = -RT \ln q_r = -RT \ln\left(\frac{207.22\ \text{cm}^{-1}}{\sigma\tilde{B}}\right) = -(2.479\ \text{kJ mol}^{-1}) \ln\left[\frac{207.22\ \text{cm}^{-1}}{2(0.379\ \text{cm}^{-1})}\right]$$

$$= -(2.479\ \text{kJ mol}^{-1}) \ln(273.4) = -13.9\ \text{kJ mol}^{-1}$$

Non-linear molecules have three moments of inertia. The rotational contribution to the internal energy, at all but the lowest temperatures, is again equivalent to the Equipartition value of $U_r - U_r(0) = {}^3/_2\,RT$. Substitution of the rotational partition function of a non-linear molecule from Eq. 30.2.35 into Eqs. 30.3.27 and 30.3.53 gives the rotational contribution to the entropy and Gibbs energy as:

$$S_r = nR\ln q + \frac{U_r - U_r(0)}{T} = nR\ln\left[\frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{\tilde{A}hc}\right)^{1/2}\left(\frac{kT}{\tilde{B}hc}\right)^{1/2}\left(\frac{kT}{\tilde{C}hc}\right)^{1/2}\right] + {}^3/_2\,nR \qquad 30.4.10$$

$$G_r - G_r(0) = -nRT\ln\left[\frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{\tilde{A}hc}\right)^{1/2}\left(\frac{kT}{\tilde{B}hc}\right)^{1/2}\left(\frac{kT}{\tilde{C}hc}\right)^{1/2}\right] \qquad 30.4.11$$

Electronic structure programs use this relationship to calculate the Gibbs energy of substances. Rotation gives a significant contribution to the Gibbs energy, does vibration also?

Low Energy Vibrations Contribute to Internal Energy and Gibbs Energy: The partition function for vibration of a diatomic molecules in the harmonic approximation is given by Eq. 30.2.25. The version of this equation written in terms of β is the most convenient form. The internal energy is given by Eq. 30.3.15°. Taking the logarithm and using the chain rule, the required derivative is:

$$\ln q_v = -\ln(1 - e^{-\beta h\nu_o}) \qquad \text{giving} \qquad \left(\frac{\partial \ln q}{\partial \beta}\right)_V = \frac{-1}{(1 - e^{-\beta h\nu_o})}\,(-h\nu_o\, e^{-\beta h\nu_o}) \qquad 30.4.12$$

Substitution of the derivative into Eq. 30.3.15° gives the final result:

$$U_v - U_v(0) = N\left(\frac{\partial \ln q}{\partial \beta}\right)_V = \frac{Nh\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}} \qquad \text{(harmonic)} \qquad 30.4.13$$

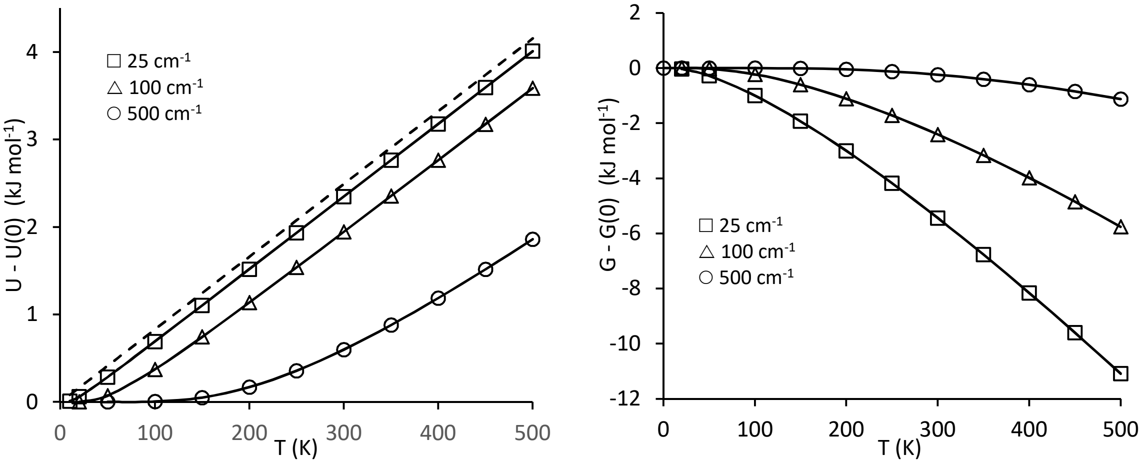
The molar zero-point vibrational energy is:

$$ZPE = \tfrac{1}{2}\, N_A h\nu_o \qquad 30.4.14$$

Converting $Nh\nu_o$ to molar terms gives: $Nh\nu_o = ({}^N/_{N_A})(N_A h\nu_o) = n(N_A h\nu_o)$. The vibrational contribution to the internal energy is:

$$U_v - U_v(0) = \frac{n(N_A h\nu_o)\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}} \qquad \text{(harmonic)} \qquad 30.4.15$$

The vibrational contribution to the internal energy is strongly dependent on the fundamental vibrational frequency, Figures 30.4.1a and 8.10.3. The vibrational contribution is largest for small fundamental vibration frequencies. However, the contribution always falls short of the Equipartition prediction of RT, for all temperatures. At room temperature the contribution of vibrations with wave numbers greater than 500 cm^{-1} is less than 1 kJ mol^{-1}. As a result, only the weakest bonds have stretching frequencies that make a significant contribution to internal energy and Gibbs energy. Low energy single-bond torsions and bending vibrations often contribute strongly to thermodynamic properties.



(a). (b).

Figure 30.4.1: Vibrational contribution to the (a) internal energy and (b) Gibbs energy of a harmonic oscillator. Three different fundamental vibration frequencies are illustrated. The dotted line is the classical limit given by Equipartition, $U_v - U_v(0) = nRT$.

The contribution of a vibration to the entropy is given using Eqs. 30.2.25, 30.3.27°, and 30.4.15:

$$S_v = -nR\ln(1 - e^{-h\nu_o/kT}) + \frac{n(N_A h\nu_o)}{T}\,\frac{e^{-h\nu_o/kT}}{1 - e^{-h\nu_o/kT}} \qquad 30.4.16$$

The contribution of a vibration to the Gibbs energy is simpler. Substitution of the vibrational partition function into the Gibbs energy, Eq. 30.3.52°, gives the vibrational contribution to the Gibbs energy as:

$$G_v - G_v(0) = -nRT\ln q_v = nRT\ln(1 - e^{-h\nu_o/kT}) \qquad \text{(per mode)} \qquad 30.4.17$$

At room temperature the Gibbs energy is conveniently calculated as:

$$G_v - G_v(0) = nRT\ln(1 - e^{-\tilde{\nu}_o/207.22\ \text{cm}^{-1}}) \qquad \text{(per mode, 298.2 K)} \qquad 30.4.18$$

where the fundamental vibration frequency is read directly from the infra-red or Raman spectrum. The connection between Gibbs energy and molecular structure is through the spectroscopic determination of $\tilde{\nu}_o$, giving the force constant for the bond from $\tilde{\nu}_o = (1/2\pi c)\sqrt{k/\mu}$. For a diatomic molecule as the bond strength increases, the force constant increases, the fundamental vibration frequency increases, the spacing between vibrational levels increases, the vibrational partition function decreases, and the absolute value of the contribution to the Gibbs energy is decreased. The vibrational contribution to the Gibbs energy of a molecule is destabilized, made more positive, by an increase in bond strength. The vibrational contribution to the Gibbs energy is strongly dependent on the fundamental vibration frequency, Figure 30.4.1b. At room temperature, vibrations with wave numbers greater than 500 cm^{-1} make a negligible contribution to the Gibbs energy.

The contribution of vibration to Gibbs energy in Eq. 30.4.17 is for a diatomic molecule or a single mode of a polyatomic. Since the total vibrational partition function of a polyatomic is the product of the partition functions of each mode, the total vibrational Gibbs energy is the sum of the Gibbs energy contributions of each mode. The overall contributions of rotation and vibration are summarized in Table 30.4.3.

Table 30.4.3: Contributions of Internal Degrees of Freedom to Internal Energy and Gibbs Energy for a Rigid Rotor and a Harmonic Oscillator.

per mole internal	Rotation	Vibration	High temperature or $h\nu_o \ll kT$
q	$q_r = \frac{kT}{\sigma\tilde{B}hc}$	$q_v = \frac{1}{1 - e^{-h\nu_o/kT}}$ $q_v = \frac{1}{1 - e^{-\beta h\nu_o}}$	$e^{-h\nu_o/kT} \cong 1 - \frac{h\nu_o}{kT}$ $q_v \cong \frac{kT}{h\nu_o}$
$U_m - U_m(0) = \frac{RT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V$	RT	$\frac{(N_A h\nu_o)\, e^{-h\nu_o/kT}}{1 - e^{-h\nu_o/kT}}$	RT
$G_m - G_m(0) = -RT \ln q$	$-RT \ln\left(\frac{kT}{\sigma\tilde{B}hc}\right)$	$RT \ln(1 - e^{-h\nu_o/kT})$	$-RT \ln\left(\frac{kT}{h\nu_o}\right)$
$G_m - G_m(0)$ at 298.15 K	$-RT \ln\left(\frac{207.22 \text{ cm}^{-1}}{\sigma\tilde{B}}\right)$	$RT \ln(1 - e^{-\tilde{\nu}_o/207.22 \text{ cm}^{-1}})$	$-RT \ln\left(\frac{207.22 \text{ cm}^{-1}}{\tilde{\nu}_o}\right)$

The High Temperature Approximation Gives the Classical Limit: The typically large quantum spacing of vibrational levels limits the influence of vibrations on thermodynamic properties. Low vibrational frequencies and high temperatures increase the vibrational contribution to internal energy and Gibbs energy. What is the maximum contribution that vibrations can make? The maximum contribution is determined by using the high temperature approximation. The approximation can be met in two ways, either with high temperatures or with low energy vibrations. At room temperature the requirement is $\tilde{\nu}_o \ll 207.22 \text{ cm}^{-1}$. The vibrational partition function is given by Eq. 30.2.25. In the limit that $h\nu_o \ll kT$ the exponential factor can be expanded in a Taylor series. Keeping only the first two terms gives:

$$e^{-h\nu_o/kT} \cong 1 - \frac{h\nu_o}{kT} \qquad (h\nu_o \ll kT) \qquad 30.4.19$$

Substitution of this approximation into the vibrational partition function gives:

$$q_v \cong \frac{1}{1 - (1 - h\nu_o/kT)} = \frac{kT}{h\nu_o} \qquad (h\nu_o \ll kT) \qquad 30.4.20$$

We also invoked the high temperature approximation in evaluating the rotational partition function, Eq. 30.2.33. As a consequence, the vibrational partition function in the high temperature approximation has the same functional form as the rotational partition function. Substitution into Eq. 30.3.12° gives the maximum contribution to the internal energy as:

$$U_v - U_v(0) = \frac{nRT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V = \frac{nRT^2}{\left(\frac{kT}{h\nu_o}\right)}\left(\frac{k}{h\nu_o}\right) = nRT \qquad (h\nu_o << kT) \quad 30.4.21$$

which is the Equipartition prediction. From the perspective of Equipartition, each quadratic term in the energy contributes ½RT to the internal energy. For vibrations, one quadratic term is the potential energy and one quadratic term is the kinetic energy. Substitution of Eq. 30.4.20 into Eq. 30.3.52° correspondingly gives the classical contribution to the Gibbs energy:

$$G_v - G_v(0) = -RT \ln q_v = -RT \ln\left(\frac{kT}{h\nu_o}\right) \qquad (h\nu_o << kT) \quad 30.4.22$$

The high temperature approximation is valid for very low frequency vibrations and acts as a point of comparison with the quantum results.

Example 30.4.3: *Gibbs Energy Contributions of Translation, Rotation, and Vibration*
Calculate the contributions of translation, rotation, and vibration to the standard state molar Gibbs energy of $H^{35}Cl$, as an ideal gas at 298.2 K. For spectroscopic constants use Table 27.6.1.

Answer: (a). Translation contributes $^3/_2$ RT to the molar internal energy. The definition of enthalpy is $H \equiv U + PV$. Assuming ideal gas behavior, the molar translational enthalpy is:

$$H_t - H_t(0) = U_t - U_t(0) + RT = {}^5/_2\, RT = 3.7184 + 2.4789 \text{ kJ mol}^{-1} \qquad 30.4.3$$

The molar translational entropy is given by the Sackur-Tetrode equation, Eq. 30.3.30°, with: $V^\circ_m = RT/P^\circ = 24.79$ L, $\mathcal{M} = 35.976678$ g mol^{-1}, and R = 8.3145 J K^{-1} mol^{-1}:

$$S^\circ_t = R \ln(V^\circ_m/_L) + {}^3/_2\, R \ln T + {}^3/_2\, R \ln(\mathcal{M}/_{g\ mol^{-1}}) + 11.1037 \text{ J K}^{-1}\text{ mol}^{-1} = 153.5398 \text{ J K}^{-1}\text{ mol}^{-1}$$

The translational contribution to the molar standard state molar Gibbs energy is:

$$G^\circ_m - G^\circ_m(0) = H_m - H_m(0) - T\, S^\circ_m$$
$$= 6.1973 \text{ kJ mol}^{-1} - 298.15 \text{ K}(153.5398 \text{ J K}^{-1}\text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -39.581 \text{ kJ mol}^{-1}$$

The preceding calculations follow the method used in electronic structure programs such as Gaussian and Spartan. Alternately, a determination of the translational contribution to the molar Gibbs energy is based directly on the partition function by Eq. 30.3.52°. Using Eqs. 30.4.1° and 30.4.2°:

$$\frac{q^\circ_{t,m}}{N_A} = \Gamma\, (\mathcal{M}/_{g\ mol^{-1}})^{3/2}\, (T/_K)^{5/2}$$
$$= 0.0259467\,(35.976678)^{3/2}\,(298.15)^{5/2} = 8.5941\text{x}10^6$$
$$G^\circ_t - G^\circ_t(0) = -RT \ln(q^\circ_{t,m}/N_A) = -8.32446 \text{ J K}^{-1}\text{mol}^{-1}(298.15 \text{ K}) \ln(8.5943\text{x}10^6)$$
$$= -39.581 \text{ kJ mol}^{-1}$$

