

Chapter 9. Introduction to Statistical Mechanics

Focus question:

If the energy levels of a helium atom in a one-dimensional box are $E_n = n^2 h^2 / 8mL^2$, what is the energy of 10^{20} helium atoms in that box at 300K?

The Statistical Approach

Quantum mechanics deals with the energy levels and wavefunctions of a single system. The system may be simple such as the particle on a line, or the system may be complex as in the molecule $\text{Ru}_3(\text{CO})_{12}$. If we know the energies and wavefunctions for these systems, how can we translate this information into typical thermodynamic concepts such as entropy and energy? That is, how can we apply quantum mechanical results to real chemical systems that contain large numbers of particles? Since chemical systems consist of a large number ($\sim 10^{23}$) of atoms or molecules, the behavior of an individual atom or molecule is relatively unimportant. What is important is the behavior of a large fraction of these atoms or molecules. The behavior of large numbers of particles can be modeled by statistical methods; therefore, statistics provides the bridge from the microscopic world of quantum phenomena (individual system) to the macroscopic world of chemistry (large numbers of systems). In this chapter, we will investigate some statistical concepts and produce relationships that we can use to calculate the energies and other properties of macroscopic systems.

The origin of statistical thermodynamics can be traced to the elegant work produced by Ludwig Boltzmann in the middle to late 1800s. Boltzmann's efforts culminated in the elegant, yet simple, definition of entropy he proposed in 1896:

$$S = k \ln W \quad (9.1)$$

This equation states that entropy, S , is related to the most probable distribution of particles among energy levels, W . According to this equation, if we know how the particles are distributed among the energy levels of the system, then we can calculate the entropy of the system. We can also calculate the other thermodynamic properties such as the internal energy (symbol: U) and Gibbs energy (symbol: G) from this most probable distribution, and ultimately, we can calculate equilibrium constants from the Gibbs energy. Equation (9.1) opens the window to all thermodynamics, but everything depends on finding the most probable distribution.

Most Probable Distribution and the Boltzmann Law

The concept of the most probable distribution is the central idea in statistical mechanics. If we place a large number of molecules in a closed container at a specific temperature, how are these molecules distributed, or arranged, among the different energy levels that are available? There are a large number of possible distributions. Out of all the possible distributions of molecules in energy levels, which distribution is most likely (most probable) to occur? We restrict our discussion to closed systems in this development; that is, a system where the number of molecules and the total energy are constant. The distribution of particles must obey these two restrictions.

Consider the systems shown in Figure 9 – 1. Is system 1, where five particles are in the lowest energy level and five more particles are in the second energy level, the most probable arrangement? Alternatively, is the most probable arrangement system 2, with the particles distributed among all three energy levels, or is system 3, with seven particles in the lowest level, the most probable distribution? How do we determine the most probable distribution?

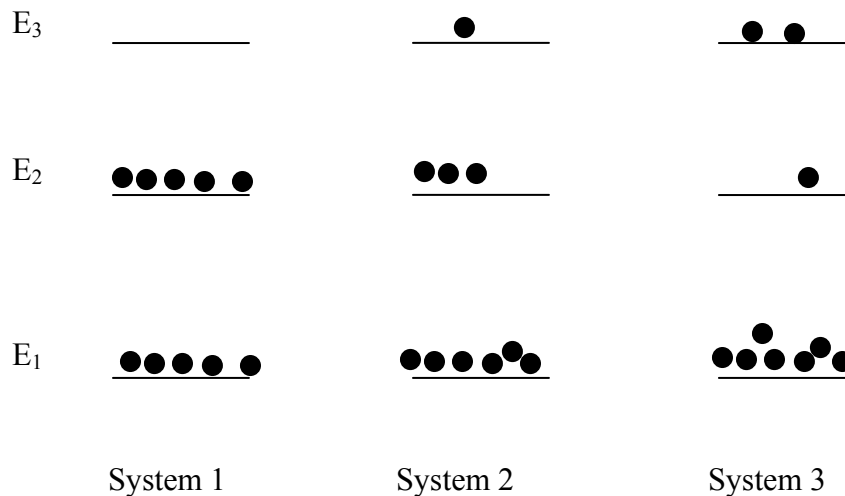


Figure 9 – 1

Since there are a very large number of possible distributions, we cannot discover the most probable distribution by trial and error; we need a method to obtain it. To find the most probable distribution, we will use statistical methods that are designed to work with large numbers of particles.

Permutations and Combinations

Since we are dealing with the distribution of particles among energy levels, we need a bit of mathematics that deal with the arrangements of objects; this is the mathematics of permutations and combinations. The factorial is central to the discussion of permutations and combinations, and the mathematical notation for n factorial is $n!$. $n!$ is defined as the product of $n(n-1)(n-2)(n-3)\dots 1$. In addition, zero factorial is defined as: $0! = 1$. For example, $5! = 5 \times 4 \times 3 \times 2 \times 1 = 120$.

Consider the number of ways that N distinguishable particles can be arranged in N boxes, assuming one particle per box (these are called permutations). Any one of the N particles can be put in the first box. That would leave us with $(N-1)$ particles for the other boxes. We could put any of these $(N-1)$ particles in the second box, leaving us with $N-2$ particles to place in box 3, and so on. For N particles, the number of possibilities is the product of the numbers: $N(N-1)(N-2)(N-3)\dots$. This result is $N!$. Therefore, $N!$ is the number of permutations of N objects, each object placed in its own box. For the case of three particles (labeled 1, 2, 3) and three boxes, a table of the possible permutations is:

Arrangement #	Box 1	Box 2	Box 3
1	1	2	3
2	1	3	2
3	2	1	3
4	2	3	1
5	3	1	2
6	3	2	1

We count six possibilities, and this is the result we get from $3!$.

As a second example, how many ways (permutations) can we assign three distinguishable particles into two boxes, with the first box containing two of the particles? A table of possibilities is:

Arrangement #	Box 1	Box 2
1	1, 2	3
2	1, 3	2
3	2, 3	1

Notice that we do not count the arrangement $\{1,2\}$ as different from $\{2,1\}$ because in both cases particles 1 and 2 are in the box. There are three possible arrangements. From statistics, the equation to calculate the number of arrangements for N particles taken n at a time is:

$$W = \frac{N!}{n!(N-n)!} \quad (9.2)$$

If we use this equation for this example we would have $N = 3$ (there are 3 particles), and $n = 2$ (we have two places to put the particles).

$$W = \frac{3!}{2!(3-2)!} = \frac{6}{2} = 3$$

Therefore, we calculate three possibilities and this is in agreement with our table of data.

