

Chapter 13: The Molecular Partition Function

In the previous treatments of thermodynamics from the preceding chapters, we have focused on the flow of energy through a system. This approach is sometimes referred to as **Classical Thermodynamics** or the “caloric approach”. In this chapter, we will use the quantum properties of molecules to develop a statistical description of thermodynamics, based on the average behavior of several molecules in a distribution of quantum states (generally determined by the temperature of the sample.)

The statistical approach is based on the distribution of energy in a system of molecules (or ions in a crystal matrix, or whatever microscopic description of matter is appropriate for a given sample.) For example, **Entropy** is a measure of the distribution of energy within a sample of matter. However, in that sample, one molecule may be storing a great deal of **kinetic energy** in the form of molecular rotation as it tumbles through space, while another might be storing a dynamic combination of both kinetic and **potential energy** in the form of molecular vibration.

In order to broach the topic of Thermodynamics from the statistical angle, we must first get a handle on how molecules can store energy within a sample of matter. The simplest case will be the gas phase of matter, since molecules in the gas phase are not hindered in their motions (except through collisions!), so we will begin there.

Quantum Levels

Ever since Niels Bohr first explained the emission spectrum of hydrogen with his simplistic model of the atom [1] [2], it has been clear that some treatment of the quantum nature of small particles would be necessary to describe matter in nature. **Quantum Theory** wasn't just for light anymore!

What the quantum theory tells us about atoms and molecules is that they can be viewed as having specific energy levels. Let's call these $\epsilon_1, \epsilon_2, \dots, \epsilon_N$. Because the total energy of a set of N_{tot} molecules must be a constant,

$$\sum_i N_i \epsilon_i = E_{tot}$$

where

$$\sum_i N_i = N_{tot}$$

The Boltzmann Distribution tells us that the fraction of molecules (N_i/N_{tot}) occupying a particular energy level (ϵ_i) is given by

$$\frac{N_i}{N_{tot}} = \frac{d_i e^{-\frac{\epsilon_i}{k_B T}}}{\sum_i d_i e^{-\frac{\epsilon_i}{k_B T}}}$$

Temperature and the Maxwell-Boltzmann Distribution

Using the Maxwell distribution of velocities, Boltzmann derived an expression for the distribution of kinetic energies [3]. The Maxwell-Boltzmann distribution is derived by making the assumption that

$$-\log\left(\frac{N_i}{N_{tot}}\right) \propto \frac{d_i \epsilon_i}{T}$$

where N_i/N_{tot} gives the fraction of molecules in a sample with energy ϵ_i , and T is the temperature of the sample.

The Molecular Partition Function

The constant of proportionality, it turns out, is a combination of $1/k_B$ and q , the **molecular partition function**. The molecular partition function, q , is given by

$$q = \sum_i d_i e^{-\frac{\epsilon_i}{k_B T}}$$

The molecular partition function can be used to calculate thermodynamic functions, such as entropy, heat capacity, and even equilibrium constants for reactions involving the compound of interest (although for these, one must also determine other molecular partition functions as determined by the stoichiometry of the particular reaction of interest).

Internal Energy

The **Internal Energy** of a sample of molecules in the gas phase is directly related to the molecular partition function. Consider that the Internal Energy (E) of N of gas particles is given by

$$E(T) = \sum_i N_i \epsilon_i$$

where

$$\sum_i N_i = N$$

But, based on the molecular partition function, we know that

$$\frac{N_i}{N} = \frac{d_i e^{-\frac{\epsilon_i}{k_B T}}}{q}$$

so

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

Plugging this into the expression for the internal energy, produces

$$E(T) = \frac{N}{q} \sum_i \varepsilon_i d_i e^{-\frac{\varepsilon_i}{k_B T}}$$

Here, it is useful to note that

$$\frac{dq}{d\left(\frac{1}{k_B T}\right)} = \frac{d}{d\left(\frac{1}{k_B T}\right)} d_i e^{-\frac{\varepsilon_i}{k_B T}} = -\varepsilon_i d_i e^{-\frac{\varepsilon_i}{k_B T}}$$