(b). The rotational contribution to the molar Gibbs energy, Eq. 30.4.9, with $\sigma = 1$ and $\tilde{B}_e = 10.5933$ cm^{-1} is:

$$G_m - G_m(0) = -RT \ln\left(\frac{207.22\ \text{cm}^{-1}}{\sigma\tilde{B}}\right) = -8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}(298.15\ \text{K}) \ln\left(\frac{207.22\ \text{cm}^{-1}}{(1)(10.5933\ \text{cm}^{-1})}\right)$$
$$= -7.371\ \text{kJ mol}^{-1}$$

(c). The observed fundamental vibration frequency is given by Eq. 27.5.11:

$$\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e\tilde{\nu}_e = 2990.925\ \text{cm}^{-1} - 2(52.800\ \text{cm}^{-1}) = 2885.325\ \text{cm}^{-1}$$

The vibrational contribution to the molar Gibbs energy using Eq. 30.4.18 is:

$$G_m - G_m(0) = RT \ln(1 - e^{-\tilde{\nu}_o/207.22\ \text{cm}^{-1}})$$
$$= 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}(298.15\ \text{K}) \ln(1 - e^{-2885.325\ \text{cm}^{-1}/207.22\ \text{cm}^{-1}}) = -2.22\text{x}10^{-3}\ \text{J mol}^{-1}$$

The vibrational contribution at room temperature is negligible. The ground state is $^1\Sigma_g^+$ with no low lying excited states giving the electronic contribution as zero. The total thermal contribution to the standard state molar Gibbs energy is:

$$G^\circ_m - G^\circ_m(0) = \underset{\textit{translation}}{-39.581\ \text{kJ mol}^{-1}} + \underset{\textit{rotation}}{-7.371\ \text{kJ mol}^{-1}} + \underset{\textit{vibration}}{0} = -46.952\ \text{kJ mol}^{-1}$$

30.5 Reaction Gibbs Energy

Reaction Gibbs Energies are Calculated from Spectroscopic Constants: The standard state reaction Gibbs energy is the difference in Gibbs energy between products and reactants: $\Delta_r G^\circ = \Sigma \nu_i\, G^\circ_i$, where ν_i are the stoichiometric coefficients and G°_i are the molar standard state Gibbs energies of each pure substance i. The expressions in the previous section determine the thermal contribution to the Gibbs energy of each substance, $G_i - G_i(0)$. The thermal contribution is the contribution above the zero kelvin reference point, $G_i(0)$. The difference in reference points between thermodynamics and quantum mechanics must be taken into account in evaluating $G_i(0)$. Using spectroscopic data, the quantum mechanical energy zero is most conveniently taken as totally dissociated atoms, Figure 30.5.1. As shown in Sec. 30.3, the thermodynamic potential energy functions are all equal at absolute zero. The primary assumption of statistical mechanics is that the quantum mechanical average energy is equal to the internal energy. As a result, for each pure substance i at absolute zero temperature:

$$G^\circ_i(0) = A^\circ_i(0) = H^\circ_i(0) = U^\circ_i(0) = \varepsilon_{o,i} = -D_{o,i} \qquad 30.5.1$$

where $\varepsilon_{o,i}$ is the quantum mechanical **zero-point electronic energy**, which is the total electronic and vibrational energy at the $\upsilon = 0$ vibrational level. $D_{o,i}$ is the dissociation energy to give atoms. The Gibbs energy at absolute zero is unaffected by the choice of standard state ensuring that $G^\circ_i(0) = G_i(0)$. Using Eqs. 30.3.52° and 30.3.53° the molar standard state Gibbs energy of each substance is then:

$$G^\circ_i = G^\circ_i(0) - RT \ln\left(\frac{q^\circ_i}{N_A}\right) = G^\circ_i(0) - RT \ln\left(\frac{q^\circ_{t,i}}{N_A}\right) - RT \ln(q_{r,i}\, q_{v,i}\, q_{e,i}) \qquad 30.5.2^\circ$$

The reaction Gibbs energy at absolute zero is determined by the spectroscopic dissociation energies. For the general reaction: aA + bB ⇄ cC + dD, the quantum mechanical **zero-point energy shift**, ΔE_o, is given by:

$$\Delta E_o = c\ \varepsilon_{oC} + d\ \varepsilon_{oD} - a\ \varepsilon_{oA} - b\ \varepsilon_{oB}$$
$$\Delta E_o = c\ (-D_{o,C}) + d\ (-D_{o,D}) - a\ (-D_{o,A}) - b\ (-D_{o,B}) \qquad 30.5.3$$

From Eq. 30.5.1 the reaction thermodynamic potentials and the quantum mechanical zero-point energy shift are equal:

$$\Delta_r G°(0) = \Delta_r A°(0) = \Delta_r H°(0) = \Delta_r U°(0) = \Delta E_o \qquad 30.5.4$$

The relationships for the simple example A ⇄ B are shown in Figure 30.5.1

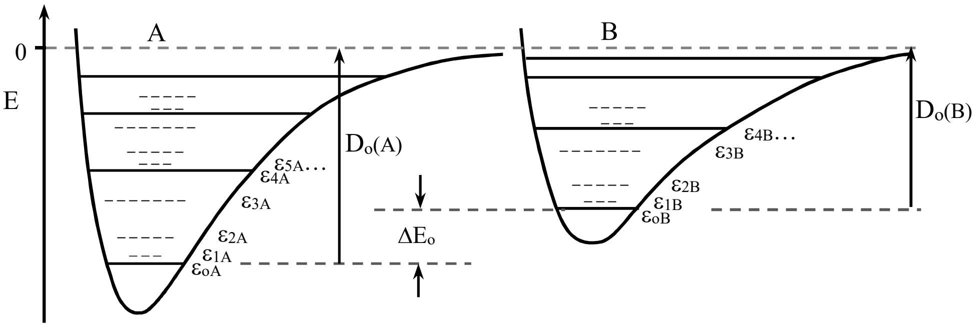


Figure 30.5.1: The potential energy curves for A ⇄ B are schematically drawn as diatomic potential curves with associated vibrational and rotational levels. The zero-point electronic energy levels are the negative of the total bond dissociation energy, $\varepsilon_{oA} = -D_o(A)$.

The reference energy difference, $\Delta_r G°(0) = \Delta E_o$, is then seen to be centrally important. Eq. 30.5.4 is the link between the microscopic world of quantum mechanics and the macroscopic world of thermodynamics. More importantly, the zero-point electronic energies are the negative of the bond dissociation energies, which are often the dominant factor in determining the reaction Gibbs energy and equilibrium constant.

Example 30.5.1: *Reaction Gibbs Energies from Spectroscopic Constants*
(a). Calculate the standard state molar Gibbs energy of formation of $H^{35}Cl$ (g) at 298.15 K. Assume ideal gases. The spectroscopic constants are given in Table 27.6.1. (b). Calculate the equilibrium constant for the formation reaction.

Answer: The reaction H_2 (g) + Cl_2 (g) → 2 HCl (g) gives 2 $\Delta_f G°$. The spectroscopic constants, partition functions, and resulting thermal contributions to the Gibbs energy of each pure substance are listed in the spreadsheet below. The input spectroscopic constants are listed at the top. The necessary fundamental constants are listed at the bottom. The equations used are listed under "*Notes*." The row labeled "G – G(0) internal" gives the contribution of the internal degrees of freedom to the Gibbs energy, $G - G(0) = -RT \ln(q_r\, q_v\, q_e)$. The next row adds in the translational contribution using Eq. 30.3.52°, $G - G(0) = -RT \ln({}^{q_t}/_{N_A}\, q_r\, q_v\, q_e)$. The reference energy, G°(0) is determined using Eq. 30.5.1, after conversion to kJ mol^{-1}. The reaction Gibbs energy is the difference:

$$\Delta_rG° = 2G°(HCl) – G°(H_2) – G°(Cl_2) = -190.818 \text{ kJ mol}^{-1}.$$

Finally $\Delta_fG^o = ½\ \Delta_rG° = -95.409$ kJ mol^{-1}.

A1	B	C	D	E	F	G	H
2		H_2	+	Cl_2	→	2 HCl	
3							*Notes:*
4	ν_o (cm^{-1})	4158.53		554.3614		2885.325	Eq. 27.5.11
5	B_e (cm^{-1})	60.853		0.2442		10.5933	Eq. 27.4.2
6	$\mathfrak{M}$ (g mol^{-1})	2.01565		69.937706		35.976678	
7	g (grnd.state)	1		1		1	
8	σ	2		2		1	
9	D_o (eV)	4.4776		2.476		4.432	Eq. 27.5.12
10							
11	q_t/N_A	113970.4		23293596.6		8594113.07	Eq. 30.4.1º
12	q_r	1.702664		424.292445		19.5618391	Eq. 30.2.33
13	q_v	1		1.07399255		1.0000009	Eq. 30.2.25
14	q_e	1		1		1	Eq. 30.2.35
15	G-G(0) internal	-1.319286		-15.1756931		-7.3713805	*r+v+e*
16	G-G(0) (kJ mol^{-1})	-30.18355		-57.2279467		-46.9518636	*t+r+v+e*
17	G(0) (kJ mol^{-1})	-432.0226		-238.897625		-427.622889	*-Do*
18	G (kJ mol^{-1})	-462.2061		-296.125557		-474.574753	Eq. 30.5.2
19							
20	T (K)	298.15		$\Delta_rG°$ (kJ mol^{-1})	=	-190.81781	
21	kT/hc (cm^{-1})	207.22443		$\Delta_fG°$ (kJ mol^{-1})	=	-95.408906	
22	R (J K^{-1}mol^{-1})	8.3144621					
23	N_A (mol^{-1})	6.02214E+23		K_p	=	5.18702E+16	
24	Γ	0.0259467					
25	h (J s)	6.62608E-34					
26	k (J K^{-1})	1.38065E-23					
27	1eV	96.485309	kJ mol^{-1}				

The literature $\Delta_fG°$ is -95.299 kJ mol^{-1}. In this case and in general, the principal error is in the bond dissociation energies. Under many circumstances, especially under extreme temperatures with reactive species, the statistical mechanical equilibrium constant is more accurate than can be measured experimentally.

The reaction Gibbs energy at absolute zero, Eqs. 30.5.3 and 30.5.4, is the difference:

$$\begin{aligned}\Delta_rG°(0) = \Delta E_o &= [2(–D_{o,HCl})] – [(–D_{o,H_2}) + (–D_{o,Cl_2})]\\ &= [2(-427.62 \text{ kJ mol}^{-1})] – [-432.02 \text{ kJ mol}^{-1} + (-238.90 \text{ kJ mol}^{-1})]\\ &= -184.33 \text{ kJ mol}^{-1}\end{aligned}$$

The final $\Delta_rG°$ at 298.2 K of -190.82 kJ mol^{-1} is dominated by the zero-point energy shift. In this example, as is often the case, just using the zero-point energy shift alone is not a bad rough estimate of the reaction Gibbs energy.

(b). The equilibrium constant is given by $\Delta_rG° = –RT \ln K_p$. Solving for K_p:

$$\Delta_rG°/RT = -95.409 \text{ kJ mol}^{-1}(1000 \text{ J}/1 \text{ kJ})/8.3145 \text{ J K}^{-1} \text{ mol}^{-1}/298.15 \text{ K} = -38.487$$

$$K_p = e^{-\Delta_rG°/RT} = e^{38.487} = 5.2\text{x}10^{16}$$

This example is a formation reaction, however the process applies equally to any reaction.

---

www Using the methods illustrated in the previous example, two applets that calculate reaction Gibbs energies and equilibrium constants are available on the text Web site and companion CD. The "*Equilibrium Constants from Molecular Structure*" or "efs.html" applet is for atomic and diatomic species. The "*Equilibrium Constants from Molecular Structure: Polyatomics*" or "efsp.html" applet extends the applet to polyatomic species. Example data is included for simple reactions. The results of Example 30.5.1 are easily validated using the diatomic version of the applet (see the Problems).

Reaction Gibbs Energies are Calculated from Electronic Structure Calculations: When experimental spectra are not available, electronic structure calculations are used to estimate the moments of inertia, vibrational frequencies, and dissociation energies. However, the zero energy reference used in electronic structure calculations is for completely dissociated nuclei and electrons. For example, the SCF total electronic energy of formaldehyde at B3LYP/cc-pVTZ corresponds to the process:

$$2\ H^+ + C^{6+} + O^{8+} + 16\ e^- \rightarrow H_2C{=}O \qquad \text{SCF total energy: } -114.5494128\ \text{H} \tag{30.5.5}$$

However, the dissociation energy, D_e, of formaldehyde corresponds to the process:

$$H_2C{=}O \rightarrow 2\ H + C + O \tag{30.5.6}$$

The SCF energies of the atoms are needed to calculate the dissociation energy, using the same method and basis set as the molecular calculation, Table 30.5.1.

Table 30.5.1: Atomic Energies in Hartrees (au) using *Ab Initio* Methods.$^{*(DS)}$

Atom	HF/6-31G*	MP2/6-311G*	B3LYP/6-311G*	B3LYP/6-311+G*	B3LYP/cc-pVTZ
H	-0.4982329	-0.4998098	-0.5021559	-0.5021559	-0.5021563
C	-37.6808603	-37.7450232	-37.8559888	-37.8572669	-37.8585746
N	-54.3854425	-54.4750512	-54.5985435	-54.6007232	-54.601781
O	-74.7839336	-74.9181455	-75.0853748	-75.0898713	-75.0918572
F	-99.3649569	-99.5541705	-99.7538101	-99.7605798	-99.7628675

* SCF atom energies are identical at the "*" and "**" levels, or equivalently at the (d) and (d,p) levels.

The dissociation energy is then given by [products] – [reactants] of the SCF electronic energies:

$$\begin{aligned} D_e &= [2(-0.5021563) + (-37.8585746) + (-75.0918572)] - [-114.5494128] \\ &= 0.594668441\ \text{H} = 1561.30045\ \text{kJ/mol} \end{aligned} \tag{30.5.7}$$

The observed spectroscopic dissociation energy, D_o, is obtained by zero-point energy correction. The molar zero-point vibrational energy is the sum over all normal modes, Figure 27.5.2:

$$ZPE = \tfrac{1}{2} N_A hc \sum \tilde{\nu}_o \qquad \text{giving} \qquad D_o = D_e - ZPE \tag{30.5.8}$$

Example 30.5.2: *Thermodynamic Parameters from Electronic Structure Calculations*
The thermodynamic analysis obtained by doing a normal mode calculation for formaldehyde at the B3LYP/cc-pVTZ level from the Spartan/Q-Chem program is shown in Figure 30.5.2.