In these two examples, we assumed that the particles were labeled and we knew into which box particle 1 goes, and the same for particle 2. In reality, molecules (the particles) are not labeled and are indistinguishable. How do we account for the indistinguishability of particles? To see how this is done, reconsider the first example, but now the particles are indistinguishable.

We have three boxes, and one particle is placed in each box. As in the table above, we have $N!$ ways of placing these particles in the boxes (if we can distinguish among them). Since we cannot distinguish between these particles, there is in reality, only one arrangement for our particles – one particle is in each box! We have overcounted the number of possibilities because we labeled the particles for our counting purposes and thus made them distinguishable. We can correct for the overcounting by dividing our answer by $N!$. Notice that our original result was $3!$, and our overcounting adjustment is $3!$, therefore, we have $3!/3!$, which is one – one arrangement of particles.

In the second example, where two particles were placed in one box, and the other particle placed in a different box, we calculated 3 arrangements. Once again, we have overcounted because the particles are labeled. There is only one arrangement possible; two particles are in one box and one particle is in the other box.

Consider another example. Ten marbles are to be placed in three boxes, arranged such that six marbles are in one box, three in another box, and one marble in the last box. How many ways can this be accomplished? The total number of particles is 10 so there are $10!$ possibilities. The marbles are indistinguishable; therefore, we must correct for overcounting as we did in the example of three particles. Because there are six marbles in the first box, we divide the $10!$ possibilities by $6!$; because there are three marbles in the second box, we divide the $10!$ possibilities by $3!$, and because there is one marble in the third box, we divide $10!$ by $1!$. Thus, we have $\frac{10!}{6!3!1!} = \frac{10 \cdot 9 \cdot 8 \cdot 7 \cdot 6!}{6! \cdot 3 \cdot 2 \cdot 1 \cdot 1} = 840$ possibilities.

We can generalize this discussion for N particles constrained such that N_1 are in box 1, N_2 in box 2 and so on, as:

$$W = \frac{N!}{N_1!N_2!N_3\dots} = \frac{N!}{\prod N_i!} \quad (9.3)$$

W is the number of possibilities for a particular arrangement and it is commonly called the distribution of the particles. The symbol Π is the multiplication symbol just as Σ is the symbol for addition.

To see an application of these ideas, consider the physical situation in Figure 9 – 2 where we have 10 particles and 3 energy levels.

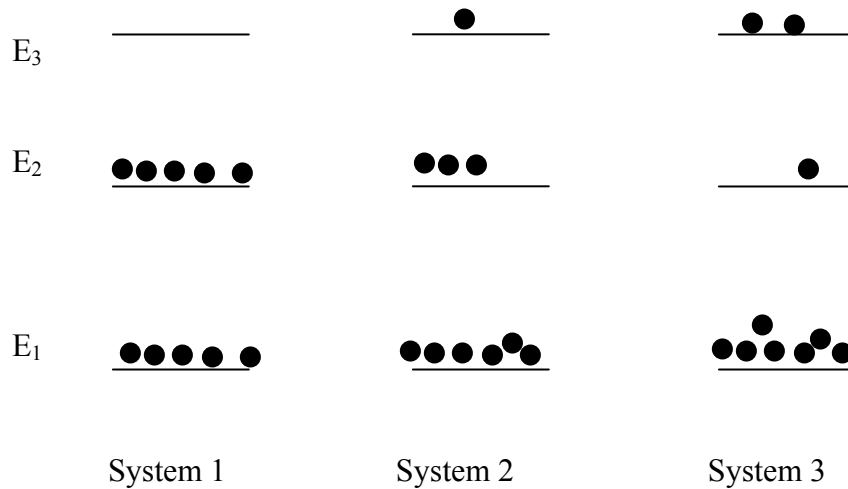


Figure 9 – 2

How many possibilities exist for each arrangement? For system 1, we have:

$W_1 = \frac{10!}{5!5!0!} = 252$; therefore, we have 252 distinct occurrences for the arrangement in system 1. As an exercise, compute W_2 and W_3 .

The number of occurrences is directly related to the probability of finding the system as system 1 or system 2, or system 3. In this example $W_1 = 252$, $W_2 = 840$ and $W_3 = 360$; the total number of possibilities is: $252 + 840 + 360 = 1452$. The probability of observing system 1 is determined from the number of occurrences for system 1 divided by the total number of occurrences for the system: $252/1452 = 17\%$. System 2 has the largest probability (58%), while system 3 has a 25% probability. The fact that system 2 is more probable might almost appear obvious to us because in system 2, most of the particles are in the ground state, fewer in the first excited state, and fewer still in the second excited state.

Derivation of the Boltzmann Distribution

We want to find an equation that describes the most probable distribution of particles – the distribution that has the maximum number of possibilities, W . For simplicity, we will

consider a nondegenerate case, solve the problem, and then generalize our results to situations that have degeneracy. There are two constraints to impose on our physical system as we look for the most probable distribution:

- The system is closed – no particles can enter or leave,
- The system is at thermal equilibrium – the total energy is constant.

The restriction that the total number of particles is constant is represented by:

$$\sum_i N_i = \text{constant}$$

The total energy of the system is the sum of the energy levels multiplied by the number of particles in that energy level:

$$\sum_i N_i \varepsilon_i$$

The restriction that the total energy is constant is represented by:

$$\sum_i N_i \varepsilon_i = \text{constant}$$

Now we can begin our work. Imagine an infinitesimal change in the most probable distribution, dW , caused by changing the number of particles, dN_i in a particular energy state. Since the total energy and total number of particles cannot change, we have, for the change in particles, dN_i :

$$\sum_i dN_i = 0 \tag{9.4}$$

and

$$\sum_i \varepsilon_i dN_i = 0 \tag{9.5}$$

Take the logarithm of the distribution, equation (9.3); recall that the logarithm of a product is the sum of the logarithms and the logarithm of a quotient is the difference of the logarithms:

$$\ln(W) = \ln(N!) - \sum_i \ln(N_i!)$$

To find the maximum, or most probable, distribution, we differentiate this result and set the differential equal to zero:

$$d \ln(W) = d \ln(N!) - d \sum_i \ln(N_i!)$$

Because N is constant, $d \ln(N!) = 0$; therefore, the most probable distribution is given by the expression:

$$d \ln(W) = d \sum_i \ln(N_i!) = 0 \quad (9.6)$$

We are working with very large numbers, and we can use Stirling's approximation to simplify the factorials. Stirling's approximation allows us to replace $N!$ by an expression in N . This approximation is useful because the derivative of a factorial would require many applications of the product rule. Stirling's approximation is:

$$\ln(N!) = N \ln(N) - N$$

For more information see Stirling's Approximation –Where did it come from? At the end of the chapter.

