6.12: Equilibria and Reversible Processes

The distinction between a system at equilibrium and a system undergoing reversible change is razor-thin. What we have in mind goes to the way we choose to define the system and centers on the origin of the forces that affect its energy. For a system at equilibrium, the forces are fixed. For a system undergoing reversible change, some of the forces originate in the surroundings, and those that do are potentially variable.

To raise a bowling ball reversibly, we apply an upward force, $+mg$, exactly equal and opposite to the downward force, $-mg$, due to gravity. At any point in this reversible motion, the ball is stationary, which is the reason we say that a reversible process is a hypothetical change. If we were to change the system slightly, by adding a shelf to support the ball at exactly the same height, the forces on the ball would be the same; however, the forces would be fixed and we would say that the ball is at equilibrium.

We can further illustrate this distinction by returning to the water–water-vapor system. If an unchanging water–water-vapor mixture is enclosed in a container whose dimensions are fixed (like a sealed glass bulb) we say that the system is at equilibrium. If a piston encloses the same collection of matter, and the surroundings apply a force on the piston that balances the pressure exerted by the mixture, we can say that the system is changing reversibly.

In Section 1.6, we used the term “primitive equilibrium” to refer to an equilibrium state in which all of the state functions are fixed. A system that can undergo reversible change without changing the number or kinds of phases present can be in an infinite number of such states. Since the set of such primitive equilibrium states encompasses the accessible equilibrium conditions in the sense of Gibb’s phase rule, we can call this set a ***Gibbsian equilibrium manifold***.