

considered in Chap. 13. A system consisting of air can be regarded as a pure substance as long as it is a mixture of gases; but if a liquid phase should form on cooling, the liquid would have a different composition from the gas phase, and the system would no longer be considered a pure substance.

EQUILIBRIUM

Classical thermodynamics places primary emphasis on equilibrium states and changes from one equilibrium state to another. Thus, the concept of equilibrium is fundamental. In mechanics,

equilibrium means a condition of balance maintained by an equality of opposing forces. In thermodynamics, the concept is more far-reaching, including not only a balance of forces but also a balance of other influences. Each kind of influence refers to a particular aspect of thermodynamic, or complete, equilibrium. Accordingly, several types of equilibrium must exist individually to fulfill the condition of complete equilibrium; among these are mechanical, thermal, phase, and chemical equilibrium.

Criteria for these four types of equilibrium are considered in subsequent discussions.

For the present, we may think of testing to see if a system is in thermodynamic equilibrium by the following procedure: Isolate the system from its surroundings and watch for changes in its observable properties. If there are no changes, we conclude that the system was in equilibrium at the moment it was isolated. The system can be said to be at an equilibrium state.

When a system is isolated, it does not interact with its surroundings; however, its state can change as a consequence of spontaneous events occurring internally as its intensive properties, such as temperature and pressure, tend toward uniform values. When all such changes

cease, the system is in equilibrium. Hence, for a system to be in equilibrium it must be a single phase or consist of a number of phases that have no tendency to change their conditions when the overall system is isolated from its surroundings. At equilibrium, temperature

is uniform throughout the system. Also, pressure can be regarded as uniform throughout as long as the effect of gravity is not significant; otherwise a pressure variation can exist, as in a vertical column of liquid.

ACTUAL AND QUASIEQUILIBRIUM PROCESSES

There is no requirement that a system undergoing an actual process be in equilibrium during the process. Some or all of the intervening states may be nonequilibrium states. For many such processes we are limited to knowing the state before the process occurs and the state after the process is completed. However, even if the intervening states of the system are not known, it is often possible to evaluate certain overall effects that occur during the process.

Examples are provided in the next chapter in the discussions of work and heat. Typically, nonequilibrium states exhibit spatial variations in intensive properties at a given time. Also, at a specified position intensive properties may vary with time, sometimes chaotically. Spatial and temporal variations in properties such as temperature, pressure, and velocity can be measured in certain cases. It may also be possible to obtain this information by solving appropriate governing equations, expressed in the form of differential equations, either analytically or by computer.

Processes are sometimes modeled as an idealized type of process called a quasiequilibrium (or quasistatic) process. A quasiequilibrium process is one in which the departure from thermodynamic equilibrium is at most infinitesimal. All states through which the system passes in a quasiequilibrium process may be considered equilibrium states. Because

nonequilibrium effects are inevitably present during actual processes, systems of engineering interest can at best approach, but never realize, a quasiequilibrium process.

equilibrium

equilibrium state

quasiequilibrium

process