Calculate the molar standard state Gibbs energy of formaldehyde at 298.2 K, with the energy reference as the dissociated atoms.

```
Formaldehyde B3LYP/cc-pVTZ  SCF Total Energy = -114.549412841

 Standard Thermodynamic quantities at 298.15 K and 1.00 atm

           Term       ZPE     Enthalpy   Entropy      Cv      % in
           cm-1     kJ/mol     kJ/mol    J/mol.K   J/mol.K  Ground IR Int.
  --   ----------   -------   -------    -------     ----
 1  B2    1201.147    7.1845    0.0438     0.1722    0.8540   99.70   3.23
 2  B1    1268.200    7.5855    0.0334     0.1304    0.6877   99.78  12.79
 3  A1    1536.772    9.1919    0.0111     0.0421    0.2754   99.94   9.98
 4  A1    1822.699   10.9022    0.0033     0.0123    0.0974   99.98 106.86
 5  A1    2878.663   17.2182    0.0000     0.0001    0.0015  100.00  68.98
 6  B1    2932.280   17.5389    0.0000     0.0001    0.0012  100.00 144.64
  --   ----------   -------   -------    -------     ----
  Total Vibrations   69.6212    0.0916     0.3573    1.9171

        Ideal Gas              2.4789
      Translation              3.7184  151.1751   12.4716
         Rotation              3.7184   66.9384   12.4716
       ----------             -------   -------   -------
           Totals             79.6286  218.4708   26.8604

 Vibrational(v) Corrections:
    Temp. Correction    Hv      79.6286
  Entropy Correction (Hv-TSv)   14.4916
```

Figure 30.5.2: Thermodynamic analysis for formaldehyde at B3LYP/cc-pVTZ using Spartan/Q-Chem '14.[3]

Answer: The thermodynamic calculations assume ideal gas behavior of one mole of substance at 298.2 K. In Spartan and Gaussian the standard state pressure is set at 1 atm, but the difference caused by the change in standard state is well within the overall error of the calculation. The Spartan listing begins with the vibrational contributions. The molar zero point vibrational energy, ZPE, is given by Eq. 30.5.8. For rotations and vibrations H – H(0) = U – U(0). The reason is that even though H ≡ U + PV, the PV correction term is included with the translational enthalpy. The vibrational contributions are given by Eqs. 30.2.25, 30.3.15, and 30.3.16. The heading "% in Ground" gives the Boltzmann probability of occupation of the $\upsilon = 0$ zero-point vibrational state. The heading "IR Int." gives the infra-red intensity of the normal mode transition. The translational contributions are given next using Eq. 30.3.37°; the "Ideal Gas" entry is the PV = RT correction and the "Translation" entry is $U_t - U_t(0) = \frac{3}{2}$ RT. The translational entropy is given by the Sackur-Tetrode equation, Eq. 30.3.30°. The "Rotation" enthalpy entry is $H_r - H_r(0) = RT$ for a linear molecule and $\frac{3}{2}$ RT for a non-linear molecule. The total enthalpy includes the zero-point vibrational energy: [ZPE + H° – H°(0)]. The "Rotation" entropy entry is given by Eq. 30.4.7. The thermal contribution to the Gibbs energy is listed as the "Entropy Correction (Hv –TSv)":

$$\begin{aligned} \text{ZPE} + G° - G°(0) &= [\text{ZPE} + H° - H°(0)] - TS° \qquad 30.5.9 \\ &= 79.6286 \text{ kJ mol}^{-1} - (298.15 \text{ K})(218.4708 \text{ J K}^{-1} \text{ mol})(1 \text{ kJ}/1000 \text{ kJ}) \\ &= 14.4916 \text{ kJ mol}^{-1} \end{aligned}$$

Since the ground state of formaldehyde is a singlet, no electronic contribution from the multiplicity is required. The zero-point vibrational energy of formaldehyde is 69.6212 kJ mol^{-1} giving the total dissociation energy, using Eqs. 30.5.7 and 30.5.8:

$$D_o = D_e - ZPE = 1561.30045 \text{ kJ mol}^{-1} - 69.6212 \text{ kJ mol}^{-1} = 1491.6792 \text{ kJ mol}^{-1}$$

The standard state Gibbs energy of formaldehyde with the energy reference as the dissociated atoms is using Eqs. 30.5.8 and 30.5.9:

$$G° = G°(0) + [G° - G°(0)] = -D_o + [G° - G°(0)] = -D_e + ZPE + [G° - G°(0)] \qquad 30.5.10$$
$$= -1561.30045 \text{ kJ mol}^{-1} + 14.4916 \text{ kJ mol}^{-1} = -1546.8089 \text{ kJ mol}^{-1}$$

The uncertainty is difficult to determine, but is at least several kJ mol^{-1}. The error is dominated by the difficulty in calculating the correlation energy. The final total Gibbs energy is then used in the calculation of reaction Gibbs energies and equilibrium constants.

Equivalently, the version of the thermodynamic analysis from Gaussian ’03 lists the spectroscopic temperatures for rotation and vibration, Figure 30.5.3. The E (Thermal) values are essentially identical to the Spartan version except that the units are in kcal mol^{-1}, with 1 cal = 4.184 J. The “Thermal correction” to the “Enthalpy” and “Gibbs Free Energy” again include the zero-point vibrational energy, ZPE + H – H(0) or ZPE + G – G(0).

```
This molecule is an asymmetric top.
 Rotational symmetry number  2.
 Rotational temperatures (Kelvin)     13.69943     1.87889     1.65228
 Rotational constants (GHZ):         285.45003    39.14976    34.42793
 Zero-point vibrational energy        69627.0 (Joules/Mol)
                                   16.64125 (Kcal/Mol)
 Vibrational temperatures:   1730.75  1824.90  2210.73  2624.49  4140.04
          (Kelvin)           4217.47

 Zero-point correction=                           0.026520 (Hartree/Particle)
 Thermal correction to Energy=                    0.029387
 Thermal correction to Enthalpy=                  0.030331
 Thermal correction to Gibbs Free Energy=         0.005523
 Sum of electronic and zero-point Energies=           -114.522888
 Sum of electronic and thermal Energies=              -114.520021
 Sum of electronic and thermal Enthalpies=            -114.519077
 Sum of electronic and thermal Free Energies=         -114.543885

                     E (Thermal)               CV              S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                   18.441                  6.419         52.213
 Electronic               0.000                  0.000          0.000
 Translational            0.889                  2.981         36.130
 Rotational               0.889                  2.981         15.998
 Vibrational             16.663                  0.457          0.085
```

Figure 30.5.3: Thermodynamic analysis of formaldehyde at B3LYP/cc-pVTZ using Gaussian 03.[4]

The preceding example is typical if reaction Gibbs energy calculations are done using spectroscopically derived dissociation energies. If the reaction Gibbs energy is to be determined using <u>only</u> information from electronic structure calculations, then dissociation energies need not be calculated. The reference in thermodynamic calculations is arbitrary as long as the chosen reference is consistent for each reactant and product. The reference state of completely dissociated nuclei and electrons, Eq. 30.5.5, can be used to find the reaction Gibbs energy as shown in the next two examples, again using the synthesis of formaldehyde as an example.

Example 30.5.3: *Reaction Gibbs Energies from Electronic Structure Calculations*
Calculate the standard state reaction Gibbs energy and equilibrium constant at 298.15 K for the reaction giving formaldehyde as the product, assuming ideal gases:

$$CO\ (g) + H_2\ (g) \rightleftarrows H_2C{=}O\ (g)$$

Use parameters entirely based on electronic structure calculations, which at B3LYP/cc-pVTZ are given in the table below from Gaussian ’03 (see Figure 30.5.3 for the formaldehyde output):

B3LYP/cc-pVTZ	CO	H_2	$H_2C{=}O$
SCF total energy (H)	-113.35725379	-1.1799987149	-114.549412841
Zero-point correction	0.005038	0.010077	0.026520
Thermal correction to Energy	0.007399	0.012437	0.029387
Thermal correction to Enthalpy	0.008343	0.013381	0.030331
Thermal correction to Gibbs Free Energy	-0.014081	-0.001410	0.005523
Sum of electronic and zero-point Energies	-113.352216	-1.169922	-114.522888
Sum of electronic and thermal Energies	-113.349855	-1.167562	-114.520021
Sum of electronic and thermal Enthalpies	-113.348911	-1.166617	-114.519077
Sum of electronic and thermal Free Energies	-113.371334	-1.181409	-114.543885

Answer: The “Thermal correction to the Gibbs Free Energy” includes the zero-point vibrational correction: ZPE + [G – G(0)]. Even though the SCF energies are with respect to the *ab initio* electronic structure reference point, the reference point is arbitrary as long as the values of all reactants and products are on a consistent basis. As a result the standard state reaction Gibbs energy is just the difference [products] – [reactants] of the “Sum of the electronic and thermal Free Energies”:

$$\Delta_r G^\circ = [-114.543885\ \text{H}] - [-113.371334\ \text{H} + -1.181409\ \text{H}] = 0.008858\ \text{H} = 23.257\ \text{kJ mol}^{-1}$$

The agreement with the thermodynamically based literature value, 27.3 kJ mol^{-1}, is better than typical at this level of *ab initio* approximation. The equilibrium constant is:

$$K_p = e^{-\Delta_r G^\circ/RT} = e^{-(23.26\ \text{kJ mol}^{-1})(1000\ \text{J}/1\ \text{kJ})/8.3145\ \text{J K}^{-1}\text{mol}^{-1}\ 298.15\ \text{K}} = 8.43\text{x}10^{-5}$$

Example 30.5.4: *Reaction Gibbs Energies from Electronic Structure Calculations*
Calculate the standard state reaction Gibbs energy and equilibrium constant at 298.15 K for the reaction giving formaldehyde as the product, assuming ideal gases:

$$CO\ (g) + H_2\ (g) \rightleftarrows H_2C{=}O\ (g)$$

Use parameters entirely based on electronic structure calculations, which at B3LYP/cc-pVTZ are given in the table below from Spartan ‘14 (see Figure 30.5.2 for the formaldehyde output):

B3LYP/cc-pVTZ	CO	H_2	$H_2C{=}O$
SCF total energy (H)	-113.357258	-1.179999791	-114.549412841
ZPE (kJ mol^{-1})	13.2370	26.4308	69.6212
Temp. Correction	21.9139	35.1071	79.6286
Entropy Correction (Hv-TSv)	-36.9627	-3.7306	14.4916

Answer: The "Temp. Correction" is the enthalpy and zero-point vibrational correction: [ZPE + H – H(0)]. The "Entropy Correction" is the Gibbs energy and zero-point vibrational correction. See the previous example for the discussion of the *ab initio* energy reference point. The difference in SCF total energies is not corrected for the vibrational zero-points:

$$\begin{aligned}\Delta_r E &= [-114.549412841\text{ H}] - [-113.357258\text{ H} + -1.179999791\text{ H}] \\ &= -0.1215505\text{ H}\,(2625.4974\text{ kJ mol}^{-1}/1\text{ H}) = -31.913\text{ kJ mol}^{-1}\end{aligned}$$

The standard state reaction Gibbs energy is just the total sum of differences [products] – [reactants] of the SCF total energies and the "Entropy Corrections":

$$\begin{aligned}\Delta_r[\text{ZPE} + G - G(0)] &= [14.4916\text{ kJ mol}^{-1}] - [-36.9627\text{ kJ mol}^{-1} + -3.7306\text{ kJ mol}^{-1}] \\ &= 55.1849\text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta_r G^\circ = -31.913\text{ kJ mol}^{-1} + 55.1849\text{ kJ mol}^{-1} = 23.27_2\text{ kJ mol}^{-1}$$

The small difference between the Gaussian and Spartan calculations is largely the result of differing default gradient convergence criteria, and is useful in estimating the corresponding uncertainty in the purely theoretical results. The corresponding equilibrium constant is:

$$K_p = e^{-\Delta_r G^\circ/RT} = e^{-(23.27_2\text{ kJ mol}^{-1})(1000\text{ J}/1\text{ kJ})/8.3145\text{ J K}^{-1}\text{mol}^{-1}\,298.15\text{ K}} = 8.37\text{x}10^{-5}$$

Equilibrium Constants are Determined by Molecular Structure: The equilibrium constant of a chemical reaction is given by $\Delta_r G^\circ = -RT \ln K_p$, with the reaction Gibbs energy given by $\Delta_r G^\circ = \Sigma \nu_i\, G_i^\circ$. In a more insightful way, the relationship between molecular structure and chemical equilibria is displayed by expressing the equilibrium constant directly in terms of the partition functions of the products and reactants. As an initial example, an ideal gas reaction with one-to-one stoichiometry displays all the important attributes of any general chemical reaction:

$$A \rightleftarrows B \qquad 30.5.11$$

Reactions of this type include isomerizations, such as the *cis-trans* isomerization of retinal in the primary process in vision or $HC{\equiv}N \rightleftarrows HN{\equiv}C$. As an introductory and schematic example, consider an equally spaced set of energy levels for the reactant and product, Figure 30.5.4a. To calculate the equilibrium constant, the product and reactant states are superimposed, Figure 30.5.4b. The equilibrium constant is calculated by establishing a Boltzmann distribution while ignoring the distinction between product and reactant states. The Boltzmann weighting factors of each level are listed in the figure. The product states and reactant states are then separated, Figure 30.5.4c. The number of accessible product states and reactant states are the sums of the corresponding Boltzmann weighting factors. The equilibrium constant is the number of accessible product states divided by the number of accessible reactant states:

$$K_p = \frac{\text{accessible product states}}{\text{accessible reactant states}} = \frac{0.368 + 0.050}{1 + 0.135 + 0.018} = 0.363 \tag{30.5.12}$$

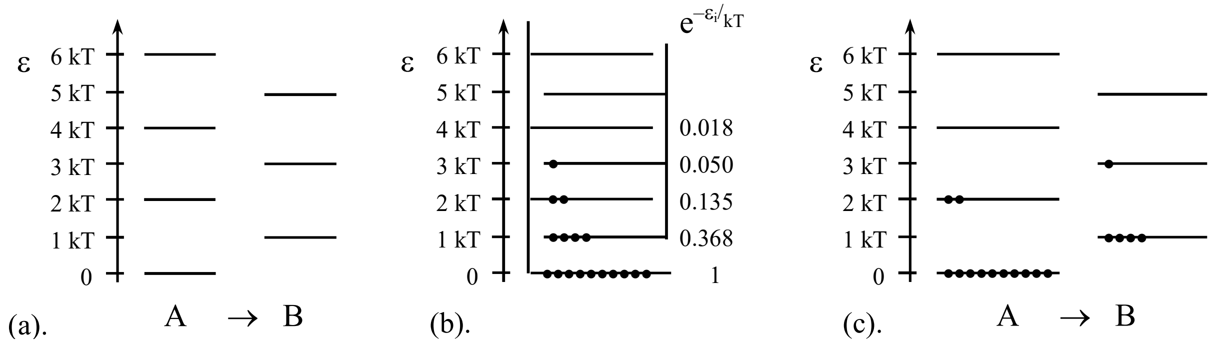


Figure 30.5.4: (a). A schematic isomerization. (b). The Boltzmann distribution is established ignoring the distinction between product and reactant states. (c). The equilibrium constant is the number of accessible product states divided by the number of accessible reactant states.