That means that the preceding equation can be rewritten

$$E(T) = -\frac{N}{q} \frac{dq}{d\left(\frac{1}{k_B T}\right)}$$

Noting that the Internal energy is generally a function of both temperature and volume, the derivative should be a partial derivative with the volume held constant. So after accounting for any offsets,

$$U(T) = U(0) - \frac{N}{q} \left(\frac{\partial q}{\partial \left(\frac{1}{k_B T}\right)} \right)_V$$

And further noting that

$$\frac{\partial q}{q} = \partial \ln q$$

this can be simplified to

$$U(T) = U(0) - N \left(\frac{\partial \ln q}{\partial \left(\frac{1}{k_B T}\right)} \right)_V$$

Translation

Molecular translation has already been discussed in Chapter 2 of this text. The **Maxwell Distribution** of velocities (And the **Maxwell-Boltzmann Distribution** of kinetic energies) give a very good description of a **thermalized** sample of gas-phase molecules that agrees with experimental measurements. The Maxwell-Boltzmann distribution of velocities is given by

$$f(v) = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 e^{-\frac{mv^2}{2k_B T}}$$

where m gives the mass of a single molecule, k_B is the Boltzmann constant.¹

The kinetic energy of a single molecule would be given by

$$E_{kin} = \frac{1}{2}mv^2$$

Rotation

Molecular rotation, like translation, involves energy only of the Kinetic variety. The simplest Quantum Mechanical model of a rotating molecule is that of a rigid rotator, in which the energy is given by

$$E_{rot} = hc B J(J + 1)$$

where h is Planck's constant, c is the speed of light in a vacuum, B is a spectroscopic constant that is a property of a given molecule ($B = \frac{h}{8\pi^2 c \mu r^2}$ for a diatomic molecule) that is related to its **moment of inertia**. And the fraction of molecules in a particular quantum state specified by the quantum number J within a thermalized sample is given by

$$\frac{N_J}{N_{tot}} = \frac{d_J e^{-B J(J+1) \frac{hc}{k_B T}}}{\sum_J d_J e^{-B J(J+1) \frac{hc}{k_B T}}}$$

We can replace the denominator on the right by the **rotational partition function**:

$$q_{rot} = \sum_J d_J e^{-B J(J+1) \frac{hc}{k_B T}}$$

which for a given molecule, at a given temperature, is a constant.

The degeneracy of a rotational energy level is given to

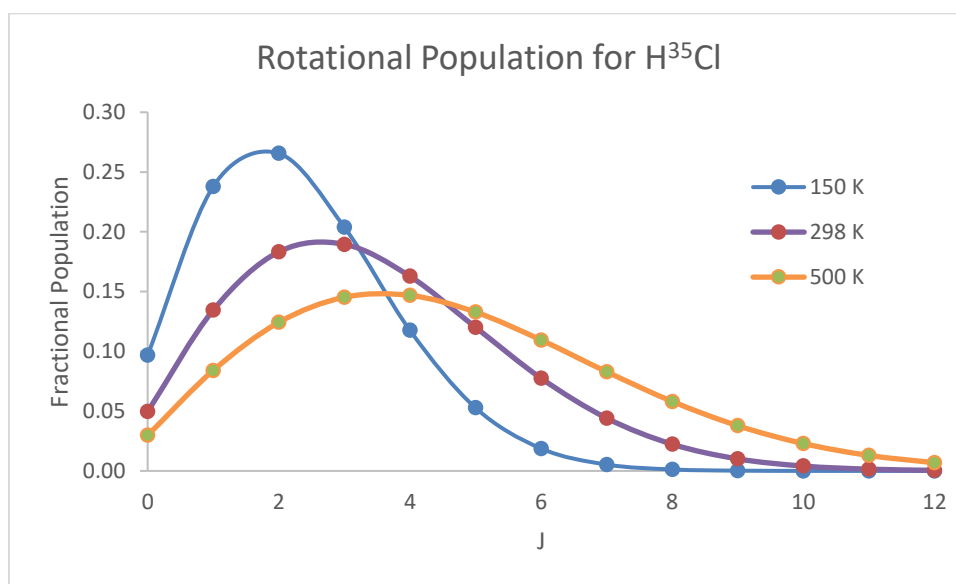
¹ $k_B = 1.38 \times 10^{-23}$ J/K and is also given by R/N_A , where R is the universal gas law constant, and N_A is Avogadro's Number.