Using Stirling's approximation, we can write the right hand side of equation (9.6), which is:

$$d \sum_i \ln(N_i!) = 0$$

as:

$$d \sum_i (N_i \ln(N_i) - N_i) = 0$$

Take the derivatives, remembering to use the product rule in the first term,

$$\sum_i \{N_i d \ln(N_i) + \ln(N_i) dN_i - dN_i\} = 0$$

Recall that $\frac{dx}{x} = d(\ln x)$ and substitute $\frac{dN_i}{N_i}$ for $d(\ln N_i)$:

$$\sum_i \left\{ N_i \frac{dN_i}{N_i} + \ln(N_i) dN_i - dN_i \right\} = 0$$

Cancel N_i in the first term:

$$\sum_i \{dN_i + \ln(N_i) dN_i - dN_i\} = 0$$

Finally, cancel dN_i to produce:

$$\sum_i \ln(N_i) dN_i = 0$$

The last equation is true for the most probable distribution.

We are not quite finished because we must include the restrictions given by equations (9.4) and (9.5) into the most probable distribution. These restrictions must also be obeyed for *any* change in the particles, dN_i . We incorporate these restrictions into the expression for the maximum distribution by using a mathematical technique called Lagrange's method of undetermined multipliers. In Lagrange's method, the equations for changes in the restrictions are multiplied by *arbitrary* constants and the results are added to the change in the original equation. We then solve the resulting equation including these undetermined multipliers. In our case, we produce three equations containing two undetermined multipliers:

1. Change in the most probable distribution that we just derived:

$$\sum_i \ln(N_i) dN_i = 0$$

2. Restriction on number of particles:

$$\alpha \sum_i dN_i = 0$$

3. Restriction on energy:

$$\beta \sum_i \varepsilon_i dN_i = 0$$

In these equations, α and β are the undetermined constants (or Lagrange multipliers). We combine these three equations and factor out the common term, dN_i :

$$\sum_i (\ln(N_i) + \alpha + \beta \varepsilon_i) dN_i = 0$$

This equation must be true for *any* change, dN_i , so:

$$\ln(N_i) + \alpha + \beta \varepsilon_i = 0$$

Take the exponential of the equation and solve for N_i :

$$N_i = e^{-\alpha} e^{-\beta \varepsilon_i} \tag{9.7}$$

We are almost finished. The sum of all the particles is equal to N , the total number of particles in the system:

$$N = \sum_i N_i$$

Substituting equation (9.7) into this expression gives,

$$N = \sum_i e^{-\alpha} e^{-\beta \varepsilon_i}$$

We can factor out $e^{-\alpha}$ since it does not depend on i :

$$N = e^{-\alpha} \sum_i e^{-\beta \varepsilon_i}$$

Solve for $e^{-\alpha}$:

$$e^{-\alpha} = \frac{N}{\sum_i e^{-\beta \varepsilon_i}}$$

Substitute this expression for $e^{-\alpha}$ into equation (9.7), to produce:

$$\frac{N_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}$$

Later in this chapter, we will show that $\beta = 1/k_B T$ where k_B is Boltzmann's constant, 1.38×10^{-23} J/K, and T is the Kelvin temperature. Accepting this fact for now, we have:

$$\frac{N_i}{N} = \frac{e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}} \quad (9.8)$$

Our derivation is finished. Equation (9.8) is the expression for the most probable distribution subject to the constraints that the total energy and the total number of particles are constant. Equation (9.8) is one form of the **Boltzmann Distribution Law**. The Boltzmann law determines the most probable distribution of particles among various energy states. It tells us the population distribution in a set of energy states – the number of particles, N_i , in any energy state at temperature, T .

The denominator in the Boltzmann distribution is commonly given the symbol, q , and is called the **molecular partition function**:

$$q = \sum_i e^{-\varepsilon_i/k_B T} \quad (9.9)$$

We can solve equation (9.8) for the number of molecules, N_i , in any state:

$$N_i = N \frac{e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}} = N \frac{e^{-\varepsilon_i/k_B T}}{q} \quad (9.10)$$

Equation (9.10) is another form of the Boltzmann distribution law. Equations (9.8) and (9.10) are valid for nondegenerate energy states; if the states are degenerate, then equation (9.10) becomes:

$$N_i = N \frac{g_i e^{-\varepsilon_i/k_B T}}{\sum_i g_i e^{-\varepsilon_i/k_B T}} = N \frac{g_i e^{-\varepsilon_i/k_B T}}{q} \quad (9.11)$$

Where we are now counting over energy levels, and g_i is the degeneracy of level i . Note that the partition function is:

$$q = \sum_i g_i e^{-\varepsilon_i/k_B T} \quad (9.12)$$

We can transform the Boltzmann distribution into a form that provides the ratio of particles in two different levels, i and j . Write equation (9.11) for levels i and j .

$$N_i = N \frac{g_i e^{-\varepsilon_i/k_B T}}{q}$$

and,

$$N_j = N \frac{g_j e^{-\varepsilon_j/k_B T}}{q}$$

Divide these two equations:

$$\frac{N_i = N \frac{g_i e^{-\varepsilon_i/k_B T}}{q}}{N_j = N \frac{g_j e^{-\varepsilon_j/k_B T}}{q}}$$

Canceling terms produces:

$$\frac{N_i}{N_j} = \left(\frac{g_i}{g_j} \right) e^{-(\varepsilon_i - \varepsilon_j)/k_B T} \quad (9.13)$$

Equation (9.13) is another common form of the Boltzmann law, but a form that relates populations in *two* energy levels. Let's apply these statistical concepts to some physical situations.

Molecular Partition Functions, Populations, and Energies

The partition function, equation (9.12), is particularly important because it tells us the number of *thermally accessible energy levels for a system at any temperature*. That is, the partition function tells us the number of energy levels that are occupied at a particular temperature. This information is important for an understanding of spectroscopic intensities, and it is important when we calculate the different thermodynamic quantities such as the enthalpy and the Gibbs energy.