The equilibrium constant is determined by the random distribution of the available thermal energy among the product and reactant states. Occupations of low energy states have higher probability than high energy states, regardless of whether the state belongs to a product or reactant. The equilibrium state is the most probable state. This example shows that the molecular basis of chemical equilibrium is remarkably simple. Our discussion so far is schematic. We now need to determine the number of accessible states by evaluating partitions functions of the products and reactants that result from accurate models of translation, rotation, vibration, and electronic degrees of freedom. How do translation, rotation, vibration, and electronic states influence chemical equilibria?

Equilibrium Constants of Ideal Gas Reactions: The standard state reaction Gibbs energy of a reaction with stoichiometry A ⇄ B is the difference of products and reactants using Eq. 30.5.2°:

$$\Delta_r G^\circ = G^\circ_B - G^\circ_A = [G^\circ_B(0) - G^\circ_A(0)] - RT \ln\left(q^\circ_B/N_A\right) + RT \ln\left(q^\circ_A/N_A\right) \tag{30.5.13°}$$

Using Eq. 30.5.4, the reaction difference at absolute zero is equal to the quantum mechanical zero-point energy shift, $G^\circ_B(0) - G^\circ_A(0) = \Delta E_o$. The zero-point energy shift is $\Delta E_o = \varepsilon_{oB} - \varepsilon_{oA}$, Figure 30.5.1. Combining the logarithmic terms in Eq. 30.5.13° gives:

$$\Delta_r G^\circ = \Delta E_o - RT \ln\left(\frac{q^\circ_B/N_A}{q^\circ_A/N_A}\right) \tag{30.5.14°}$$

Using $\Delta_r G^\circ = -RT \ln K_p$, we can solve for the logarithm of the equilibrium constant by dividing the previous equation by $-RT$:

$$\ln K_p = \frac{-\Delta E_o}{RT} + \ln\left(\frac{q^\circ_B/N_A}{q^\circ_A/N_A}\right) \tag{30.5.15°}$$

Exponentiation of both sides of this last equation gives the equilibrium constant:

$$K_p = \left(\frac{q^\circ_B/N_A}{q^\circ_A/N_A}\right) e^{-\Delta E_o/RT} \qquad 30.5.16^\circ$$

The result is the ratio of the number of accessible product states divided by the number of reactant states. The partition functions are defined relative to the zero-point energies, Eq. 30.2.25. The "**zero-point energy shift term**," $e^{-\Delta E_o/RT}$, adjusts for the difference in zero-point energies to put the reactants and products on a common energy scale.

Eq. 30.5.16° is derived for the special case of an $A \rightleftarrows B$ reaction. For a more general reaction:

$$aA + bB \rightleftarrows cC + dD \qquad \Delta E_o = c\,\varepsilon_{oC} + d\,\varepsilon_{oD} - a\,\varepsilon_{oA} - b\,\varepsilon_{oB} \qquad 30.5.17^\circ$$

where the ε_{oA}, ε_{oB}, etc. are the zero-point electronic energy levels of each product and reactant. Repeating the steps taken in Eqs. 30.5.13°-30.5.16° gives the more general result:

$$K_p = \frac{\left(q^\circ_C/N_A\right)^c \left(q^\circ_D/N_A\right)^d}{\left(q^\circ_A/N_A\right)^a \left(q^\circ_B/N_A\right)^b} e^{-\Delta E_o/RT} \qquad 30.5.18^\circ$$

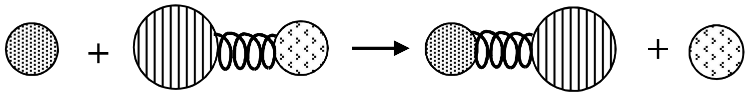
This last equation is so central to our understanding of chemical equilibria that we should do several examples. In particular, Eq. 30.5.18° allows us to focus on the relationship between molecular structure and the position of equilibrium.

An atom-diatom exchange reaction is a good first example, Figure 30.5.5:

$$A + BC \rightleftarrows AB + C \qquad \Delta E_o = \varepsilon_o(AB) - \varepsilon_o(BC) \qquad 30.5.19$$

where A, B, and C are atoms. The zero energy reference-point is chosen as the dissociated atoms, Figure 30.5.1. As a result ΔE_o is the difference in zero-point electronic energies of the product diatomic and the reactant diatomic molecules. The zero-point electronic energies are given by the negative of the bond dissociation energies, $\varepsilon_o(AB) = -D_o(AB)$ and $\varepsilon_o(BC) = -D_o(BC)$, giving the zero-point energy shift as:

$$\Delta E_o = \varepsilon_o(AB) - \varepsilon_o(BC) = [-D_o(AB)] - [-D_o(BC)] \qquad 30.5.20$$



Rotation:	A	R_{BC}	R_{AB}	C
Vibration:		$\tilde{\nu}_o(BC)$	$\tilde{\nu}_o(AB)$	
Electronic:	g_A	g_{BC}	g_{AB}	g_C
Bond energy:		$D_o(BC)$	$D_o(AB)$	

Figure 30.5.5: An atom-diatom exchange reaction. The required spectroscopic information is listed for each species.

The equilibrium constant is the ratio of accessible product and reactant states:

$$K_p = \frac{\left(q^{\circ}_{AB}/N_A\right)\left(q^{\circ}_{C}/N_A\right)}{\left(q^{\circ}_{A}/N_A\right)\left(q^{\circ}_{BC}/N_A\right)}\, e^{-\Delta E_o/RT} \tag{30.5.21°}$$

where the standard state partition functions are q°_{A} for atom-A, q°_{BC} for diatomic-BC, q°_{AB} for diatomic-AB, and q°_{C} for atom-C. The partition function of each diatomic molecule factors into translation, rotation, vibration, and electronic terms. For example with BC the partition function is $q^{\circ}_{BC} = [q^{\circ}_{t}(BC)/N_A]q_r(BC)q_v(BC)q_e(BC)$. All four species have translational and electronic partition functions. The equilibrium constant expression may be correspondingly rearranged into a product of terms for translation, rotation, vibration, and electronic degrees of freedom. The translational partition function is given by Eq. 30.2.19°. In the equilibrium constant, Eq. 30.5.21°, the common factors of $(2\pi kT)^{3/2}V^{\circ}_{m}/h^3$ cancel between products and reactants to give the translational contribution as:

$$q^{\circ}_{t,i} = \frac{(2\pi m_i kT)^{3/2}}{h^3} V^{\circ}_{m} \quad \text{gives} \quad \frac{\left(q^{\circ}_{t}(AB)/N_A\right)\left(q^{\circ}_{t}(C)/N_A\right)}{\left(q^{\circ}_{t}(A)/N_A\right)\left(q^{\circ}_{t}(BC)/N_A\right)} = \left(\frac{m_{AB}\, m_C}{m_A\, m_{BC}}\right)^{3/2} \tag{30.5.22°}$$

with masses m_A, m_{BC}, m_{AB}, and m_C. In the rotational contribution, the common factors of k/hc in the rotational partition functions, Eq. 30.2.33, cancel between products and reactants:

$$q_{r,i} = \frac{kT}{\sigma \tilde{B}_i hc} \quad \text{gives} \quad \frac{q_r(AB)}{q_r(BC)} = \left(\frac{\dfrac{1}{\sigma_{AB}\tilde{B}_{AB}}}{\dfrac{1}{\sigma_{BC}\tilde{B}_{BC}}}\right) \tag{30.5.23}$$

The vibrational partition functions are given by Eq. 30.2.25, and are substituted directly into Eq. 30.5.21°. For this simple example, we assume that there are no low lying excited electronic states, giving the electronic partition functions as the ground state degeneracies g_A, g_{BC}, g_{AB}, and g_C. For atomic species with low energy excited states, the full electronic partition function, Table 30.2.2, must be used. Substitution of Eqs. 30.5.22° and 30.5.23, the vibrational partition functions, and ground state electronic degeneracies into Eq. 30.5.21° gives the equilibrium constant of the atom-diatom reaction as:

$$K_p = \left(\frac{m_{AB}\, m_C}{m_A\, m_{BC}}\right)^{3/2} \left(\frac{\dfrac{1}{\sigma_{AB}\tilde{B}_{AB}}}{\dfrac{1}{\sigma_{BC}\tilde{B}_{BC}}}\right) \left(\frac{\dfrac{1}{1 - e^{-hc\tilde{\nu}_o(AB)/kT}}}{\dfrac{1}{1 - e^{-hc\tilde{\nu}_o(BC)/kT}}}\right) \left(\frac{g_{AB}\, g_C}{g_A\, g_{BC}}\right) e^{-\Delta E_o/RT} \tag{30.5.24°}$$

translation *rotation* *vibration* *electronic* *zero-point energy shift*

The first comment is to note that all parameters needed to calculate the equilibrium constant are derived from spectroscopy of the pure substances. Secondly, even though this relationship is restricted to ideal gas reactions of rigid-rotors and harmonic oscillators, the underlying principles govern all reactions, whether in gas or condensed phases. Lastly, we can build our insight into chemical equilibria by considering “what-if scenarios,” as illustrated in the next example.

Example 30.5.5: *Molecular Structure and Chemical Equilibria*
For the reaction A + BC $\rightleftarrows$ AB + C, consider the shift in equilibrium position, towards products or reactants, after making the following changes. (a). The bond length of AB is increased. (b). BC is changed from a heteronuclear to a homonuclear diatomic. (c). The bond force constant of AB is increased. (d). The ground state of BC is a triplet state instead of a singlet. (e). The bond dissociation energy of AB is increased. [In reality changing just one molecular parameter is impossible, bond strength changes have multiple effects. However, for the purposes of this exercise assume that the given change is done without changes in other parameters.]

Answer: The plan is to note if the change increases or decreases the number of accessible states and if the change is for a product or reactant.

(a). The rotational constant of a diatomic molecule is given by Eq.30.1.34: $\tilde{B} = \frac{\hbar}{4\pi\, \mu R^2\, c}$

If the bond length of AB is increased, the moment of inertia is increased, the rotational constant is decreased, the rotational energy level spacing is decreased, and the number of accessible states is increased for AB. Since AB is a product, increasing the number of accessible states shifts the equilibrium towards products. Equivalently, in Eq. 30.5.24°, decreasing the rotational constant increases the numerator in the accessible states ratio, favoring products.

(b). If BC is changed from heteronuclear to a homonuclear diatomic, the symmetry number increases from one to two, and the number of accessible rotational states is decreased for BC. Since BC is a reactant, decreasing the number of accessible states shifts the equilibrium towards products. Equivalently, in Eq. 30.5.24°, increasing the symmetry number of BC, σ_{BC}, decreases the denominator in the accessible states ratio, favoring products. The number of distinguishable states is always greater than the number of indistinguishable states.

(c). If the bond force constant of AB is increased, the fundamental vibration frequency of AB is increased, the vibrational energy level spacing is increased, and the number of accessible states is decreased. Since AB is a product, decreasing the number of accessible states shifts the equilibrium towards reactants. Equivalently, in Eq. 30.5.24°, increasing the fundamental vibration frequency, $\tilde{\nu}_o(AB)$, decreases the numerator in the accessible states ratio, favoring reactants.

(d). If the ground state of BC is a triplet state instead of a singlet, the ground state degeneracy increases, and the number of accessible electronic states increases. Since BC is a reactant, increasing the number of accessible states shifts the equilibrium towards reactants. Equivalently, in Eq. 30.5.24°, increasing the ground state degeneracy of BC, g_{BC}, increases the denominator in the accessible states ratio, favoring reactants.

(e). The zero-point energy shift is: $\Delta E_o = [-D_o(AB)] - [-D_o(BC)] = D_o(BC) - D_o(AB)$.

If the bond dissociation energy of AB is increased, the zero-point energy shift is decreased, the overall energy states of AB are lowered, and the number of accessible AB states are increased. Since AB is a product, increasing the number of accessible states shifts the equilibrium towards products. Equivalently, in Eq. 30.5.24°, decreasing ΔE_o increases the exponential factor, which favors products. Increasing the bond dissociation energy of a product makes that product more stable, which favors products.

Example 30.5.6: *Molecular Structure and Chemical Equilibria*

Calculate the equilibrium constant of the ideal gas reaction $Na_2 \rightleftarrows Na + Na$ at 1000.0 K. The dissociation of Na_2 is an important process in sodium vapor street lamps. The spectroscopic constants for Na_2 are $R_e = 3.07859$ Å, $\tilde{\nu}_o = 157.66\ cm^{-1}$, and $D_e = 0.759$ eV. The ground state of Na_2 is ${}^1\Sigma_g^+$ and the ground state of Na-atoms is ${}^2S_{½}$.

