

## 1.8: Equilibrium and Classical Thermodynamics

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We develop classical thermodynamics by reasoning about **reversible processes**—processes in which a system passes through a series of equilibrium states. Any such process corresponds to a path on one or more of the Gibbsian manifolds that are available to the system. The resulting theory consists of equations that relate the changes in the values of the system's state functions as the system undergoes a reversible change. For this reason, the body of theory that we are calling classical thermodynamics is often called **equilibrium thermodynamics** or **reversible thermodynamics**.

As we discuss further in Chapter 6, any change that we can actually observe in a real system must be the result of a **spontaneous process**. In a reversible process, both the initial and the final states are equilibrium states. In a spontaneous process, the initial state of the system is not an equilibrium state. A spontaneous process begins with the system in a non-equilibrium state and proceeds until an equilibrium state is reached.

The domain of classical thermodynamics—reversible processes—is distinct from the domain of real observations, because real observations can be made only for spontaneous processes. We bridge this gap by careful selection of real-world systems to serve as models for the reversible systems that inhabit our theory. That is, we find that we can make measurements on non-equilibrium systems and irreversible processes from which we can estimate the properties of equilibrium systems and reversible processes. Saying almost the same thing from another perspective, we find that the classical thermodynamic equations that apply to equilibrium states can also be approximately valid for non-equilibrium states. For many non-equilibrium states, notably those whose individual phases are homogenous, the approximations can be very good. For other non-equilibrium states, notably those whose individual phases are markedly inhomogeneous, these approximations may be very poor.

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