For simplicity, we will express energy in terms of the ratio, ε/k_B , which has units of kelvins. As an example, consider a system with three nondegenerate levels: level 1 has energy $\varepsilon/k_B = 0$ K, level 2 has $\varepsilon/k_B = 30$ K, and level 3 has $\varepsilon/k_B = 100$ K. The partition function is, from (9.12):

$$q = \sum_i g_i e^{-\varepsilon_i/k_B T}$$

Inserting the known quantities produces:

$$q = e^{-0/T} + e^{-30/T} + e^{-100/T} = 1 + e^{-30/T} + e^{-100/T}$$

Let's calculate q at some different temperatures. At 0 K, $q = 1$. Since q is the number of thermally accessible levels, this result means that at 0 K only the first level (the ground level) is occupied. We should have anticipated this result; because at 0 K, there is no thermal energy available to populate any higher energy levels. At 100 K, we calculate that $q = 2.11$ (You should check this result). We interpret this number, 2.11, by stating that the first two levels are thermally occupied at 100 K, and the third level is essentially unoccupied (due to the 0.11). At $T = 300$ K, we find that $q = 2.62$. This value means that level 3 is becoming more occupied at this higher temperature, which we would expect because there is more thermal energy at 300 K than at 100 K. At $T = 3000$ K, we find $q = 2.96$, and all three levels are essentially occupied. At 3000 K, there is enough thermal energy available to occupy all three energy levels.

✎ **Exercise:** Use the partition function, $q = e^{-0/T} + e^{-300/T} + e^{-1500/T}$ to determine the number of occupied energy levels at 100 K, 300 K, and 3000 K. How do these data, at each temperature, compare with the values we previously calculated from $q = e^{-0/T} + e^{-30/T} + e^{-100/T}$ at the same temperatures? What do you think causes the differences? 🙌

✎ **Exercise:** Given the partition function, $q = e^{-0/T} + e^{-15/T} + e^{-185/T}$, what *fraction* of the total molecules would be in each state at: 300 K, at 1000 K? 🙌

Previously, we used quantum mechanics to investigate vibrational energy states. Let's combine the quantum information with our statistics to look at the populations of some vibrational states.

Example: From organic chemistry, you may recall that a C = O stretching mode has a vibrational wavenumber of about 1700 cm^{-1} . Which of the carbonyl vibrational energy levels 0, 1, 2, or 3, are thermally occupied at room temperature (300 K)? Which are occupied at 1500 K?

Solution: The energy of vibration is $\varepsilon = 3.38 \times 10^{-20} \text{ J}$. (Verify this result). Recall that the harmonic oscillator vibrational energy levels are equally spaced with $\Delta\varepsilon = hc\bar{\omega}$, so $\Delta\varepsilon = 3.38 \times 10^{-20} \text{ J}$, and $\Delta\varepsilon/k_B = 2447 \text{ K}$. The partition function for the first four levels is:

$$q = e^{-\frac{1}{2}hc\bar{\omega}/T} + e^{-\frac{3}{2}hc\bar{\omega}/T} + e^{-\frac{5}{2}hc\bar{\omega}/T} + e^{-\frac{7}{2}hc\bar{\omega}/T}$$

We subtract the ground state energy, $\frac{1}{2}\varepsilon$, from each energy term so that the first term in the partition function is e^0 :

$$q = e^{-\frac{(\frac{1}{2}hc\bar{\omega} + \frac{1}{2}hc\bar{\omega})}{T}} + e^{-\frac{(\frac{3}{2}hc\bar{\omega} + \frac{1}{2}hc\bar{\omega})}{T}} + e^{-\frac{(\frac{5}{2}hc\bar{\omega} + \frac{1}{2}hc\bar{\omega})}{T}} + e^{-\frac{(\frac{7}{2}hc\bar{\omega} + \frac{1}{2}hc\bar{\omega})}{T}}$$

Write the expression in terms of $\Delta\varepsilon$:

$$q = e^{-0/T} + e^{-\Delta\varepsilon/T} + e^{-2\Delta\varepsilon/T} + e^{-3\Delta\varepsilon/T}$$

Substitute in the numerical values:

$$q = e^0 + e^{-2447/300} + e^{-2(2447)/300} + e^{-3(2447)/300}$$

At 300 K, $q = 1$ and only the ground vibrational state is occupied at room temperature. At 1500 K, $q = 1.24$. Note that for this vibrational frequency, only the first energy level is essentially populated even at 1500 K.

Exercise: The fundamental vibrational wavenumber for $^{35}\text{Cl}_2$ is 559.71 cm^{-1} . Which of the first four vibrational levels are populated at 300 K and at 1500 K? How do these results compare to the results for the carbonyl group? What causes the difference in behavior?

Ψ: Explain the meaning of each term in the partition function in the example problem. What does it mean to have $q = 1$ at 300 K as in this example?

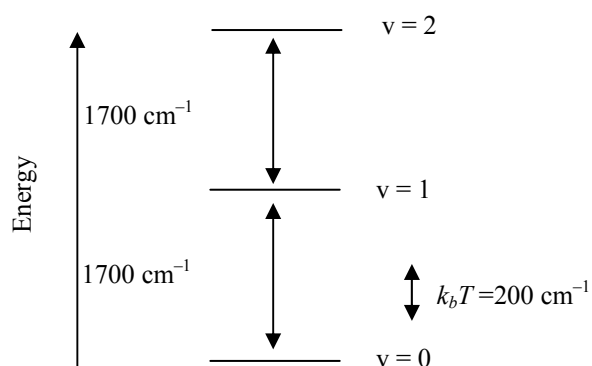
Example: At what temperature would the first two vibrational levels be occupied for the C = O stretch?

Solution: The expression for q is: $q = e^0 + e^{-2447/300} + e^{-2(2447)/300} + e^{-3(2447)/300}$. Since we want two levels to be occupied, we substitute $q = 2$ into the expression:

$$2 = 1 + e^{-2447/T} + e^{-2(2447)/T} + e^{-3(2447)/T}$$

Solving for T by iteration yields $T = 4015$ K. This temperature is needed to occupy the first two vibrational energy levels for a carbonyl stretch. You can see why only the lowest vibrational level is populated at room temperature, and only the fundamental vibration is typically observed in the spectrum. 🙌

In the previous example, we saw that to occupy the second vibrational level required a temperature of about 4000 K. We could have anticipated this result. At room temperature, $k_B T \sim 200 \text{ cm}^{-1}$, so there is not nearly enough thermal energy to populate the first excited state that lies at 1700 cm^{-1} above the ground state.



