UNIT IIIA

EQUILIBRIUM —A Microscopic Understanding

Equilibrium, the condition attained by every isolated system, is a state for which all fundamentally intensive properties are spatially uniform and temporally constant. From a macroscopic perspective, we observe that isolated systems attain equilibrium but we cannot provide a fundamental explanation of how or why. With a microscopic approach, i.e., a study of the behavior of the system's particles, we can examine both the condition of equilibrium and explain the spontaneous processes that drive isolated systems toward equilibrium. In addition, microscopic analysis provides a means of calculating properties from knowledge of the energy levels accessible to particles of the system. In many instances these predicted properties are more accurate, less expensive to obtain, and much more easily extrapolated over wide ranges of conditions than properties obtained by macroscopic measurement. Equally significant, microscopic models give insight into why a particular substance exhibits its characteristic macroscopic properties.

I. THE BEHAVIOR OF INDIVIDUAL PARTICLES

Although real systems are invariably composed of large numbers of particles, we choose not to begin our study with such large groups. Rather we will study single particles, then small groups, and finally we will statistically extrapolate our findings to real systems. Our first task is to select a *particle*.

A. The Particle

The term *particle* is used to mean some part, component, subdivision, entity, etc., the concept of which facilitates the understanding of the nature of matter. Depending on the questions that a study seeks to answer, the system particles might be stars, planets, billiard balls, raindrops, molecules, atoms, ions, electrons, photons, mesons, and so on. Thermodynamics defines the particle to be the largest system subdivision, the knowledge of whose individual behavior is sufficient to predict the statistical overall behavior of the group, i.e., the system's thermodynamic properties.

Example 1. As we have stated, the choice of a system particle depends upon the system definition and the question(s) to be answered. Suppose the system is the sixteen balls of a game of pool. (a) What is a suitable choice of particle definition for the player? The manufacturer of the balls must design a process that transforms molten plastic into a hard spherical ball. The rate at which the ball is cooled must be controlled to prevent distortion. (b) What is a suitable choice of particle definiton for the designer?

(a) To the player, the particle is obvious. To make a shot he must know in what manner, in what direction, and how hard to hit the cue ball. His shot will involve energy interactions between the balls and its dissipation via frictional processes.