

The Partition Function: If That's What It Is *Why Don't They Say So!*

Addison Ault, Cornell College, Mount Vernon, IA 52314

Not long ago a former student was telling me about the Stat Mech course he had just finished in grad school, and how he had struggled to figure out the meaning of the partition function. When he finally got it figured out his reaction was “If that's what it is *why don't they say so!*” That was my own reaction, forty-some years ago, when I helped a couple of students work through the second edition of Gordon Barrow's Physical Chemistry.

I believe the main reason that the partition function appears mysterious is that *it has no dimension*. Most quantities have a dimension, and the dimension indicates what the quantity “is”, or represents: it represents a mass, a length, or a volume, and so on. On the other hand, for example, the Reynolds number, like the partition function, has no dimension. The fact that the Reynolds number is 2500 has no meaning unless you know that the Reynolds number is the ratio of inertial forces to viscous forces in a liquid flowing in a pipe.

The origin of the partition function

The partition function comes from a way of counting the particles of a system when the particles are distributed over the available energy levels in accord with the Boltzmann distribution.

The way to count the particles

Count the particles like this. First, represent the total number of particles by N . Then represent the number in the lowest energy level, or ground state, by

n_0 , represent the number in the first excited state by n_1 , the number in the second excited state by n_2 , and so on. Then represent the total number of particles, N , as the sum of the numbers in each energy level:

$$N = n_0 + n_1 + n_2 + n_3 + n_4 \dots \quad \text{Equation 1}$$

In the Boltzmann distribution the number of particles in the first excited state is a fraction of the number of particles in the ground state, and that fraction is $(1/e^{\epsilon_1/kT})$, where ϵ_1 is the energy of the first excited state, relative to the ground state, k is Boltzmann's constant, and T is the absolute temperature. Represent the number of particles in the first excited state as n_0 times this fraction: $n_0(1/e^{\epsilon_1/kT})$.

The number of particles in the second excited state is also a fraction of the number of particles in the ground state, and this second fraction is $1/e^{\epsilon_2/kT}$. This second fraction, however, is smaller than the first fraction because ϵ_2 is greater than ϵ_1 . Represent the number of particles in the second excited state as n_0 times this second fraction: $n_0(1/e^{\epsilon_2/kT})$. Continue in this way and then substitute the resulting expressions for the numbers of particles in each state into Equation 1 to form Equation 2.

$$N = n_0 + n_0(1/e^{\epsilon_1/kT}) + n_0(1/e^{\epsilon_2/kT}) + n_0(1/e^{\epsilon_3/kT}) + n_0(1/e^{\epsilon_4/kT}) \dots \quad \text{Equation 2}$$

Next, factor out n_0 to give Equation 3.

$$N = n_0 (1 + 1/e^{\epsilon_1/kT} + 1/e^{\epsilon_2/kT} + 1/e^{\epsilon_3/kT} + 1/e^{\epsilon_4/kT} \dots) \quad \text{Equation 3}$$

Finally, divide both sides of equation 3 by n_0 to convert it to Equation 4.

$$\frac{N}{n_0} = 1 + 1/e^{\epsilon_1/kT} + 1/e^{\epsilon_2/kT} + 1/e^{\epsilon_3/kT} + 1/e^{\epsilon_4/kT} \dots \quad \text{Equation 4}$$

The partition function

The sum of terms on the right of Equation 4 is called the partition function.

When you let Q stand for the partition function you can rewrite Equation 4 in a very concise form, as Equation 5.

$$\frac{N}{n_0} = Q \quad \text{Equation 5}$$

The partition function is thus seen to be the ratio of the total number of particles to the number of particles in the ground state. The partition function is the number of times larger the total number of particles is than the number of particles in the ground state. The partition function is a measure of the degree to which the particles are spread out over, *or partitioned among*, the energy levels.

The partition function can also be seen to be the total number of particles expressed as the sum of the numbers of particles of each energy, with the population of the ground state being the unit of measure of population.

$$Q = 1 + 1/e^{\epsilon_1/kT} + 1/e^{\epsilon_2/kT} + 1/e^{\epsilon_3/kT} + 1/e^{\epsilon_4/kT} \dots \quad \text{Equation 6}$$

The population of the ground state (the most highly populated state) is taken to be 1, and the populations of the other energy states are expressed as fractions of the population of the ground state. Considered in this way the partition function can be seen as a sum of the relative occupancies of states. It is for this reason that the partition function is also called the sum-over-states, or *Zustandsumme*.