✎ **Exercise:** What temperature is needed to populate the third vibrational level for a CO stretch? Answer: 11650 K. 🙌

Molecular Partition Functions and the Total Energy

Partition functions are directly related to the total energy of the system. The average energy of a system of particles is given by:

$$E = \sum_i N_i \epsilon_i \quad (9.14)$$

Using equation (9.11) to substitute for N_i in equation (9.14), we get:

$$E = \frac{N}{q} \sum_i \epsilon_i g_i e^{-\epsilon_i / k_B T} \quad (9.15)$$

To proceed further, we use some mathematical sleight of hand. Take the derivative, $\frac{\partial q}{\partial T}$ in equation (9.9),

$$\frac{\partial q}{\partial T} = \frac{\partial}{\partial T} \sum_i g_i e^{-\epsilon_i / k_B T}$$

Evaluating the derivative produces:

$$\frac{\partial q}{\partial T} = \sum_i \frac{-\epsilon_i}{k_B} g_i e^{-\epsilon_i / k_B T} \frac{-1}{T^2}$$

Factor out the constants:

$$\frac{\partial q}{\partial T} = \frac{1}{k_B T^2} \sum_i \epsilon_i g_i e^{-\epsilon_i / k_B T}$$

Isolate the summation term in the last expression:

$$k_B T^2 \frac{\partial q}{\partial T} = \sum_i \epsilon_i g_i e^{-\epsilon_i / k_B T}$$

The summation term in this equation is the same summation that is in equation (9.15), so we can substitute the expression, $k_B T^2 \frac{\partial q}{\partial T}$, into equation (9.15) for the summation to produce:

$$E = k_B T^2 \frac{N}{q} \frac{\partial q}{\partial T} \quad (9.16)$$

or

$$E = Nk_B T^2 \frac{\partial \ln q}{\partial T} \quad (9.17)$$

Therefore, the energy of the system is related to the derivative of the natural logarithm of the partition function with respect to temperature. Equations (9.16) and (9.17) are the fundamental equations that relate the partition function to the total energy of the system. Both forms are used, but the logarithmic form is more common.

Molecular Partition Functions and Molecular Motion

Now that we have a sense of what partition functions are and how they are related to the energy of a system, we can set out to find the partition functions for different kinds of molecular motion. With these equations, we can observe the change in energy as physical variables such as temperature and volume are changed. We will calculate partition functions for different types of molecular energy (translational vibrational rotational and electronic). We will also calculate the total energy for a system of particles by using the partition function and equations (9.16) or (9.17). From these calculations, we can determine how these different energies contribute to the total energy of a system.

Translational Partition Function

What is the energy of a monatomic gas such as argon? Since argon is monatomic, it has no rotational or vibrational motion; consequently, it has only translational motion (electronic energy will be considered later). On the quantum level, the translational energy is obtained from a one-dimensional Schrödinger equation such as the particle on a line, where the energies are:

$$\varepsilon_n = \frac{n^2 h^2}{8mL^2}$$

The partition function for this system is, from equation (9.9),

$$q = \sum_n e^{-\varepsilon_n/k_B T} = \sum_n \exp(-n^2 h^2 / 8mL^2 k_B T)$$

Numerically, this sum can be evaluated using a spreadsheet.

Ψ: Set up a spreadsheet to calculate the energy of an argon atom on a 1.00 m line as a function of n . Evaluate q at 300 K for $n = 10$, $n = 50$, and $n = 100$. Does q change significantly as you change n ? How many energy levels are needed to calculate q with reasonable precision?

Ψ: Show that at 300 K, $\epsilon_2 - \epsilon_1 \ll k_B T$ for this system.

Since the translational energy level spacing is small compared to $k_B T$, we can assume that these levels are essentially continuous and the translational energy is a continuous function of the quantum number, n . With this approximation, the partition function becomes an integral over n :

$$q = \sum_{n=1}^{\infty} \exp(-n^2 h^2 / 8mL^2 k_B T) = \int_1^{\infty} \exp(-n^2 h^2 / 8mL^2 k_B T) dn$$

Since there are a large number of occupied energy levels, little error is incurred by extending the lower limit to zero:

$$\int_0^{\infty} \exp(-n^2 h^2 / 8mL^2 k_B T) dn = \frac{L}{h} \sqrt{2\pi m k_B T}$$

$$q = \frac{L}{h} \sqrt{2\pi m k_B T} \quad (9.18)$$

Equation (9.18) is the partition function for the translational motion of a particle in one dimension. The advantage of equation (9.18) over the sum computed by a spreadsheet is that in equation (9.18) we can deduce the effects of mass, temperature, and length on the partition function. The energy is given by equation (9.17), and we substitute equation (9.18) into equation (9.17):

$$E = N k_B T^2 \frac{\partial \ln q}{\partial T} = N k_B T^2 \frac{\partial \ln \left(\frac{L}{h} \sqrt{2\pi m k_B T} \right)}{\partial T}$$

Use the relation that $\ln(xyz) = \ln(x) + \ln(y) + \ln(z)$ to separate terms:

$$E = N k_B T^2 \frac{\partial}{\partial T} \left(\ln \left(\frac{L}{h} \right) + \ln \left(\sqrt{2\pi m k_B} \right) + \ln \sqrt{T} \right)$$

The first two terms in the derivative expression do not contain T ; and their derivatives are zero. The derivative of the last term is $1/(2T)$, so the energy is:

$$E = N k_B T^2 \left(\frac{1}{2T} \right)$$

$$E = \frac{1}{2} N k_B T$$

If we take N to be Avogadro's number, then $Nk = N_A k = R$ and the energy per mole is:
 $E = \frac{1}{2} RT$.

✎ **Exercise:** Calculate the partition function (equation (9.18)) at 300 K for an argon atom on a 1.00 m line and compare the result to the results of your spreadsheet calculation. 🙌

📌 **Ψ:** Calculate the energy of an argon atom on a 1.00 m line. Compare the energy to $k_B T$ at room temperature. Is $\varepsilon < k_B T$?

In reality, argon is not constrained to move in one dimension; it moves in three dimensions. The energy levels for a particle in a three-dimensional system with lengths a , b , c , are:

$$\varepsilon_{n_x, n_y, n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

For these energies, the partition function is:

$$q = \int_0^\infty \exp(-n_x^2 h^2 / 8ma^2 k_B T) dn_x \int_0^\infty \exp(-n_y^2 h^2 / 8mb^2 k_B T) dn_y \int_0^\infty \exp(-n_z^2 h^2 / 8mc^2 k_B T) dn_z$$

These integrals are evaluated in the same manner as in the one-dimensional case to give:

$$q = \frac{abc}{h^3} \left(\sqrt{2\pi m k_B T} \right)^3 = \frac{V}{h^3} (2\pi m k_B T)^{3/2} \quad (9.19)$$

Where $V = abc$, is the volume of the container. Equation (9.19) is the translational energy of an ensemble of molecules in three dimensions. Once again, the energy of the system is obtained from equation (9.17):

$$E = N k_B T^2 \frac{\partial \ln q}{\partial T} = N k_B T^2 \frac{\partial \ln \left(\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right)}{\partial T}$$

Separating terms:

$$E = N k_B T^2 \frac{\partial}{\partial T} \left(\ln \left(\frac{V}{h^3} \right) + \ln (2\pi m k_B)^{3/2} + \ln (T^{3/2}) \right)$$

Only the last term depends on T , so the derivative is:

$$E = N k_B T^2 \frac{\partial}{\partial T} \ln (T^{3/2}) = \frac{3}{2} N k_B T^2 \left(\frac{1}{T} \right)$$

or

$$E = \frac{3}{2} N k_B T \quad (9.20)$$

The energy of argon in a container is $3/2 N k T$, or on a molar basis: $E = 3/2 R T$, which is the classical thermodynamic expression.