$$d_J = (2J + 1)$$

So the fractional population of a rotational level at a given temperature is given by

$$\frac{N_J}{N_{tot}} = \frac{(2J + 1) e^{-B J(J+1) \frac{hc}{k_B T}}}{q_{rot}}$$

This function is interesting because the population will increase as J increases due to the degeneracy, but decrease as J increases due to the exponential term. At low J, the degeneracy will win, whereas at higher J values, the exponential term will take over. This leads to the following kind of pattern for the rotational distribution in H³⁵Cl at several temperatures.



Determining the Rotational Temperature

One can determine the rotational temperature by fitting the population distribution to the distribution function, using the temperature as an adjustable parameter. Another method, albeit less precise, is to use the apparent population maximum [4]. The distribution maximum can be determined by differentiating the function with respect to J and setting the result equal to zero:

$$\frac{d}{dJ} \left[\frac{(2J + 1) e^{-B J(J+1) \frac{hc}{k_B T}}}{q_{rot}} \right] = 0$$

Solving this for J yields

$$J_{max} = \sqrt{\frac{k_B T}{2 B h c}} - \frac{1}{2}$$

Example: From the 298 K data in the figure above, Find the rotational temperature based on the J value for which the maximum population is observed. ($B = 10.44 \text{ cm}^{-1}$)

Solution: The J value that shows the highest population is $J = 3$. So, using the above relationship:

$$3 = \sqrt{\frac{\left(1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}\right) T}{2(10.44 \text{ cm}^{-1})(6.626 \cdot 10^{-34} \text{ J s}) \left(2.998 \cdot 10^{10} \frac{\text{cm}}{\text{s}}\right)}} - \frac{1}{2}$$

Solving for T:

$$\frac{\left(3 + \frac{1}{2}\right)^2 (2)(10.44 \text{ cm}^{-1})(6.626 \cdot 10^{-34} \text{ J s}) \left(2.998 \cdot \frac{10^{10} \text{ cm}}{\text{s}}\right)}{1.38 \cdot 10^{-23} \text{ J/K}} = 368 \text{ K}$$

Note: This temperature came out a bit high, because the maximum of the distribution function actually occurs between $J=2$ and $J=3$.

Vibration

$$\frac{N_v}{N_{tot}} = \frac{d_v e^{-\omega_e \left(v + \frac{1}{2}\right) \frac{hc}{k_B T}}}{\sum_v d_v e^{-\omega_e \left(v + \frac{1}{2}\right) \frac{hc}{k_B T}}}$$

Electronic States

	Expression	Approx. Exp.	Magnitude Estimate
q_{elec}	$q = \sum_i d_i e^{-\frac{E_i}{k_B T}}$	d_0	1
q_{vib}	$q = \sum_v d_v e^{-\frac{hc\omega_e \left(v + \frac{1}{2}\right)}{k_B T}}$	$\left(1 - e^{-\frac{\omega_e hc}{k_B T}}\right)^{-1}$	1-10
q_{rot}	$q = \sum_J (2J + 1) e^{-\frac{hcBJ(J+1)}{k_B T}}$	$\frac{kT}{B}$	100-1000

References

- [1] N. Bohr, "On the Constitution of Atoms and Molecules," *Philosophical Magazine*, vol. 26, no. 6, pp. 1-25, 1913.
- [2] N. Bohr, "On the Constitution of Atoms and Molecules. Part II - systems containing only a Single Nucleus," *Philosophical Magazine*, vol. 26, pp. 476-502, 1913.
- [3] L. Boltzmann, "Über die Beziehung zwischen dem zweiten Hauptsatz der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht," *Mathematisch-Naturwissenschaftliche Classe. Abt. II*, vol. 76, p. 373–435, 1877.
- [4] R. J. Le Roy, "Where Is the Intensity Maximum in a Pure Rotational Spectrum?," *Journal of Molecular Spectroscopy*, vol. 192, pp. 237-238, 1998.

Vocabulary and Concepts

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Problems