UNIT IIIB

ENTROPY, EQUILIBRIUM DISTRIBUTIONS, AND THE SECOND LAW OF THERMODYNAMICS

Unit IIIA initiated our study of macroscopic systems from the viewpoint that the behavior of real systems results from the collective microscopic behaviors of the particles of the system. By studying successively larger systems we surmised that real systems have unimaginably enormous numbers of microstates and enormous numbers of macrostates. With no reason to expect the (isolated) system to prefer any specific microstate, it was assumed that all microstates of an isolated system are equally probable. With this single assumption, it was shown that a relatively small percentage of the macrostates possesses a vast majority of the system's microstates, that the properties of the macrostates in this group are virtually identical, and that whenever a system is in a macrostate not belonging to this group, collisions drive the system overwhelmingly toward distributions (and consequent properties) of these probable, equilibrium group macrostates. This characteristic behavior of isolated systems of particles is the Second Law of Thermodynamics.[1] To express these concepts quantitatively this unit defines the property, *entropy*, and uses it to formulate the second law. This formulation is used to develop tools for the calculation of macroscopic properties in terms of entropy and to evolve statements of the second law for nonisolated systems.

I. ENTROPY DEFINED

The microscopic property that determines if a macrostate (i) is a member of the equilibrium group is the relative magnitude of its number of microstates, W_i. Therefore, W_i is a property that can be used to describe the approach to equilibrium, $W_i \rightarrow W_{eq}$, where eq represents equilibrium or a member of the most probable group. Since W_i is proportional to the number of particles in the system it is an extensive property. We also know that W_i is proportional to the probability of macrostate i. The probability of occurrence of two independent events is the product of probability of each. So if the particles of a system were partitioned into parts A and B, then W_i would equal $W_{A,i} \cdot W_{B,i}$, where $W_{A,i}$ and $W_{B,i}$ are the number of microstates in macrostate space for portions A and B. This multiplicative nature of W_i is inconvenient; no other extensive property we have encountered behaves this way (other extensive properties are additive). To eliminate this difficulty we define a new property that increases as W_i increases (i.e., when the isolated system ap-

[1]The second law can be stated as "all microstates of an isolated system are equally probable" since this is the single assumption of the statistical approach.