Proof that $\beta = 1/kT$

Earlier, you were asked to accept that $\beta = 1/kT$. Let's now prove this. If we write the partition function in terms of β , we get, from equation (9.9),

$$q = \sum_i g_i e^{-\varepsilon_i \beta}$$

Take the derivative:

$$\frac{\partial q}{\partial \beta} = - \sum_i g_i \varepsilon_i e^{-\varepsilon_i \beta}$$

The average energy is given by the expression:

$$E = \sum_i N_i \varepsilon_i = \frac{N \sum_i g_i \varepsilon_i e^{-\varepsilon_i \beta}}{q}$$

The summation in the energy expression is identical to $-\partial q / \partial \beta$. Substituting $-\partial q / \partial \beta$ into the expression for the energy gives:

$$E = - \frac{N}{q} \frac{\partial q}{\partial \beta}$$

Recall that from equation (9.17):

$$E = \frac{Nk_B T^2}{q} \frac{\partial q}{\partial T}$$

Equating these two expressions for the energy:

$$- \frac{N}{q} \frac{\partial q}{\partial \beta} = k_B T^2 \frac{N}{q} \frac{\partial q}{\partial T}$$

Simplifying the result,

$$- \frac{\partial q}{\partial \beta} = k_B T^2 \frac{\partial q}{\partial T}$$

Eliminating ∂q from both sides and rearranging produces: $\partial T = -k_B T^2 \partial \beta$

Since there are no other variables, replace the partial derivative with full derivatives. Separate the variables to yield:

$$- \frac{dT}{k_B T^2} = d\beta$$

Integrate the expression to obtain:

$$\beta = \frac{1}{k_B T}$$

Vibrational Partition Function

Now we consider the partition function for vibrational motion of a diatomic molecule. The simple harmonic oscillator model will be used as a model because the energy expressions are easier to calculate, and we know that under normal circumstances, the model works well. The energies of the system are:

$$\varepsilon_v = (v + \frac{1}{2})hc\bar{\omega}$$

where v is the vibrational quantum number and $\bar{\omega}$ is the fundamental vibrational wavenumber. Vibrational motion has a zero-point energy of $\frac{1}{2} hc\bar{\omega}$; subtracting this value from the vibrational energy expression gives:

$$\varepsilon_v - \varepsilon_0 = vhc\bar{\omega}$$

The partition function is:

$$q = \sum_v g_v e^{-\Delta\varepsilon/k_B T} = \sum_v g_v e^{-vhc\bar{\omega}/k_B T}$$

There are no degeneracies in diatomic vibrations, so $g_i = 1$. Since v is an integer, the partition function becomes:

$$q = e^{-hc\bar{\omega}/k_B T} + e^{-2hc\bar{\omega}/k_B T} + e^{-3hc\bar{\omega}/k_B T} + \dots$$

Make the substitution, $x = e^{-hc\bar{\omega}/k_B T}$, so that:

$$q = 1 + x + x^2 + x^3 + \dots = \sum_v x^v$$

This is the sum of a geometric series and the result is:

$$\sum_v x^v = \frac{1}{1-x}$$

Using this result, the vibrational partition function for a diatomic molecule is:

$$q = \frac{1}{1-x} = \frac{1}{1 - e^{-hc\bar{\omega}/k_B T}} \quad (9.21)$$


The energy associated with *any* partition function is given by equation (9.17). If we apply equation (9.17) to vibration, we obtain:

$$E = Nk_B T^2 \frac{\partial \ln q}{\partial T} = Nhc\bar{\omega} \frac{e^{-hc\bar{\omega}/k_B T}}{1 - e^{-hc\bar{\omega}/k_B T}}$$


Therefore, the vibrational energy of a diatomic molecule is:

$$E = Nhc\bar{\omega} \frac{e^{-hc\bar{\omega}/k_B T}}{1 - e^{-hc\bar{\omega}/k_B T}} \quad (9.22)$$

Example: Which vibrational levels of $^{35}\text{Cl}_2$ are populated at room temperature?

Solution: We can look up the fundamental vibrational wavenumber of Cl_2 in a table; it is 559.71 cm^{-1} . The vibrational energy, $hc\bar{\omega}$, is $1.11 \times 10^{-20} \text{ J}$. At room temperature, 300K , $k_B T$ is $4.14 \times 10^{-21} \text{ J}$, so $hc\bar{\omega}/k_B T = 2.68$, and, from equation (9.21), $q = 1.07$. Only the first vibrational level is populated at room temperature. 

We can make a rough estimate of a population in a vibrational level by comparing the vibrational wavenumber to the quantity, $k_B T/hc$. At 300 K , the thermal energy, $k_B T/hc \sim 200 \text{ cm}^{-1}$. Since the vibrational spacing, $\bar{\omega}$, of 565 cm^{-1} is greater than the thermal energy, the upper vibrational levels essentially are unoccupied because there is not enough thermal energy available to populate these levels.

Exercise: Compare the partition functions for H_2 and HBr at 300 K and explain the differences. Which molecule has the greater number of populated vibrational energy levels at 300 K ? 

Example: Calculate the vibrational energy of $^{35}\text{Cl}_2$ at 300 K .

Solution: We know the vibrational wavenumber of $^{35}\text{Cl}_2$ is 559.71 cm^{-1} , so that the vibrational energy, $hc\bar{\omega}$, is $1.11 \times 10^{-20} \text{ J}$. At room temperature, 300K , $k_B T$ is $4.14 \times 10^{-21} \text{ J}$; hence $hc\bar{\omega}/k_B T = 2.68$. Substitute this information into equation (9.22):

$$E = Nhc\bar{\omega} \frac{e^{-hc\bar{\omega}/k_B T}}{1 - e^{-hc\bar{\omega}/k_B T}}$$

$$E = 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.11 \times 10^{-20} \text{ J} \times \frac{e^{-2.68}}{1 - e^{-2.68}}$$

$$E = 492 \text{ J mol}^{-1} = 0.492 \text{ kJ mol}^{-1}$$



Rotational Partition Function

You should now be familiar with the overall procedure to obtain partition functions and energies; we will use this method to obtain expressions for the rotational energy.

