

1.4: Statistical Thermodynamics

Statistical thermodynamics is a theory that uses molecular properties to predict the behavior of macroscopic quantities of compounds. While the origins of statistical thermodynamics predate the development of quantum mechanics, the modern development of statistical thermodynamics assumes that the quantized energy levels associated with a particular system are known. From these energy-level data, a temperature-dependent quantity called the **partition function** can be calculated. From the partition function, all of the thermodynamic properties of the system can be calculated. We begin our development of statistical thermodynamics by using the energy levels of an individual molecule to find its molecular partition function and the thermodynamic properties of a system that contains N non-interacting molecules of that substance. Later, we see that the partition function of a system containing molecules that do interact with one another can be found by very similar arguments.

Statistical thermodynamics has also been applied to the general problem of predicting reaction rates. This application is called **transition state theory** or **the theory of absolute reaction rates**. In principle, we should be able to predict the rate of any reaction. To do so, we need only to solve the quantum mechanical equations that give the energy levels associated with the reactants and the energy levels associated with a transitory chemical structure called the **transition state** for the reaction. From the energy levels we calculate partition functions; from partition functions we calculate thermodynamic functions; and from these thermodynamic functions we obtain the reaction rate. There is a big difference between “in principle” and “in practice.” While increases in computer speed make it increasingly feasible to do quantum mechanical calculations to useful degrees of accuracy, the results of such calculations remain too inaccurate to give generally reliable reaction rate predictions. The theory of absolute reaction rates is an important application of statistical thermodynamics. However, it is not included in this book.

Quantum mechanical calculations are not the only way to obtain the energy-level information that is needed to evaluate partition functions. Particularly for small molecules, these energy levels can be deduced from spectroscopic data. In these cases, the theory of statistical thermodynamics enables us to calculate thermodynamic properties from spectroscopic measurements. Excellent agreement is obtained between the values of thermodynamic functions obtained from classical thermodynamic (thermochemical) measurements and those obtained from statistical-thermodynamic calculations based on energy levels derived from spectroscopic measurements. In Chapter 24, we consider a particular example to illustrate this point.

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