Answer: The mass of Na_2 is 45.97954 g mol^{-1} and with Eqs. 30.3.1° and 30.3.2°:

$$\frac{q^{\circ}_{t,Na_2}}{N_A} = \Gamma\,(\mathfrak{M}/g\ mol^{-1})^{3/2}(T/K)^{5/2} = 0.0259467\ (45.97954)^{3/2}\ (1000.0)^{5/2} = 2.5582x10^{8}$$

For Na-atoms: $\dfrac{q^{\circ}_{t,Na}}{N_A} = 0.0259467\ (22.98977)^{3/2}\ (1000.0)^{5/2} = 9.0445x10^{7}$

The reduced mass of Na_2 is: $\mu = \dfrac{m_1\,m_2}{m_1 + m_2} = \dfrac{\mathfrak{M}_{Na}/2}{N_A}\ (1\ kg/1000\ g) = 1.90877x10^{-26}$ kg.

With Eqs. 24.4.10 and 24.5.41: $\tilde{B}_e = \dfrac{\hbar}{4\pi\,\mu R_e^2\,c}$

$$\tilde{B}_e = \frac{1.05457266x10^{-34}\ J\ s}{4\pi(1.90877x10^{-26}\ kg)(3.07859x10^{-10}\ m)^2(2.99792458x10^{10}\ cm\ s^{-1})} = 0.154735\ cm^{-1}$$

Using Table 30.4.1, kT/hc = 695.03 cm^{-1} at 1000 K and with Eq. 30.2.33:

$$q_{r,Na_2} = \frac{kT}{\sigma\tilde{B}hc} = \frac{695.03\ cm^{-1}}{2(0.154735\ cm^{-1})} = 2245.9$$

At 1000.0 K, using Eq. 30.2.25: $q_v = \dfrac{1}{1 - e^{-h\tilde{\nu}_o c/kT}} = \dfrac{1}{1 - e^{-157.66\ cm^{-1}/695.03\ cm^{-1}}} = 4.9275$

The reaction products are atoms, while the reference point is for totally dissociated atoms. The zero-point energy shift is then just $\Delta E_o = -\varepsilon_o(Na_2) = -\,[-D_o(Na_2)] = 0.759$ eV. In terms of bond energy, the reactions runs uphill from Na_2. Using Table 30.4.1, kT/e = 0.08617 eV at 1000 K giving the zero-point energy sift term as:

$$e^{-\Delta E_o/RT} = e^{-0.759\ eV/0.08617\ eV} = e^{-8.81} = 1.450\ x10^{-4}$$

Even though the bond dissociation energy is unusually small and the temperature is 1000 K, the zero-point energy shift term is still unfavorable. Considering each degree of freedom separately, the overall equilibrium constant is:

$$K_p = \frac{q^{\circ}_{Na}\,q^{\circ}_{Na}}{q^{\circ}_{Na_2}}\,e^{-\Delta E_o/RT}$$

$$= \left(\frac{q^{\circ}_{t,Na}\,q^{\circ}_{t,Na}}{q^{\circ}_{t,Na_2}}\right)\left(\frac{1}{q^{\circ}_{r,Na_2}}\right)\left(\frac{1}{q^{\circ}_{v,Na_2}}\right)\left(\frac{q^{\circ}_{e,Na}\,q^{\circ}_{e,Na}}{q^{\circ}_{e,Na_2}}\right)e^{-\Delta E_o/RT}$$

$$= \underbrace{\left(\frac{(9.0445x10^{7})(9.0445x10^{7})}{2.5582x10^{8}}\right)}_{translation}\underbrace{\left(\frac{1}{2245.9}\right)}_{rotation}\underbrace{\left(\frac{1}{4.9275}\right)}_{vibration}\underbrace{\left(\frac{2\cdot 2}{1}\right)}_{electronic}\ \underbrace{1.450\ x10^{-4}}_{zero\text{-}point\ energy\ shift}$$

$$K_p = 1.676$$

Na_2 is only 79% dissociated at 1000 K. This example shows the ability of statistical mechanics to easily handle reactions of reactive species at high temperatures that are difficult to study in the laboratory.

To this point we have assumed that the system is always exactly at equilibrium. That restriction has allowed us to work through important issues including the effects of molecular structure on chemical equilibrium. We know that we live in a dynamic universe. Molecules are constantly undergoing collisions and the interactions between molecules are constantly changing, especially in the gas phase. We need to broaden our perspective to consider the extent of deviations from equilibrium in otherwise thermodynamically time-invariant systems.

30.6 Fluctuations[5]

The equilibrium state is the most probable state. The most probable state is the overwhelmingly predominant distribution. The most probable state is given by the Boltzmann distribution. If a fluctuation occurs, then the distribution is perturbed from the Boltzmann distribution. In the canonical ensemble, each system has the same volume, number of molecules, and average energy, but the energy of each system can vary. The ensemble average energy of the system is given by Eqs. 30.3.2, 30.3.4, and 30.3.9:

$$U - U(0) = \langle E \rangle = \frac{\Sigma\, E_i\, e^{-\beta E_i}}{Q} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V = \frac{kT^2}{Q}\left(\frac{\partial Q}{\partial T}\right)_V \qquad (30.2.2,30.2.4,30.2.9)$$

Fluctuations of the energy of the system are given by the ensemble average of the standard deviation of the system energy, $\langle\sigma_E\rangle$. In analogy with Eq. 23.4.36, the square of the standard deviation is:

$$\langle\sigma_E\rangle^2 = \langle(E - \langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 \qquad 30.6.1$$

The ensemble average of the squared energy is given by the sum:

$$\langle E^2\rangle = \frac{\Sigma\, E_i^2\, e^{-\beta E_i}}{Q} \qquad 30.6.2$$

In an analogous fashion to Eqs. 30.3.3 and 30.3.4, this sum is also related to a derivative of the partition function with respect to β. Starting with Eq. 30.3.3, the second derivative of the partition function with respect to β is:

$$\left(\frac{\partial^2 Q}{\partial \beta^2}\right)_V = -\left(\frac{\partial[\Sigma\, E_i\, e^{-\beta E_i}]}{\partial \beta}\right)_V = \Sigma\, E_i^2\, e^{-\beta E_i} \qquad 30.6.3$$

The square of the standard deviation is then given by substituting this last equation into Eq. 30.6.2 and then substituting the result and Eq. 30.3.4 into Eq. 30.6.1:

$$\langle\sigma_E\rangle^2 = \langle E^2\rangle - \langle E\rangle^2 = \frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \beta^2}\right)_V + \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)_V^2 \qquad 30.6.4$$

This last expression is, surprisingly, an old friend in disguise. First, using Eq. 30.3.8, the constant volume heat capacity is given by the derivative of the internal energy with respect to β by:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_V \qquad 30.6.5$$

In turn, since U(0) is a constant, using the last expression and the internal energy as given by Eq. 30.3.4 gives:

$$C_v = -\frac{1}{kT^2}\left(\frac{\partial[U - U(0)]}{\partial \beta}\right)_V = \frac{1}{kT^2}\left[\frac{\partial}{\partial \beta}\left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right)\right]_V \qquad 30.6.6$$

Using the product rule in the second derivative gives:

$$C_v = \frac{1}{kT^2}\left[\frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \beta^2}\right)_V + \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)_V^2\right] \qquad 30.6.7$$

Comparing this last expression with Eq. 30.6.4 gives the squared standard deviation of the system energy as:

$$<\sigma_E>^2 = kT^2\, C_v = \left(\frac{RT^2}{N_A}\right) C_v \qquad 30.6.8$$

with N_A as Avogadro's Number. Who would have guessed? The direct relationship between fluctuations of the energy of the system and the heat capacity is quite remarkable. Heat capacities are the fundamental building blocks of all thermodynamic properties. For example, Third Law absolute entropies are based entirely on the heat capacity of the substance and the enthalpies of the phase transitions. Eq. 30.6.8 shows that without fluctuations, the heat capacity of the system is zero; the system cannot absorb energy from the surroundings. Fluctuations are seen to be central to the system, central to the establishment of equilibrium. The importance of fluctuations does not invalidate the concept of time-invariant equilibrium, however.

Fluctuations are Small for Macro-Scale Systems: While fundamentally important, fluctuations of the system away from the most probable distribution are very small. For example, for a monatomic ideal gas, the internal energy is $^3/_2$ RT and the heat capacity is $^3/_2$ R. The ratio of the fluctuation of the energy to the average energy is:

$$\frac{<\sigma_E>}{<E>} = \frac{\sqrt{(RT^2/N_A)(^3/_2\, R)}}{^3/_2\, RT} = \frac{1}{(^3/_2 N_A)^{1/2}} = 1.05\text{x}10^{-12} \qquad \text{(monatomic ideal)} \quad 30.6.9°$$

which shows that the distribution of states around the most probable state is sharply peaked. Excursions of the probability distribution away from the Boltzmann distribution are exceedingly rare, and the Boltzmann averaged energy and corresponding temperature give the time-invariant equilibrium state. Equilibrium, on the other hand, is maintained through energy exchange with other systems in the ensemble, as enabled by tiny fluctuations in the system energy. In an isolated system, non-equilibrium distributions relax to the equilibrium state by fluctuations (*General Pattern* ℘**11**).

To this point we have considered each molecule from a quantum perspective. However, we have viewed the system as essentially a classical collection of molecules. We have also neglected the influence of a final molecular degree of freedom, that being the spin configuration of the nuclei. As a final discussion in this chapter, we need to consider if we can consider the system as a collection of weakly interacting quantum molecules or if we need to consider the system of N molecules together as a completely quantum system, including the nuclear degree of freedom.

30.7 Indistinguishability, Quantum Statistics, and Statistical Thermodynamics

The total energy of a molecule includes nuclear interactions, which we have neglected up to this point. The intrinsic spins of the nuclei interact with each other, interact with the intrinsic spin of the electrons, and interact with electric fields at each nucleus. These electric fields are created by the electron distribution. Nuclear interactions are probed in various forms of spectroscopy including NMR, ESR, nuclear quadrupole resonance, and rotational spectroscopy. For nuclear-nuclear and nuclear-electron interactions the spin quantum number of the nuclei must be greater than zero, $I > 0$. For nuclear interaction with electric fields the spin quantum number must be one or greater, $I > ½$. Common nuclei with $I = ½$ include ^{1}H, ^{13}C, ^{15}N, ^{18}O, ^{19}F, and ^{29}Si, Table 30.7.1. Common nuclei with $I = 1$ include ^{2}H (deuterium), and ^{14}N. However, the most abundant isotope of ^{12}C, ^{16}O, and ^{32}S has $I = 0$. Except for H_2, the energetic consequences of nuclear interactions are negligible in thermodynamic considerations near room temperature. However, nuclear based symmetry constraints do have important effects in rotational and vibrational spectroscopy and in determining the symmetry number in the rotational partition function.

Table 30.7.1: Nuclear Spin Quantum Number, I, for Example Nuclei.

I	Examples*
0	^{4}He, ^{12}C, ^{16}O, ^{18}O, ^{20}Ne, ^{24}Mg, ^{28}Si, ^{32}S, ^{40}Ca, ^{40}Ar, ^{48}Ti, ^{52}Cr, ^{56}Fe, ^{58}Ni, ^{64}Zn, ^{74}Ge, ^{80}Se, ^{88}Sr, ^{90}Zr, ^{208}Pb
½	^{1}H, ^{3}He, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P, ^{43}Ca, ^{57}Fe, ^{77}Se, ^{111}Cd, ^{113}Cd, ^{117}Sn, ^{119}Sn, ^{123}Te, ^{129}Xe, ^{195}Pt, ^{199}Hg, ^{207}Pb
1	^{2}H, ^{6}Li, ^{14}N
3/2	^{9}Be, ^{7}Li, ^{11}B, ^{23}Na, ^{33}S, ^{35}Cl, ^{37}Cl, ^{39}K, ^{63}Cu, ^{65}Cu, ^{69}Ga, ^{71}Ga, ^{75}As, ^{79}Br, ^{81}Br, ^{87}Rb, ^{137}Ba
5/2	^{17}O, ^{27}Al, ^{55}Mn, ^{47}Ti, ^{121}Sb, ^{127}I, ^{185}Re, ^{187}Re
3	^{10}B
7/2	^{45}Sc, ^{49}Ti, ^{51}V, ^{59}Co, ^{123}Sb, ^{133}Cs, ^{181}Ta, ^{139}La
9/2	^{93}Nb, ^{113}In, ^{115}In, ^{209}Bi

* For $I = 0$: examples of which the most abundant isotope of the element has $I = 0$. The list is not exhaustive.

Particles are Fermions or Bosons: Fundamental particles and atomic nuclei are divided into two types. Particles that have half-integer spin are called **Fermions**. Examples of Fermions include the electron, proton, neutron, and atomic nuclei with half-integer spin. Particles with integer spin are called **Bosons**. Examples of Bosons include photons and nuclei with zero and integer spin. Fermions are governed by **Fermi-Dirac statistics**, in that the wave functions of Fermions are antisymmetric with respect to exchange of nuclear labels. Bosons are governed by **Bose-Einstein statistics**, in that the wave functions of Bosons are symmetric with respect to exchange of nuclear labels. The consequence of Fermi-Dirac statistics for atomic and molecular structure is summarized by the Pauli Exclusion Principle; to ensure wave function anti-symmetry, no two electrons can have the same set of quantum numbers. As a result, no quantum state can hold more than one electron, having either $m_s = +½$ or $m_s = -½$. The consequence of Bose-Einstein statistics is that a quantum state can hold any number of Bosons. However, at high temperature the probability of multiple occupancy is negligible. An analogy is helpful:[6]

> *Imagine you and a friend are placed at random in rooms in the largest building you can imagine. (Each room represents a unique quantum state, and you are a molecule.) If both of you follow Fermi-Dirac rules, you are not allowed to be in the same room. However, if you adhere to Bose-Einstein rules, double occupancy is allowed. If you are both placed at random, and if the number of rooms in huge, the odds that you both land in the same room are quite small. [John S. Winn, Physical Chemistry, ref. 6]*

In determining the partition functions of systems of Fermions, the sum over states must exclude any configuration that has more than a single particle in the same spin-specific energy state. The distribution function of the occupancy of such states is not the Boltzmann distribution. For Bosons, many particles can occupy the same energy state, but then indistinguishability must be taken into account for each individual state. Once again the Boltzmann distribution is not valid. The effects of Bose-Einstein statistics are significant at low temperatures or for volume restricted systems. Luckily, at high temperature in macrosocopic systems there are many more accessible quantum states than particles and the dilute limit is applicable. The Boltzmann distribution is the "classical" average of the Fermi-Dirac and Bose-Einstein distributions and is entirely adequate in describing room temperature macroscopic chemical systems.