- We will use the quantum mechanical rotational energy expression:
- Put that expression into the equation for the partition function:
- Try to simplify the result:
- Finally, we will use equation (9.17) to obtain the rotational energy.

Let's limit our discussion to diatomic molecules as we had done previously. The rigid rotor model will be used because the model is simple and the model works well at low energies. Recall that the quantum mechanical energies of the rigid rotor are:

$$\varepsilon_J = J(J+1)\tilde{B}hc$$

Where \tilde{B} is the rotational constant in wavenumbers, $\tilde{B} = \frac{h}{8\pi^2 Ic}$, and I is the moment of inertia. The degeneracies of the rotational energy levels are $g_J = 2J + 1$, so the partition function (9.12) for rotational motion is:

$$q = \sum_J (2J+1) e^{-J(J+1)\tilde{B}hc/k_B T}$$

Ψ: Set up a spreadsheet to calculate the energy of H₂ as a function of J . Evaluate q at 300 K for $J = 10$, $J = 20$, and $J = 50$. How does q change significantly as you change J ? How many energy levels are needed to calculate q with reasonable precision?

Remember that the rotational energy levels are closely spaced, and at temperatures near 300 K, most of the levels are occupied. Under these conditions, the summation can be replaced by an integral (similar to the approach taken for translational motion).

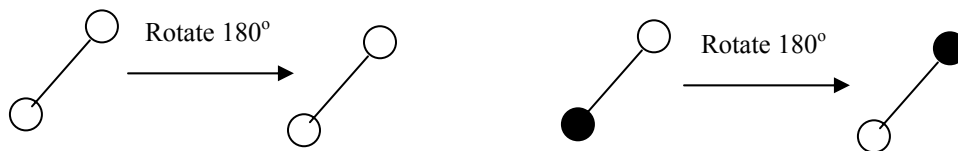
$$q = \int_0^{\infty} (2J+1) e^{-J(J+1)\tilde{B}hc/k_B T} dJ$$

Evaluating the integral produces:

$$q = \frac{k_B T}{\tilde{B}hc} \quad (9.23)$$

The rotational partition function depends only on the temperature and nature of the molecule (through the rotational constant).

One additional factor should be added to the expression for the partition function, equation (9.23). When counting possible arrangements, homonuclear molecules produce different results than heteronuclear molecules. Consider these models of rotation for the homonuclear and heteronuclear cases.



Remember that we are attempting to count *indistinguishable* arrangements of molecules. Obviously, the rotation by 180° for homonuclear molecules produces an identical

configuration as the original configuration and we have overcounted by including it. The overcounting does not occur in heteronuclear diatomic molecules as you can see by the picture to the right (the two arrangements are clearly distinguishable). To compensate for this effect, we introduce a symmetry parameter, σ , into the partition function, equation (9.23). For homonuclear molecules, $\sigma = 2$, while for heteronuclear molecules, $\sigma = 1$. The corrected rotational partition function is:

$$q = \frac{k_B T}{\sigma \tilde{B} h c} \quad (9.24)$$

Exercise: Look up the bond length and calculate the reduced mass of H₂. Use your data to calculate the rotational constant (in cm⁻¹) and then the partition function. What is the value of q at 300 K? How many rotational levels are occupied at this temperature? At what temperature would $q = 3$? Answers: $\tilde{B} = 60.7 \text{ cm}^{-1}$; $q = 1.7$; ~ two; 345 K

The total rotational energy is obtained, as usual, from equation (9.17).

$$E = N k_B T^2 \frac{\partial \ln q}{\partial T}$$

Substitute equation (9.24) for the partition function.

$$E = N k_B T^2 \frac{\partial \ln \left(\frac{k_B T}{\sigma \tilde{B} h c} \right)}{\partial T}$$

Separate terms:

$$E = N k_B T^2 \frac{\partial}{\partial T} \left\{ \ln \left(\frac{k_B}{\sigma \tilde{B} h c} \right) + \ln T \right\}$$

Take the derivative:

$$E = N k_B T^2 \frac{1}{T} = N k_B T$$

Or, on a molar basis:

$$E = RT$$

Therefore, the rotational energy of a diatomic molecule is RT .

Electronic Partition Function

The average electronic energy spacing is very large compared to thermal energy ($k_B T$) at normal temperatures and consequently the excited electronic states are unoccupied. Therefore, electronic partition functions are generally equal to one. There may be a few exceptions to this rule. These exceptions would be caused by a ground state that is not

singly degenerate or by the rare case of small spacing in the electronic energy levels – cases we will not consider.

Ψ: Show that the electronic energy is large relative to $k_B T$ for the iodine molecule. I_2 absorbs energy at ~ 550 nm. What is the energy gap corresponding to this wavelength? Is $\Delta\varepsilon > k_B T$?

Calculation of Thermodynamic Properties

Now that we have, or can obtain, expressions for the partition functions of atoms and molecules, we can use that information to calculate thermodynamic properties. A few examples will be given in this section, but the connection between statistical mechanics and thermodynamics will be illustrated in the next few chapters that deal with energy, entropy, and other thermodynamic variables.

As we have demonstrated earlier, equations (9.14) – (9.17), the energy is related to the partition function:

$$E = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_v \quad (9.25)$$

In equation (9.25), we show explicitly that the volume is constant. Where did this restraint come from? Although it was not apparent in earlier derivations, the energy, E , is a function of both temperature and volume. The temperature dependence is obvious from the temperature in the Boltzmann law, but the origin of the volume dependence is more subtle. We can observe this volume dependence from a simple example, the particle in a three-dimensional box. The quantum mechanical energy expression is inversely related to the volume of the container, and this is the origin of the volume dependence of E .

To relate the statistical energy expression to thermodynamics, we need to relate E in equation (9.25) to the thermodynamic quantity called the internal energy, U . At absolute zero, $E = 0$. As we will see, thermodynamics does not allow the internal energy at absolute zero to be zero. This means that $U = E + E_0$, or $E = U - E_0$. Substituting this expression into equation (9.25) produces:

$$U - E_0 = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_v \quad (9.26)$$

for the internal energy of a system. This is the first connection between the microscopic world of quantum mechanics and the macroscopic world of thermodynamics.

The second thermodynamic quantity we can obtain is the entropy, S . You may recall from general chemistry that entropy is a measure of disorder in a system.

