

## 10.1: Fractional Population of Quantum States

A molecule will exist in a quantum state with an energy determined by that quantum state. For a sample containing a large number of molecules, several quantum states will be available, and the molecules will be distributed among them. If the sample is thermalized<sup>1</sup>, the distribution will follow the Maxwell-Boltzmann distribution law.

### Maxwell-Boltzmann Distribution Law

According to the **Maxwell-Boltzmann distribution** law, the fraction of the number of molecules in the sample that are in a specific quantum state will be given by

$$\frac{N_i}{N_{tot}} \propto d_i e^{-\frac{E_i}{kT}}$$

where  $N_i/N_{tot}$  is the fraction of the total number of molecules in the  $i^{th}$  quantum state which has energy  $E_i$  relative to the lowest energy the molecule can attain. If the fraction of molecules in each quantum state is added, the result must be unity.

$$\sum_i \frac{N_i}{N_{tot}} = 1$$

### Partition Functions

To ensure this, a **partition function** is introduced to normalize the distribution.

$$q = \sum_i d_i e^{-\frac{E_i}{kT}}$$

And so

$$\frac{N_i}{N_{tot}} = \frac{d_i e^{-\frac{E_i}{kT}}}{q}$$

The partition function, which is a function of temperature as well as the physical properties of the molecules under consideration, can be expressed as a product of partition functions for each type of motion available in the molecule. If electronic, vibrational and rotational energy levels only are considered, the partition function can be expressed as

$$q_{tot} = q_{elec} q_{vib} q_{rot}$$

When considering each type of motion, it is important to consider both the energy levels and the degeneracies of states. As was seen in the case of rotational motion (Chapter IV), at low energies, the degeneracy part of the expression dominates, but at higher energies, the exponential part of the function takes over. If the energy  $E_i$  is very large (relative to  $kT$ ) then there will be essentially no population in the  $i^{th}$  level. This is the case, in general, for electronic excitation; the energy level is so high in energy relative to  $kT$  that there are essentially no molecules in excited electronic state *except at extraordinarily high temperatures*. In this case, where the energy is very large relative to  $kT$

$$\begin{aligned} q &= d_1 e^{-\frac{0}{kT}} + \sum_{i \neq 1} d_i e^{-\frac{E_i}{kT}} \\ &\approx d_1 \cdot 1 + \sum_{i \neq 1} d_i e^{-\infty} \\ &= d_1 + \sum_{i \neq 1} d_i \cdot 0 \\ &= d_1 \end{aligned}$$

Naturally,  $q$  will become larger for motions with small energy level differences (such as rotational motion) where the word “small” is always considered relative to  $kT$ .

Based on the above equations and the degeneracies and energy level expressions for the harmonic oscillator (for  $q_{vib}$ ) and the rigid rotor (for  $d_{rot}$ ) the following approximate expressions can be used to estimate partition functions for each type of motion.

	Expression	Approx. Exp.	Magnitude Estimate
$q_{elec}$	$q = \sum_i d_i e^{-\frac{E_i}{kT}}$	$d_1$	1
$q_{vib}$	$q = \sum_v d_v e^{-\frac{hc\omega_e(v+1/2)}{kT}}$	$\left(1 - e^{-\frac{\omega_e hc}{kT}}\right)^{-1}$	1-10
$q_{rot}$	$q = \sum_J (2J+1) e^{-\frac{hcBJ(J+1)}{kT}}$	$kT/B$	100-1000

## Rotational and Vibrational Temperatures

The above discussion suggests that the temperature of a system can be determined by measuring the populations of individual quantum states. This can be done using spectroscopic intensity data. A line or band in spectrum will be more intense if there are a larger number of molecules in the originating state of the transition. (This is essentially Beer's Law that says that spectral intensity is proportional to concentration.)

Sometimes these analyses will yields results that are not consistent between different types of motion within the molecule. For example, analysis of the vibrational intensity distribution may yield a temperature that is different than the analysis of the rotational intensity distribution. For this reason, scientists often refer to the “**vibrational temperature**” or the “**rotational temperature**” of a sample. These are non-equilibrium situations and are usually dependent on the dynamics of how a molecule was formed within a sample. Some pathways may leave an excess of energy in vibrational modes whereas other may lead to rotationally hot product molecules due to an excess of energy in rotational motion. Typically after a large number of collisions which energy may be transferred from one molecule to another, these temperatures will equilibrate and the Maxwell-Boltzmann distribution law will describe all fractional populations irrespective of the type(s) of motion that dominate(s) an energy level.

## Population Inversion

In the case where all available energy levels are singly degenerate, the **Maxwell-Boltzmann distribution** law suggests that fractional population should decrease with increasing energy. In some cases, the non-equilibrium distribution of molecules through the available quantum states becomes inverted. Again, this situation can be created by the specific dynamics of how a system is prepared. In the case that a population inversion can be created, a laser can be made that uses the sample of molecules with this inverted population as a gain medium to create the laser light output.

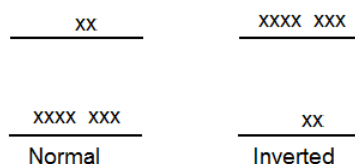


Figure 10.1.1

Theoretically, any system in which a **population inversion** can be induced can be used as a gain medium for a laser.

1. The word “Thermalized” means that all of the molecules in the sample are in “thermal contact” with one another (typically due to a large frequency of collisions with other molecules in the sample) so that there is an equilibrium established for the exchange of energy between molecules in the sample.

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