The Dilute Limit Requires Many More Available Energy States than Molecules: In Sec. 30.2 we determined that the canonical ensemble and molecular partition functions of a system containing N identical molecules is $Q = q^N/N!$, where N! is the number of permutations of N particles among the N filled states. The validity of the factor of N! to account for indistinguishability requires the dilute limit. The number of available quantum states must be much greater than the number of molecules. Consider just translation as given by the 3D-particle in a box. For one mole of gas at one bar pressure and 298 K, the volume is 24.8 L. The corresponding cubical box of that volume is 2.96 m on a side. For CO_2 with molar mass of 44.0 g mol^{-1}, the spacing between the lowest two particle in a box states, which are $(n_x, n_y, n_z) = (1, 1, 1)$ and $(2, 1, 1)$, is only $h^2/(8ma^2)\ (2^2 - 1^2) = 2.57\text{x}10^{-44}$ J or equivalently $1.30\text{x}10^{-20}$ cm^{-1}. At room temperature the available thermal kinetic energy is 207.22 cm^{-1}, which is 22 orders of magnitude larger than the energy level spacing. An instructive case is for equal n_x, n_y, and n_z quantum numbers. Assuming equal n_x, n_y, and n_z, energy state $(10^{11}, 10^{11}, 10^{11})$ has an energy equal to the available thermal kinetic energy at room temperature. At least $(10^{11})^3$ states are available. In a macroscopic chemical system at room temperature with $\approx 6.02\text{x}10^{23}$ molecules, the dilute limit is clearly valid. Rotation adds many more accessible states.

In the dilute limit, occupation of a given state by more than one molecule is highly improbable. Under these circumstances the distinction between Fermi-Dirac and Bose-Einstein statistics is irrelevant. The system is then essentially classical from the statistical perspective and the Boltzmann distribution is an accurate representation of the probability distribution. In counting the number of indistinguishable states, the number of permutations of N particles is accurate, because there are no multiply occupied states. In fact most states are unoccupied.

For most chemical applications the distinction between Fermions and Bosons is irrelevant in terms of the energy of the system. However, the distinction is important in rotational spectroscopy and in counting the number of accessible rotational states. A good example to aid our discussion is diatomic H_2.

There are Two Kinds of H_2: For the diatomic molecule composed of two ^{1}H-atoms, the two nuclei can have either parallel or anti-parallel nuclear spins, in much the same way as electrons can fill atomic or molecule orbitals with parallel or anti-parallel electron spins, Figure 30.7.1.

Ortho-hydrogen results if the nuclear spins are parallel and *para*-hydrogen results if the nuclear spins are anti-parallel.

$$\Psi_{ns} = \begin{pmatrix} \alpha\alpha \\ \alpha\beta + \beta\alpha \\ \beta\beta \end{pmatrix} \qquad \Psi_{ns} = \alpha\beta - \beta\alpha$$

Figure 30.7.1: In *ortho*-H_2 the nuclear spins are parallel. In *para*-H_2 the nuclei have anti-parallel spins. At 298 K, *ortho*-H_2 is three times as abundant as *para*-H_2.

The conversion between *ortho*- and *para*-forms is slow; the conversion is catalyzed by inhomogeneous magnetic fields or the molecule must dissociate and then recombine. The *para*-form is slightly lower in energy, but that energy difference is negligible at room temperature. The two forms have some important differences in their behavior. The rotational Raman spectrum of H_2 clearly shows the effects of nuclear-spin symmetry.

The Symmetry Number in Rotational Spectroscopy: Since the nuclei of ${}^1H–{}^1H$ have spin ½, the nuclei are Fermions. What observable consequences result from symmetry restrictions required by Fermi-Dirac statistics? The protons that constitute the nuclei are given the wave functions: α for $m_I = +½$ or spin "up" and β for $m_I = –½$ or spin "down." These nuclear-spin wave functions are analogous to the spin wave functions of electrons. The two nuclei are indistinguishable, and so we cannot determine which is specifically "up" and which is specifically "down." We must form symmetry-adapted combinations that don't violate indistinguishability. The combination $\Psi_{ns} = \alpha\beta - \beta\alpha$ is then antisymmetric with respect to exchange of nuclear labels. The three combinations $\Psi_{ns} = \alpha\alpha$, $\alpha\beta + \beta\alpha$, or $\beta\beta$ are symmetric with respect to exchange of labels. In considering the effect of the nuclear-spin symmetry on the properties of the complete molecular wave function, we note that the exchange of nuclear labels in H_2 is identical to a rotation of 180° about an axis perpendicular to the internuclear axis that runs through the molecule's center of mass. The complete wave function of the molecule is the product of electronic, vibrational, rotational, and nuclear-spin wave functions:

$$\Psi = \Psi_{electronic}\,\Psi_{vibration}\,\Psi_{rotation}\,\Psi_{ns} \qquad 30.7.1$$

For ${}^1H–{}^1H$, the overall wave function must be antisymmetric with respect to rotation by 180°. The electronic portion is given by the occupied molecular orbitals. The ground state of H_2 is ${}^1\Sigma_g^+$. Rotation of 180° leaves the electronic wave function unchanged, giving a symmetric electronic part.[7] The ground state vibrational wave function is always totally symmetric (see Problem 38.39 and Figure P28.39.1). The symmetry of the overall wave function for H_2 is then determined by the rotational and nuclear-spin wave functions. The rotational wave functions are given by the spherical harmonics with angular momentum quantum number J, Table 24.5.1.

The symmetry of the rotational wave functions under rotation by 180° can be conveniently determined through analogy with atomic orbitals. The angular portion of the atomic orbitals and the rotational wave functions have identical forms, with the angular momentum quantum number alternately given by ℓ or J. Reference to Figure 25.2.2 shows that s- and d-orbitals are symmetric with respect to rotation by 180°. On the other hand, p-orbitals are antisymmetric with respect to rotation by 180°. By extension, orbitals with even ℓ or J are symmetric with respect to rotation by 180° and orbitals with odd ℓ or J are antisymmetric with respect to rotation by 180°.[7] Now comes the important point. Given the nuclei are Fermions, if the overall molecular wave function is to be antisymmetric, then even J states must be combined with the antisymmetric nuclear-spin wave function, $\Psi_{ns} = \alpha\beta - \beta\alpha$. Correspondingly, odd J states must be combined with the symmetric nuclear-spin wave functions, $\Psi_{ns} = \alpha\alpha$, $\alpha\beta + \beta\alpha$, or $\beta\beta$.

In rotational spectroscopy, *para*-hydrogen, which corresponds to $\Psi_{ns} = \alpha\beta - \beta\alpha$ can only have even J rotational states. Correspondingly, *ortho*-hydrogen can only have odd J rotational states. In addition, there are three symmetric nuclear combinations, giving that at room temperature the probability of occurrence of *ortho*-hydrogen is three times that of *para*-hydrogen. The rotational Raman spectrum then consists of two separate sub-spectra. The even-J transitions correspond to *para*-hydrogen and the odd-J transitions correspond to *ortho*-hydrogen. The rotational transitions alternate in intensity in the ratio 3:1 for odd and even J.

For *para*-hydrogen since only even J-states are possible, when calculating the rotational partition function the sum must include only even J-states. As a result the total partition function is half that of a non-symmetrical molecule. This restriction is the fundamental reason that we must assign the rotational symmetry number of two for symmetrical diatomics, $\sigma = 2$. The rotational symmetry number of *ortho*-hydrogen is also two; only odd J-states are accessible.

The influence of nuclear-spin symmetry on rotational spectra and the rotational partition function is even more striking in the case of CO_2. The careful treatment of nuclear-spin symmetry is beyond the scope of this text. However, the general argument is similar to the case of molecular hydrogen. The nuclei of $^{12}C^{16}O_2$ all have zero spin. As a result the nuclei are all Bosons and the overall wave function must be symmetric. The nuclear-spin wave functions are necessarily symmetric (there are no nuclear spin "ups" and "downs"). The result is that CO_2 can have only even J-states. Every other line is missing in the rotational Raman spectrum and in the rotational fine-structure of vibrational spectra of CO_2. Once again, when calculating the rotational partition function, only even J-states are possible, which corresponds to assigning the rotational symmetry number as $\sigma = 2$. The thermodynamic consequence is a decrease of $-R \ln \sigma$ in the contribution of rotation to the entropy of the molecule (see Problem 30.27).

30.8 Summary – Looking Ahead

Classical thermodynamics guides us by determining the important interrelationships in energy transfer between chemical systems. In particular, Gibbs energy is the appropriate spontaneity criterion at constant temperature and pressure. However, using statistical mechanics we have discovered that all thermodynamics can be insightfully related to molecular properties. Molecular properties determine the number of accessible energy states. The mysteries of thermodynamics have hopefully been dispelled by relating the Gibbs energy of a system to the spectroscopic constants of the molecules. The spectroscopic constants are read directly from experimental spectra. Alternately, spectroscopic constants can be determined by careful electronic structure calculations. We are now able to sit at our desks while calculating the reaction Gibbs energy and equilibrium constant of any reaction of interest, at least in the ideal gas limit. Assuming accurate spectroscopic constants, the calculated equilibrium constant is likely to be better than is available from measurements in the laboratory. This achievement is remarkable and brings many of the goals of chemistry to fruition. However, these advances bring into stark contrast the work that remains to be done before we can truly say that we have a fundamental understanding of all chemical phenomena. We still need accurate theories to determine solvent effects in condensed phase reactions. In addition, much work remains in achieving accurate predictions of the rates of chemical reactions and relaxation phenomena. Non-equilibrium systems relax towards equilibrium through fluctuations in the microscopic properties of the system. Fluctuations in the energy of the system are measured thermodynamically by the heat capacity.

The chemical insight available through statistical mechanics should leave a lasting impression. The interpretation of the equilibrium constant as the ratio of the number of accessible states of the products divided by the number of accessible states of the reactants is powerful. As chemists, our major goal is often to increase the production of products from a chemical reaction. Enhancing the production of products then reduces to molecular structure changes that decrease the energies of the accessible states of the products or increase the energies of the accessible states of the reactants. This insight is the foundation of structure-function relationships in chemical equilibria.

Chapter Summary

1. For independent molecules the ensemble and molecular partition functions are related by: $Q = q^N/N!$ for N indistinguishable molecules. If the molecules are distinguishable, for example by position within a solid lattice, $Q = q^N$.

2. For an ideal gas with independent translation, rotation, vibration, and electronic energies, the molecular partition function is the product of each degree of freedom: $q = q_t\, q_{int} = q_t\, q_r\, q_v\, q_e$, and the canonical ensemble partition function is $Q = (q_t^N/N!)q_r^N\, q_v^N\, q_e^N$.

3. For independent, rigid rotor, harmonic molecules, the molecular partition functions are:

$$q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

$$q_r = \frac{kT}{\sigma\tilde{B}hc} \quad \text{linear} \qquad \text{or} \qquad q_r = \frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{\tilde{A}hc}\right)^{1/2}\left(\frac{kT}{\tilde{B}hc}\right)^{1/2}\left(\frac{kT}{\tilde{C}hc}\right)^{1/2} \quad \text{non-linear}$$

$$q_v = \frac{e^{-h\nu_o/2kT}}{1 - e^{-h\nu_o/kT}} \qquad \text{per mode, with reference } \varepsilon_o = \tfrac{1}{2}h\nu_o$$

$$q_v = \frac{1}{1 - e^{-\beta h\nu_o}} = \frac{1}{1 - e^{-h\nu_o/kT}} = \frac{1}{1 - e^{-hc\tilde{\nu}_o/kT}} \qquad \text{per mode, with reference } \varepsilon_o = 0$$

4. The rotational symmetry number, σ, is the number of indistinguishable orientations produced by rotations about the center of mass of the molecule.

5. The rotational symmetry number is the order of the rotational sub-group of the point group of the molecule. The rotational sub-group is comprised of the proper rotations and the identity.

6. The electronic partition function is the sum of the Boltzmann weighting factors over all electronic energy levels with energy ε_i and degeneracies g_i, with the energy of the ground state as the reference energy, $\varepsilon_{gs} = 0$: $q_e = \Sigma\, g_i\, e^{-\varepsilon_i/kT}$

7. For a system at equilibrium, the internal energy is the Boltzmann average energy. The internal energy and entropy are direct functions of the ensemble partition function or, assuming independent molecules of a pure substance, a direct function of the molecular partition function:

Ensemble: General	Molecular: Ideal gas°
$Q = \Sigma\, e^{-E_i/kT}$	$q = \Sigma\, e^{-\varepsilon_i/kT}$
$p_i = \dfrac{e^{-E_i/kT}}{Q}$	$p_i = \dfrac{e^{-\varepsilon_i/kT}}{q}$
$U - U(0) = \Sigma\, p_i E_i = \dfrac{\Sigma\, E_i\, e^{-E_i/kT}}{Q}$	$U - U(0) = N\, \Sigma\, p_i \varepsilon_i = N \dfrac{\Sigma\, \varepsilon_i\, e^{-\varepsilon_i/kT}}{q}$
$U - U(0) = -\dfrac{1}{Q}\left(\dfrac{\partial Q}{\partial \beta}\right)_V$	$U - U(0) = -\dfrac{N}{q}\left(\dfrac{\partial q}{\partial \beta}\right)_V$
$U - U(0) = \dfrac{kT^2}{Q}\left(\dfrac{\partial Q}{\partial T}\right)_V$	$U - U(0) = \dfrac{nRT^2}{q}\left(\dfrac{\partial q}{\partial T}\right)_V$
$U - U(0) = -\left(\dfrac{\partial \ln Q}{\partial \beta}\right)_V$	$U - U(0) = -N\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V$
$U - U(0) = kT^2\left(\dfrac{\partial \ln Q}{\partial T}\right)_V$	$U - U(0) = nRT^2\left(\dfrac{\partial \ln q}{\partial T}\right)_V$
$S = -k\, \Sigma\, p_i \ln p_i$	$S = -nR\, \Sigma\, p_i \ln p_i$
$S = k \ln Q + \dfrac{U - U(0)}{T}$	$S = nR \ln\left(\dfrac{qe}{N}\right) + \dfrac{U - U(0)}{T}$

8. The molar entropy of an ideal monatomic gas or the translational entropy of any ideal gas is given by the Sackur-Tetrode Equation:

$$S_m = nR \ln\left[\frac{(2\pi mkT)^{3/2} e}{Nh^3}\, V\right] + {}^{3}\!/_{2}\, nR = R \ln\left[\frac{(2\pi mkT)^{3/2} e^{5/2}}{N_A h^3}\, V_m\right]$$

$$S_m = R \ln(V_{m/L}) + {}^{3}\!/_{2}\, R \ln T + {}^{3}\!/_{2}\, R \ln(\mathcal{M}_{/g\ mol^{-1}}) + 11.1037\ J\ K^{-1}\ mol^{-1}$$

9. All thermodynamic potential functions are directly related to the partition function, because internal energy and entropy are directly related to the partition function.

