25.1: Quantum Statistics

In developing the theory of statistical thermodynamics and the Boltzmann distribution function, we assume that molecules are distinguishable and that any number of molecules in a system can have the same quantum mechanical description. These assumptions are not valid for many chemical systems. Fortunately, it turns out that more rigorous treatment[1,2] of the conditions imposed by quantum mechanics usually leads to the same conclusions as the Boltzmann treatment. The Boltzmann treatment can become inadequate when the system consists of low-mass particles (like electrons) or when the system temperature is near absolute zero.

In this chapter, we introduce some modifications that make our statistical model more rigorous. We consider systems that contain large numbers of particles. We address the effects that the principles of quantum mechanics have on the equilibrium states that are possible, but we continue to assume that the particles do not otherwise exert forces on one another. We derive distribution functions for statistical models that satisfy quantum-mechanical restrictions on the number of particles that can occupy a particular quantum state. Our primary objective is to demonstrate that the more rigorous models reduce to the Boltzmann distribution function for most chemical systems at common laboratory conditions.

We have been using the quantum mechanical result that the discrete energy levels of a molecule or other particle can be labeled ϵ_1, ϵ_2,..., ϵ_i,.... We have assumed that we can put any number of identifiable particles into any of these energy levels. We have assumed also that we can distinguish one particle from another, so that we can know the energy of any particular particle. In fact, we may not be able to tell the particles apart. In this case, we can know how many particles have a given energy, but we cannot distinguish the particles that have this energy from one another. Moreover, there is a quantum-mechanical theorem about the number of particles that can occupy a quantum state. If the particles have integral $(0,\ 1,\ 2,\ \dots.)$ spin, any number of them can occupy the same quantum state. Such particles are said to follow ***Bose-Einstein statistics***. If on the other hand, the particles have half-integral $(1/2,\ 3/2,\ 5/2,\dots.)$ spin, then only one of them can occupy a given quantum state. Such particles are said to follow ***Fermi-Dirac statistics***.

Protons, neutrons, and electrons all have spin $1/2$. The spin of an atom or molecule is just the sum of the spins of its constituent elementary particles. If the number of protons, neutrons, and electrons is odd, the atom or molecule obeys Fermi-Dirac statistics. If it is even, the atom or molecule obeys Bose-Einstein statistics. For most molecules at temperatures that are not too close to absolute zero, the predicted difference in behavior is negligible. However, the isotopes of helium provide an important test of the theory. Near absolute zero, the behavior of He^3 differs markedly from that of He^4. The difference is consistent with the expected difference between the behavior of a spin-$1/2$ particle (He^3) and that of a spin-0 particle (He^4).