The size of the partition function

The *size* of the partition function depends upon the sizes of the fractional populations, and the size of each fraction depends upon both the *energy* of the excited state and the *temperature* of the system.

Energy dependence

The size of the fractional population of each energy level depends upon the energy of the level, and this fractional population of the level *decreases* as the energy, ϵ , of the level increases. This is because the energy, ϵ , is in the *numerator* of the exponent of e . A larger ϵ makes a larger exponent and a smaller fraction.

Temperature dependence

The size of the fractional population of each energy level also depends upon the temperature of the system, and the fractional population of the level *increases* as the temperature, T , of the system increases. This is because the temperature, T , is in the *denominator* of the exponent of e . A larger T makes a smaller exponent and a larger fraction. The fraction, however, can never become as large as 1.¹

The range of the partition function

The lowest possible value for the partition function is 1, the value it could have when the temperature of the system is 0 K, the temperature at which all particles in the system are in the ground state and the fractions in the excited states are zero.

The highest value for the partition function can be very large, but not infinite. In a real system the number of particles is not infinite, and so the partition function cannot be infinite. The largest values are attained when the spacing of the energy levels is very small and the temperature is very high.

An illustration

The following table, Table 1, illustrates the relationships between energy levels, the absolute temperature, the Boltzmann distribution, and the partition function.

Table 1

state	ϵ/kT	$1/e^{\epsilon/kT}$	number
fourteenth excited	14	0.000 001	0
thirteenth excited	13	0.000 002	0
twelfth excited	12	0.000 006	0
eleventh excited	11	0.000 017	0
tenth excited	10	0.000 045	0
ninth excited	9	0.000 123	1
eighth excited	8	0.000 335	2
seventh excited	7	0.000 911	6
sixth excited	6	0.002 478	16
fifth excited	5	0.006 737	43
fourth excited	4	0.018 315	116
third excited	3	0.049 787	315
second excited	2	0.135 335	855
first excited	1	0.367 879	2325
ground state	0	1.000 000	6321 = n_0

$$\text{sum} = Q = 1.581\,98 \quad \text{sum} = N = 10,000$$

In this example the energy levels are uniformly spaced, and the difference in energy between successive levels is kT . The first column lists the levels in order of increasing energy, from the bottom to the top. The second column gives the ratio of the energy of each level, ϵ , to kT . The third column gives the fractional population of each state relative to the population of the ground state. And the fourth column gives the Boltzmann distribution of 10,000 particles over these energy levels. The sum of the numbers in the third column, 1.58198, is Q ; the sum of the numbers in the fourth column, 10,000, is N ; and the number at the bottom of the fourth column, 6321, is n_0 .

You can see that the ratio of the total number of particles, N , to the number in the ground state, n_0 , does equal the partition function, Q .

$$\frac{N}{n_0} = Q$$

$$\frac{10,000}{6321} = 1.58198$$

Alternatively, you can see that the total number of particles, N , does equal the product of the number of particles in the ground state, n_0 , and the partition function, Q .

$$N = n_0Q$$

$$10,000 = (6321)(1.58198)$$

The importance of the partition function

Quoting Andrews (Reference 1): “The sum Q has a central role in statistical thermodynamics because once it is known as a function of the variables on which it depends, all thermodynamic quantities may be calculated from it directly”. Q is a function of the energies, ϵ , of the quantum states and of the absolute temperature, T . “The set of states in turn is found in principle by using quantum mechanics and is a function of only the number and nature of the particles comprising the system and the constraints”.

Reference

1. Andrews, Frank C., *Equilibrium Statistical Mechanics*, John Wiley & Sons, Inc., 1963, page 35.

Footnote

- 1 When there are fractions of *exactly* the same size (when there are two or more levels with *exactly* the same energy; when there are *degeneracies*), these identical fractions are often combined and the total of the combined fractions can be more than 1.

Acknowledgments

The author acknowledges helpful conversations with real physical chemists and mathematicians. These include, in alphabetical order, Truman Jordan, William Klemperer, Leon Tabak, and Craig Teague.