Definition	Ensemble: General	Molecular: Ideal gas°
$H \equiv U + PV$	$H - H(0) = U - U(0) + PV$	$H - H(0) = U - U(0) + nRT$
$A \equiv U - TS$	$A - A(0) = -kT \ln Q$	$A - A(0) = -nRT \ln\left(\dfrac{qe}{N}\right)$
$G \equiv A + PV$	$G - G(0) = -kT \ln Q + PV$	$G - G(0) = -nRT \ln\left(\dfrac{q}{N}\right)$

10. Canonical ensemble partition function relationships apply in general for any system, real or ideal. Relationships in terms of the molecular partition function apply only to ideal gases.

11. For a real gas or condensed phase, the pressure and Gibbs energy are:

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T \qquad G - G(0) = -kT \ln Q + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

12. Assuming translation, rotation, vibration, and electronic degrees of freedom are independent, entropy and the thermodynamic potentials can be separated into additive terms for the center of mass translation and internal degrees of freedom, $q_{int} = q_r\, q_v\, q_e$:

$$S = \left[nR \ln\left(\frac{q_t e}{N}\right) + \frac{U_t - U_t(0)}{T}\right] + \left[nR \ln q_{int} + \frac{U_{int} - U_{int}(0)}{T}\right]$$

$$G - G(0) = -nRT \ln\left(\frac{q_t}{N}\right) - nRT \ln q_{int} = -nRT \ln\left(\frac{q_t}{N}\right) - nRT \ln(q_r\, q_v\, q_e)$$

13. For molar mass in g mol^{-1} the molar standard state translational partition function of an ideal gas is conventionally given in the form:

$$\frac{q^\circ_{t,m}}{N_A} = \frac{(2\pi mkT)^{3/2}}{h^3}\, RT/P^\circ = \Gamma\, (\mathcal{M}/\text{g mol}^{-1})^{3/2}\, (T/K)^{5/2} \qquad (P^\circ = 1 \text{ bar})$$

with the units conversion factor (gamma): $\Gamma = \left(\frac{2\pi k}{N_A\, 1000 \text{ g kg}^{-1}}\right)^{3/2} \frac{R}{N_A P^\circ h^3} = 0.0259467$

14. The spectroscopic rotational temperature is: $\Theta_r = \frac{\tilde{B}hc}{k}$ giving $q_r = \frac{T}{\sigma\Theta_r}$ for a linear molecule.

The spectroscopic vibrational temperature is: $\Theta_v = \frac{\tilde{\nu}_o hc}{k}$ giving $q_v = \frac{1}{1 - e^{-\Theta_v/T}}$ for each mode.

15. The typical sizes of partition functions of small molecules are:

$q_t \cong 10^{28} - 10^{29}$ V/L $\qquad q^\circ_t/N_A \cong 10^6 - 10^7 \qquad q_r \cong 10 - 100 \qquad q_v \cong 1 - 10$

16. In the high temperature approximation, energy levels approach a continuum of available energy states, which gives the classical limit. The approximation can be met with high temperatures or low energy rotations and vibrations, $\tilde{B}hc \ll kT$ or $\tilde{\nu}_o hc \ll kT$.

17. The contribution of rotation and vibration to the molar internal energy and Gibbs energy of an ideal diatomic gas, under the rigid-rotor and harmonic approximations are:

per mole internal	Rotation	Vibration	High temperature or $h\nu_o \ll kT$
q	$q_r = \frac{kT}{\sigma\tilde{B}hc}$	$q_v = \frac{1}{1 - e^{-h\nu_o/kT}}$	$e^{-h\nu_o/kT} \cong 1 - \frac{h\nu_o}{kT}$
		$q_v = \frac{1}{1 - e^{-\beta h\nu_o}}$	$q_v \cong \frac{kT}{h\nu_o}$
$U_m - U_m(0) = \frac{RT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V$	RT	$\frac{(N_A h\nu_o)\, e^{-h\nu_o/kT}}{1 - e^{-h\nu_o/kT}}$	RT
$G_m - G_m(0) = -RT \ln q$	$-RT \ln\left(\frac{kT}{\sigma\tilde{B}hc}\right)$	$RT \ln(1 - e^{-h\nu_o/kT})$	$-RT \ln\left(\frac{kT}{h\nu_o}\right)$
$G_m - G_m(0)$ at 298.15 K	$-RT \ln\left(\frac{207.22 \text{ cm}^{-1}}{\sigma\tilde{B}}\right)$	$RT \ln(1 - e^{-\tilde{\nu}_o/207.22 \text{ cm}^{-1}})$	$-RT \ln\left(\frac{207.22 \text{ cm}^{-1}}{\tilde{\nu}_o}\right)$

18. For each pure substance i: $G^\circ_i(0) = A^\circ_i(0) = H^\circ_i(0) = U^\circ_i(0) = \varepsilon_{o,i} = -D_{o,i}$, where $\varepsilon_{o,i}$ is the zero-point electronic energy, which is the total electronic and zero-point vibrational energy, and $D_{o,i}$ is the dissociation energy to give atoms. The molar standard state Gibbs energy is:

$$G^\circ_i = G^\circ_i(0) - RT \ln\left(\frac{q^\circ_{t,i}}{N_A}\right) - RT \ln(q_{r,i}\, q_{v,i}\, q_{e,i})$$

19. The observed dissociation energy is: $D_o = D_e - ZPE$, with the molar zero-point vibrational energy summed over all modes, $ZPE = \frac{1}{2} N_A hc \sum \tilde{\nu}_o$.

20. The equilibrium constant for a chemical reaction is the number of accessible product states divided by the number of accessible reactant states.

21. For $aA + bB \rightleftarrows cC + dD$, the zero-point energy shift is $\Delta E_o = c\, \varepsilon_{oC} + d\, \varepsilon_{oD} - a\, \varepsilon_{oA} - b\, \varepsilon_{oB}$,

where ε_{oC}, ε_{oD}, ε_{oA}, and ε_{oB} are the zero-point energy levels of each product and reactant, respectively. The equilibrium constant is:

$$K_p = \frac{\left(q^\circ_C/N_A\right)^c \left(q^\circ_D/N_A\right)^d}{\left(q^\circ_A/N_A\right)^a \left(q^\circ_B/N_A\right)^b}\, e^{-\Delta E_o/RT}$$

where q°_C, q°_D, q°_A, and q°_B are the standard-state molecular partition functions of each product and reactant, respectively.

22. The equilibrium constant for an atom-diatom exchange of ideal gas molecules in the rigid rotor-harmonic approximation is:

$$K_p = \left(\frac{m_{AB}\, m_C}{m_A\, m_{BC}}\right)^{3/2} \left(\frac{\dfrac{1}{\sigma_{AB}\tilde{B}_{AB}}}{\dfrac{1}{\sigma_{BC}\tilde{B}_{BC}}}\right) \left(\frac{\dfrac{1}{1-e^{-hc\tilde{\nu}_o(AB)/kT}}}{\dfrac{1}{1-e^{-hc\tilde{\nu}_o(BC)/kT}}}\right) \left(\frac{g_{AB}\, g_C}{g_A\, g_{BC}}\right) e^{-\Delta E_o/RT}$$

translation rotation vibration electronic zero-point energy shift

23. The constant volume heat capacity is:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_V = \frac{1}{kT^2}\left[\frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \beta^2}\right)_V + \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)_V^2\right]$$

24. Fluctuations are given by the squared standard deviation of the system energy as:

$$<\sigma_E>^2 = <E^2> - <E>^2 = kT^2\, C_v = \left(\frac{RT^2}{N_A}\right) C_v$$

25. Without fluctuations, the heat capacity of the system is zero; the system cannot absorb energy from the surroundings. Fluctuations, while thermodynamically negligible, allow the establishment of equilibrium.

26. The complete wave function of the molecule is the product of the electronic, vibrational, rotational, and nuclear wave-spin functions: $\Psi = \Psi_{electronic}\, \Psi_{vibration}\, \Psi_{rotation}\, \Psi_{ns}$.

27. Half-integer spin particles are Fermions. Integer spin particles are Bosons. Under Fermi-Dirac statistics, wave functions of Fermions are antisymmetric with respect to exchange of nuclear labels. Under Bose-Einstein statistics, wave functions of Bosons are symmetric.

28. In dilute systems, Boltzmann statistics are valid; there are many more energy states than molecules so that multiple occupancy of a state is highly improbable. The distinction between Fermi-Dirac and Bose-Einstein statistics is energetically irrelevant at high temperature in macroscopic volumes, except for H_2.

29. Indistinguishability requires that nuclear-spin wave functions of symmetrical molecules are combined as symmetry adapted combinations, symmetric for Bosons and antisymmetric for Fermions. The result decreases the available rotational states in symmetrical molecules giving rise to the symmetry number in the rotational partition function.

Literature Cited:

1. J. E. Sansonetti, W. C. Martin, Handbook of Basic Atomic Spectroscopic Data, *J. Phys. Chem. Ref. Data*, **2005**, *34(4)*, 1560-2259: http://www.nist.gov/data/PDFfiles/jpcrd690.pdf (last accessed 6/2015)

2. A. Kramida, Y. Ralchenko, J. Reader, *NIST Atomic Spectra Database (version 5.2)*, National Institute of Standards and Technology, Gaithersburg, MD, 2014, http://physics.nist.gov/asd, last accessed 6/2015.
3. Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Daschel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khaliullin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill, M. Head-Gordon, "Advances in quantum chemical methods and algorithms in the Q-Chem 3.0 program package," *Phys. Chem. Chem. Phys.*, **2006**, *8,* 3172.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.
5. T. L. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960, Sec. 2.1.
6. J. S. Winn, *Physical Chemistry,* Harper Collins, New York, NY, 1995, Sec. 22.1.
7. J. H. Noggle, *Physical Chemistry, 3rd.Ed.*, Harper Collins, New York, NY, 1996, Sec. 15.5.

Further Reading:

K. A. Dill, S. Bromberg, *Molecular Driving Forces: Statistical Thermodynamics in Chemistry and Biology, 2nd Ed.,* Garland Science, New York, NY, 2011.

R. M. Hanson, S. Green, *Introduction to Molecular Thermodynamics*, University Science, Sausalito, CA, 2008.

L. K. Nash, *Elements of Statistical Thermodynamics, 2nd. Ed.*, Addison-Wesley, Reading, Mass, 1974. Reprinted by Dover, Mineola, NY, 2006.

D. A. McQuarrie, *Statistical Mechanics*, Harper and Row, New York NY, 1976.

D. Chandler, *Introduction to Modern Statistical Mechanics*, Oxford, New York NY, 1987.

Chapter 30: Statistical Mechanics Problems

1. For a diatomic molecule, the rotational energy is $\varepsilon_J = \tilde{B}hc\ J(J+1)$. (a.) Evaluate the rotational partition function of a heteronuclear diatomic molecule at 298.15 K by numerically summing the Boltzmann weighting factors over many energy levels in a spreadsheet. Take $\tilde{B}hc/kT = 0.00200$. The degeneracy of each level is $g_J = 2J + 1$. (b.) Compare your numerical answer to the partition

function using the high temperature approximation: $q_r = kT/(\sigma\tilde{B}hc)$. (c). Which rotational level has the maximum population of molecules? Why?

2. The fundamental vibration frequency for $H^{35}Cl$ is 2885.3 cm^{-1}. Calculate the ratio of the number of molecules in the first excited vibrational state to the number in the ground vibrational state at 298.2 K.

3. The rotational constant for the linear molecule H–C≡N is 1.4782 cm^{-1}.[2] Calculate the ratio of the number of molecules in excited rotational level J = 3 to the number in the ground rotational level J = 0 at 298.2 K. [Hint: take the rotational degeneracy 2J + 1 into account.]

4. Verify the units conversion factor, $\Gamma = 0.0259467$, for the translational partition function in Eqs. 30.3.1-30.3.2 for a P° = 1 bar standard state.

5. (a). Calculate the translational partition function in the form $q^{\circ}_{t,m}/N_A$ for hydrocyanic acid, H–C≡N, at 298.2 K. (b). Calculate the rotational partition function of H–C≡N at 298.2 K. Hydrocyanic acid is linear with rotational constant 1.4782 cm^{-1}.[2]

6. Does anharmonicity have a significant effect on the vibrational partition function? The vibrational constants for diatomic Mg_2 are $\tilde{\nu}_e = 51.12$ cm^{-1}, $\chi_e\tilde{\nu}_e = 1.64$ cm^{-1}, and $\mathcal{Y}_e\tilde{\nu}_e = 0.0162$ cm^{-1}. Using the zero-point energy as the zero in energy, determine the vibrational partition function at 298.2 K by explicit summation for three cases. (a). Assume a harmonic oscillator with the observed vibrational frequency $\tilde{\nu}_o$. Calculate $\tilde{\nu}_o$ using the first and second anharmonicity corrections, extending Eq. 27.5.11 as: $\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e\tilde{\nu}_e + {}^{13}/_{4}\,\mathcal{Y}_e\tilde{\nu}_e$. (b). Assume an anharmonic oscillator including only the first anharmonicity correction, Eq. 27.5.8. (c). Assume an anharmonic oscillator including the first and second anharmonicity corrections, Eq. 27.5.5. [Hint: for the anharmonic oscillator cases, extend the sums until the vibrational energy reaches a maximum, which corresponds to the dissociation limit.]

7. Calculate the electronic partition function of atomic carbon at 298.2 K. The spectroscopic constants for the low-lying electronic states are given in Table 30.2.2.

8. Calculate the contribution of translation to the molar standard state entropy of H–C≡N at 298.2 K. Compare this translation-only result to the literature value of the thermodynamic standard state absolute entropy.

