20.4: How can Infinitely Many Probabilities Sum to Unity?

There are an infinite number of successively greater energies for a quantum mechanical system. We infer that the probability that a given energy level is occupied is a property of the energy level. Each of the probabilities must be between 0 and 1. When we sum the fixed probabilities associated with the energy levels, the sum contains an infinite number of terms. By the nature of probability, the sum of this infinite number of terms must be one:

$$\begin{aligned} 1 &= P_1 + P_2 + \dots + P_i + \dots \\ &= P\left(\epsilon_1\right) + P\left(\epsilon_2\right) + \dots + P\left(\epsilon_i\right) + \dots \\ &= \sum_{i=1}^{\infty} P\left(\epsilon_i\right) \end{aligned}$$

That is, the sum of the probabilities is an infinite series, which must converge: The sum of all of the occupancy probabilities must be unity. This can happen only if all later members of the series are very small. In the remainder of this chapter, we explore some of the thermodynamic ramifications of these facts. In the next chapter, we use this relationship to find the functional dependence of the P_i on the energy levels, ϵ_i. To obtain these results, we need to think further about the probabilities associated with the various population sets that can occur. Also, we need to introduce a new fundamental postulate.

To focus on the implications of this sum of probabilities, let us review geometric series. A **geometric series** is a sum of terms, in which each successive term is a multiple of its predecessor. A geometric series is an infinite sum that can converge:

$$T = a + ar + ar^2 + \dots + ar^i \dots = a\left(1 + r + r^2 + \dots + r^i + \dots\right) = a + a\sum_{i=1}^{\infty} r^i$$

Successive terms approach zero if $|r| < 1$. If $|r| \geq 1$, successive terms do not become smaller, and the sum does not have a finite limit. If $|r| \geq 1$, we say that the infinite series **diverges**.

We can multiply an infinite geometric series by its constant factor to obtain

$$\begin{aligned} rT &= ar + ar^2 + ar^3 + \dots + ar^i + \dots \\ &= a\left(r + r^2 + r^3 + \dots + r^i + \dots\right) \\ &= a\sum_{i=1}^{\infty} r^i \end{aligned}$$

If $|r| < 1$, we can subtract and find the value of the infinite sum:

$$T - rT = a$$

so that

$$T = a/(1 - r)$$

In a geometric series, the ratio of two successive terms is $r^{n+1}/r^n = r$ The condition of convergence for a geometric series can also be written as

$$\left|\frac{r^{n+1}}{r^n}\right| < 1$$

We might anticipate that any other series also converges if its successive terms become smaller at least as fast as those of a geometric series. In fact, this is true and is the basis for the ***ratio test*** for convergence of an infinite series. If we represent successive terms in an infinite series as t_i, their sum is

$$T = \sum_{i=0}^{\infty} t_i$$

The ratio test is a theorem which states that the series converges, and T has a finite value, if

$$\lim_{n\to\infty}\left|\frac{t_{n+1}}{t_n}\right|<1$$

One of our goals is to discover the relationship between the energy, ϵ_i, of a quantum state and the probability that a molecule will occupy one of the quantum states that have this energy, $P_i=g_i\rho\left(\epsilon_i\right)$. When we do so, we find that the probabilities for all of the quantum mechanical systems that we discuss in Chapter 18 satisfy the ratio test.