Boltzmann postulated that the entropy of a system was given by equation, (9.1):

$$S = k_B \ln W$$

Since

$$W = \frac{N!}{\prod N_i!}$$

we have:

$$\ln W = \ln N! - \sum_i \ln N_i!$$

Using Stirling's approximation for the factorials, we get:

$$\ln W = N \ln N - N - \sum_i N_i \ln N_i + \sum_i N_i$$

The last term in this expression, $\sum_i N_i$, is equal to N , so the second and last terms cancel, and the equation becomes:

$$\ln W = N \ln N - \sum_i N_i \ln N_i$$

Substitute the Boltzmann equation, (9.11), $\ln N_i = \ln(N) - \varepsilon_i / k_B T - \ln(q)$ into this expression for $\ln N_i$:

$$\ln W = N \ln N - \sum_i N_i \{ \ln N - \varepsilon_i / k_B T - \ln q \}$$

$$\ln W = N \ln N - \sum_i N_i \ln N + \sum_i \frac{-\varepsilon_i N_i}{k_B T} + \sum_i N_i \ln q$$

The first summation is just $N \ln N$ and cancels with the first term. The last term reduces to $N \ln q$, and the result is:

$$\ln W = N \ln q + \sum_i \frac{\varepsilon_i N_i}{k_B T}$$

However, $\sum_i \varepsilon_i N_i$ is the average energy of the system, now designated as $U - E_0$:

$$\ln W = N \ln q + \frac{U - E_0}{k_B T}$$

Multiply by k_B :

$$k_B \ln W = k_B N \ln q + \frac{U - E_0}{T}$$

Therefore:

$$S = k_B N \ln q + \frac{U - E_0}{T} \quad (9.27)$$

We have an expression for the entropy of the system.

As a practical example of equations (9.26) and (9.27), consider 15g of helium in a closed box of volume 2.5 m^3 at 325K. What are the entropy and internal energy of these helium molecules? Since helium is a monatomic gas, we only have translational energy. Assuming that $E_0 = 0$ for simplicity, the translational partition function is, from equation (9.19):

$$q = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$$

Using equations (9.26) for U , and (9.27) for S , produces:

$$U = N k_B T^2 \left(\frac{\partial \ln \left\{ \frac{V}{h^3} (2\pi m k_B T)^{3/2} \right\}}{\partial T} \right)_V = N v T^2 \frac{\partial \ln T^{3/2}}{\partial T} = N k_B T^2 \frac{3/2 \partial \ln T}{\partial T} = \frac{3/2 N k_B T^2}{T}$$

or

$$U = \frac{3}{2} N k_B T$$

$N = 9.0 \times 10^{24}$ molecules, so $U = 1.5 \times 9.0 \times 10^{24} \times 1.38 \times 10^{-23} \text{ J/K} \times 325 \text{ K} = 40 \text{ kJ}$.

For the entropy, we need the logarithm of q : $\ln q = \ln \left(\frac{V}{h^3} \right) + \frac{3}{2} \ln (2\pi m k_B T)$.

Substituting this expression and the expression for U into equation (9.27) produces:

$$S = k_B N \ln \left(\frac{V}{h^3} \right) + \frac{3}{2} k_B N \ln (2\pi m k_B T) + \frac{3}{2} N k_B$$

This expression shows that the entropy of the system depends on the volume, V , temperature, T , and the number of molecules, N . Increasing any of these quantities will increase the entropy.

✍ **Exercise:** Use the data to calculate the entropy of the helium. 🙌

Interacting Particles

The equations that we have derived ((9.26) and (9.27)) are for noninteracting particles. In a real system, particles interact and exchange both their positions and energies. Such a collection of particles is an ensemble. For an ensemble of N interacting and distinguishable particles, the partition function for the ensemble, Q , is related to the molecular partition function, q , by:

$$Q = q^N \quad \text{distinguishable particles} \quad (9.28)$$

If the particles are indistinguishable, we have overcounted and we must include the factor of $N!$ as we had done previously:

$$Q = \frac{q^N}{N!} \quad (9.29)$$

With these modifications, we write the energy and entropy relations as:

$$U - E_0 = Nk_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V \quad (9.30)$$

and

$$S = k_B N \ln Q + \frac{U - E_0}{T} \quad (9.31)$$

What Have We Learned?

In this chapter, we have used quantum mechanical energy expressions to obtain the macroscopic energies of a collection of atoms or molecules. During this transition from the microscopic to the macroscopic, we have introduced and used the techniques of statistical mechanics. The partition function was defined and shown to be of central significance in these calculations. For simplicity, we only calculated quantities for monatomic and diatomic species, but these techniques can be generalized to polyatomic molecules.

The purpose of this chapter was to introduce you to the statistical approach. Statistical mechanics is quite a bit more involved than what was presented here. However, if you

grasp the ideas of most probable distribution, partition function, and their relationship to macroscopic energy, you have a foundation for further study in other courses. In the next few chapters, we will use some of these statistical ideas in thermodynamics.

Useful Equations

Number of arrangements of n objects taken N at a time	$W = \frac{N!}{n!(N-n)!}$
Number of arrangements of N indistinguishable particles taken N at a time	$W = \frac{N!}{N_1!N_2!N_3\dots} = \frac{N!}{\prod N_i!}$
Boltzmann Law	$N_i = N \frac{g_i e^{-\varepsilon_i/k_B T}}{q}$
Molecular Partition function	$q = \sum_i g_i e^{-\varepsilon_i/k_B T}$
Ensemble Partition Function (Indistinguishable particles)	$Q = \frac{q^N}{N!}$
Energy expression	$E = Nk_B T^2 \frac{\partial \ln q}{\partial T}$
Translational partition function	$q = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$
Vibrational partition function	$q = \frac{1}{1-x} = \frac{1}{1 - e^{-hc\bar{\nu}/k_B T}}$
Rotational partition function	$q = \frac{k_B T}{\sigma \tilde{B} h c}$
Entropy	$S = k_B N \ln q + \frac{U - E_0}{T}$

Additional Information – Stirling’s Approximation

Consider $\ln(N!)$,

$$N! = 1 \times 2 \times 3 \times 4 \times \dots \times N$$

Recall that if $x = ab$, then $\ln(x) = \ln(a) + \ln(b)$

$$\ln(N!) = \ln(1) + \ln(2) + \ln(3) + \dots = \sum \ln(x)$$

where we use x as a dummy variable. If we approximate the sum by an integral,

$$\ln(N!) \approx \int_1^N \ln(x) dx$$

The integral of $\ln(x)$ is $x \ln(x) - x$, so

$$\ln(N!) \approx \int_1^N \ln(x) dx = x \ln(x) - x \Big|_1^N$$

Evaluate at the limits:

$$\ln(N!) \approx N \ln(N) - N + 1$$

If N is large, we can neglect the 1 and we get:

$$\ln(N!) \approx N \ln(N) - N$$

This is Stirling’s approximation. It allows us to replace the logarithm of $N!$ with $N \ln N$ and $-N$.