9. Calculate the contribution of rotation to the molar entropy of H–C≡N at 298.2 K. Combine the translational contribution from the previous problem with the rotational contribution. Compare this translation-rotation only result to the literature value of the thermodynamic standard state absolute entropy. Hydrocyanic acid is linear with rotational constant 1.4782 cm^{-1}.[9]

10. Determine the contribution of a vibration to the internal energy of a substance. Use the zero-point vibrational level, $\upsilon = 0$, as the zero in energy. Repeat the derivation giving Eq. 30.4.13. However, this result was derived using Eq. 30.3.15°; use Eq. 30.3.6° as the basis of your derivation, instead.

11. Find the contribution of a vibration to the enthalpy, $H_v - H_v(0)$. Assume the energy zero is at the bottom of the vibrational potential, giving the zero-point $\upsilon = 0$ vibrational level at $\varepsilon_o = ½\, h\nu_o$. For vibrations $H_v - H_v(0) = U_v - U_v(0)$. The reason vibrational enthalpy and internal energy are

equal is that even though $H \equiv U + PV$, the PV correction term is included in calculating the translational enthalpy. [Hint: Eq. 30.3.15° is most convenient for this problem. Note that Eq. 30.4.13 was derived with the $\upsilon = 0$, zero-point vibrational level as the reference energy.]

12. For one mole of an ideal gas at 25°C and constant volume, the number of accessible states increases by 10% with a temperature increase of 20°C. Estimate to a single significant figure (don't use a calculator) the internal energy of the substance. Based on Equipartition neglecting vibration, the value of $U_m - U_m(0)$ for a monatomic ideal gas is $^3/_2$ RT, for a diatomic ideal gas is $^5/_2$ RT, for a linear triatomic is $^5/_2$ RT, and for a bent triatomic is $^6/_2$ RT. To which case does this result most closely correspond?

13. We can find an approximate formula for the internal energy based on the order of magnitude of the change in accessible states by converting Eq. 30.3.16° to base-ten log: ln x = 2.303 log x:

$$U - U(0) = 2.303\ nRT^2 \left(\frac{\partial \log q}{\partial T}\right)_V$$

and at 298.2 K: $U_m - U_m(0) = 1702 \text{ kJ K mol}^{-1}\left(\frac{\partial \log q}{\partial T}\right)_V \approx 2000 \text{ kJ K mol}^{-1}\left(\frac{\partial \log q}{\partial T}\right)_V$

For one mole of an ideal gas at 298 K and constant volume, the number of accessible states increases by a factor of ten for a temperature increase of 20 K. Estimate to a single significant figure (don't use a calculator) the internal energy of the substance.

14. A quick estimate of the rotational contribution to the Gibbs energy of a linear molecule at room temperature is available by converting ln x to log x and using $2.303RT = 5.71 \text{ kJ mol}^{-1}$:

$$G_m - G_m(0) = -2.303\ RT \log\left(\frac{207.2 \text{ cm}^{-1}}{\sigma\tilde{B}}\right) \cong -6 \text{ kJ mol}^{-1} \log\left(\frac{207.2 \text{ cm}^{-1}}{\sigma\tilde{B}}\right)$$

Without using a calculator estimate the contribution of rotation to the molar Gibbs energy of CO_2. The rotational constant for CO_2 is 0.379 cm^{-1}. [Hint: use $\log 10^n = n$]

15. The atomic energy levels for low-lying states of atomic oxygen are given in Figure 30.2.6. These low-lying states are an example of a three-level system. Consider a three level system with energies ε_o, ε_1, and ε_2 with corresponding degeneracies g_o, g_1, and g_2, respectively. The lowest energy level is defined as the energy zero, $\varepsilon_o = 0$. (a). Show that the contribution of the electronic degree of freedom of a three-level system to the molar internal energy is given by:

$$U_m - U_m(0) = N_A \frac{g_1\,\varepsilon_1\, e^{-\varepsilon_1/kT} + g_2\,\varepsilon_2\, e^{-\varepsilon_2/kT}}{g_o + g_1\, e^{-\varepsilon_1/kT} + g_2\, e^{-\varepsilon_2/kT}}$$

(b). Plot the electronic contribution to the molar internal energy of O-atoms as a function of temperature, in the range 10 K to 800 K.

16. Calculate the contribution of the electronic degree of freedom to the molar internal energy of atomic carbon at 298.2 K. The spectroscopic constants for the low-lying electronic states are in Table 30.2.2.

17. Calculate the contribution of the electronic degree of freedom to the molar Gibbs energy of atomic oxygen at 298.2 K. The spectroscopic constants for the low-lying electronic states are in Table 30.2.2.

18. The nucleus of a deuterium atom has a spin of one, I = 1. In a magnetic field of strength B_o, a deuterium nucleus has energy levels $\varepsilon = \gamma\hbar B_o m_I$, with $m_I = +1, 0, -1$. The magnetogyric ratio, γ, is a constant for each isotope of each element. For deuterium, $\gamma = 41.065$ radians s^{-1} T^{-1}, with the magnetic field strength given in tesla, T. For thermodynamic calculations, setting the lowest energy level at $\varepsilon = 0$ is most convenient. With the shifted zero in energy, the deuterium nuclear energies are at $\varepsilon = 0$ for $m_I = +1$, $\varepsilon = \gamma\hbar B_o$ for $m_I = 0$, and $\varepsilon = 2\gamma\hbar B_o$ for $m_I = -1$. Find the partition function and the contribution of the nuclear energy to the internal energy. [This three-level system is the basis of ^{2}H NMR spectroscopy. ^{2}H NMR is common, especially for locking and shimming operations while doing conventional proton and ^{13}C NMR.]

19. The translational partition function of a mobile species on a surface is:

$$q_t = \frac{2\pi mkT}{h^2}\,\sigma$$

where σ is the surface area (not to be confused with the rotational symmetry number). Find the contribution of translation to the molar internal energy of the species, $U_t - U_t(0)$.

20. Find the relationship between the Helmholtz energy and the molecular partition function. Start with $A - A(0) = -kT \ln Q$, Eq. 30.3.40. Find the relationship between the Helmholtz energy and the molecular partition functions of rotation, vibration, and electronic degrees of freedom (just in the form $q_r\, q_v\, q_e$).

21. Find the relationship between the Helmholtz energy and the molecular partition function. Start with $A - A(0) = -kT \ln Q$, Eq. 30.3.40. (See also Problem 30.20). From the resulting equation, derive Eq. 30.3.51°.

22. Calculate the rotational partition function for HF at 298.15 K. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of HF.

23. Calculate the rotational spectroscopic temperature and partition function for HF at 298.15 K. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of HF.

24. Calculate the rotational partition function for $^{24}Mg_2$ at 298.15 K. The bond length is R_e = 3.07859 Å. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy.

25. Calculate the contribution of vibration to the molar entropy at 298.15 K for HCN, given the literature value of the observed bending vibration frequency at $\tilde{\nu}_o = 711.98\ cm^{-1}$ and the two stretching vibrations at 2096.85 cm^{-1} and 3311.47 cm^{-1}.[3] The bending vibration is doubly degenerate. (See also Problems 8 and 9 for the contributions of translation and rotation.)

26. Calculate the vibrational partition function at 298.15 K for Mg_2, given the literature value of the fundamental vibration frequency, $\tilde{\nu}_o = 47.89\ cm^{-1}$. Calculate the contribution of vibration to the zero point energy, and molar internal energy, entropy, and Gibbs energy of Mg_2.

27. The symmetry number, σ, in the rotational partition function may seem arbitrary at first. This problem is designed to explore the effects of the symmetry number on the properties of molecules. A good test case is to consider N_2 and CO. We will look at the contribution of rotation to the entropy of these two very similar diatomic molecules. The mass of N_2 is 28.02 g mol^{-1} and the mass of CO is 28.01 g mol^{-1}, so the contribution of translation to the entropy is essentially identical. The fundamental vibration frequencies of the two are very similar, $\tilde{\nu}_o$ for N_2 is 2359.6 cm^{-1} and for CO is 2170.2 cm^{-1}. The vibrational contribution to the entropy is essentially identical. Both molecules have singlet ground states. The rotational constants are also very similar, $\tilde{B}_e$ for N_2 is 2.010 cm^{-1} and for CO is 1.9314 cm^{-1}. So, the only major difference is the symmetry.

(a). Prove that the contribution of rotation to the molar entropy of a diatomic gas is:

$$S_m = R \ln\left(\frac{kT}{\tilde{B}_e hc}\right) + R - R \ln \sigma$$

(b). Using the result from part a, and assuming that the differences in $\tilde{B}_e$ of N_2 and CO are negligible, calculate the theoretical difference in entropy of N_2 and CO. The experimental entropies are 191.61 J K^{-1} mol^{-1} for N_2 and 197.67 J K^{-1} mol^{-1} for CO. Compare theory and experiment.

(c). Evaluate the contribution of just the symmetry part of the rotational partition function to the equilibrium constant for the reaction: $N_2 + CO_2 \rightleftarrows CO + N_2O$

28. Write your own spreadsheet that reproduces Example 30.5.1.

29. The equilibrium constant expression in Eq. 30.5.24° can be related directly to the bond lengths of the diatomic molecules: R_{AB} for the product and R_{BC} for the reactant. (a). Express Eq. 30.5.24° directly in terms of the bond lengths of the diatomic species. The result clearly shows the relationship between molecular structure and the position of equilibrium. (b). For atom-diatom exchange on the basis of rotation alone, if $R_{AB} > R_{BC}$ are products or reactants favored?

30. Use typical values of the partition functions, Eq. 30.4.5°, to estimate the equilibrium constant of the ideal gas reaction: $O_2 + F \rightleftarrows OF + O$ at 298 K. This reaction is a possible reaction in ozone depletion in the stratosphere. Use $q_t/N_A = 1\text{x}10^7$, $q_r = 100$, and $q_v = 1$. Since OF has an odd number of electrons, assume the ground state of OF is a doublet, $^2\Pi$. The bond dissociation energies are: $D_o(O_2) = 5.126$ eV = 494.6 kJ mol^{-1} and $D_o(OF) = 1.61$ eV = 155 kJ mol^{-1}.

31. Use the "*Equilibrium Constants from Molecular Structure*" applet, "efs.html," on the textbook Web site and companion CD to calculate the equilibrium constant for the reaction in the previous problem: $O_2 + F \rightleftarrows OF + O$ at 298 K. The spectroscopic parameters are available as examples, or the values given in the previous problem can be input by hand. Compare with the approximate results from the previous problem.

32. Consider the reaction AB → A + B, where A and B are atoms. Predict the effect on the equilibrium constant if the following changes are made. (a). The AB molecule is a ground state triplet (like O_2) instead of a singlet. (b). The AB bond length is increased. (c). The AB force constant is increased. (d). The AB bond dissociation energy is increased. [Changing just one molecular parameter is impossible, bond strength changes have multiple effects. For the purposes of this exercise assume that the given change is done without changes in other parameters.]

33. Calculate the equilibrium constant of the ideal gas dissociation $Mg_2 \rightleftarrows Mg + Mg$ at 298.15 K. Assume the isotope is ^{24}Mg. The spectroscopic constants for Mg_2 are $R_e = 3.8905$ Å, $\tilde{\nu}_o = 47.89\ cm^{-1}$, and $D_e = 0.04979(4)$ eV.[1] The ground state of Mg_2 is $^1\Sigma_u^+$ and the ground state of Mg-atoms is ^1S_o.

34. Heat capacities are the fundamental building blocks of all thermodynamic properties. For example, Third Law absolute entropies are based entirely on the temperature dependence of the heat capacity of the pure substance and enthalpies of the phase transitions, which in turn require heat capacities for their measurement. (a). Prove that the constant volume heat capacity of a pure substance is given by:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 2nRT\left(\frac{\partial \ln q}{\partial T}\right)_v + nRT^2\left(\frac{\partial^2 \ln q}{\partial T^2}\right)_v$$

(b). Show that the constant volume heat capacity of rotation of a linear molecule is nR.

35. The Equipartition prediction of the contribution of a vibration to the molar heat capacity of a diatomic molecule is $C_v = R$, which is the maximum contribution at high temperatures. More accurately, the contribution of vibration to the internal energy of a diatomic molecule, in the harmonic approximation, is given by Eq. 30.4.13. (a). Determine the heat capacity of a diatomic molecule, in the harmonic oscillator approximation, usng the following steps. (a). To make the derivation easier, start by showing that the vibrational contribution is given by:

$$U - U(0) = \frac{Nh\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}} = \frac{Nh\nu_o}{e^{\beta h\nu_o} - 1}$$

(b). Then, convert the heat capacity derivative to one written in terms of β:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial U}{\partial \beta}\right)_v\left(\frac{\partial \beta}{\partial T}\right)_v = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_v$$

(c). Show that: $C_v = \frac{N(h\nu_o)^2}{kT^2}\left(\frac{e^{\beta h\nu_o}}{(e^{\beta h\nu_o} - 1)^2}\right)$

(d). Finally show that: $C_v = \frac{N(h\nu_o)^2}{kT^2}\left[\frac{e^{-h\nu_o/kT}}{(1 - e^{-h\nu_o/kT})^2}\right]$

(e). Plot the molar heat capacity from T = 10 to 1000 K for a vibration frequency of 200.0 cm^{-1}. At what temperature, compared to $\tilde{\nu}_o$, does the vibration begin to make a significant contribution to the heat capacity?

Literature Cited:

1. J. G. Speight, *Lange's Handbook of Chemistry, 16th Ed.*, McGraw-Hill, New York, NY, 2005. Table 4.11

2. M. S. Lojko, Y. Beers, "A Table of Rotational Constants of Symmetric Top Molecules Giving Rise to Microwave Spectra," *J. Research National Bureau of Standards – A. Physics and Chemistry*, **1969**, *73A(2)*, 233-239. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6658462/ (last accessed 9/10/2021)

3. T. Shimanouchi, "Tables of Molecular Vibrational Frequencies, Consolidated Volume I, NSRDS-NBS 39," *Nat. Stand. Ref. Data Ser.*, **1972**, *39*, 1-164. https://nvlpubs.nist.gov/nistpubs/Legacy/NSRDS/nbsnsrds39.pdf (last accessed 9/10/2021)