18.7: Particle Spins and Statistics- Bose-Einstein and Fermi-Dirac Statistics

Our goal is to develop the theory of statistical thermodynamics from Boltzmann statistics. In this chapter, we explore the rudiments of quantum mechanics in order to become familiar with the idea that we can describe a series of discrete energy levels for any given molecule. For our purposes, that is all we need. We should note, however, that we are not developing the full story about the relationship between quantum mechanics and statistical thermodynamics. The spin of a particle is an important quantum mechanical property. It turns out that quantum mechanical solutions depend on the spin of the particle being described. Particles with integral spins behave differently from particles with half-integral spins. When we treat the statistical distribution of these particles, we need to treat particles with integral spins differently from particles with half-integral spins. Particles with integral spins are said to obey ***Bose-Einstein statistics***; particles with half-integral spins obey ***Fermi-Dirac statistics***.

Fortunately, both of these treatments converge to the Boltzmann distribution if the number of quantum states available to the particles is much larger than the number of particles. For macroscopic systems at ordinary temperatures, this is the case. In Chapters 19 and 20, we introduce the ideas underlying the theory of statistical mechanics. In Chapter 21, we derive the Boltzmann distribution from a set of assumptions that does not correspond to either the Bose-Einstein or the Fermi-Dirac requirement. In Chapter 25, we derive the Bose-Einstein and Fermi-Dirac distributions and show how they become equivalent to the Boltzmann distribution for most systems of interest in chemistry.