6.1: The Thermodynamic Perspective

Classical thermodynamics does not consider the atomic and molecular characteristics of matter. In developing it, we focus exclusively on the measurable properties of macroscopic quantities of matter. In particular, we study the relationship between the thermodynamic functions that characterize a system and the increments of heat and work that the system receives as it undergoes some change of state. In doing so, we adopt some particular perspectives. The first is to imagine that we can segregate the macroscopic sample that we want to study from the rest of the universe. As sketched in Figure 1, we suppose that we can divide the universe into two mutually exclusive pieces: the ***system*** that we are studying and the ***surroundings***, which we take to encompass everything else.

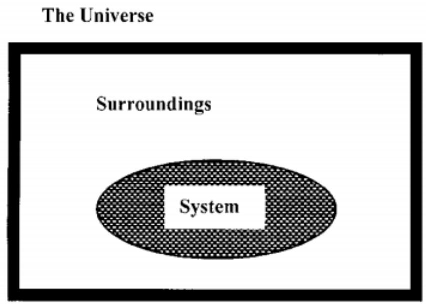

Figure 1. The thermodynamic universe.

We imagine the system to be enclosed by a boundary, which may or may not correspond to a material barrier surrounding the collection of matter that we designate as the system. (For our purposes, a system will always contain a macroscopic quantity of matter. However, this is not necessary; thermodynamic principles can be applied to a volume that is occupied only by radiant energy.) Everything inside the boundary is part of the system. Everything outside the boundary is part of the surroundingssurroundings. Every increment of energy that the system receives, as either heat or work, is passed to it from the surroundings, and conversely.

An ***open system*** can exchange both matter and energy with its surroundings. A ***closed system*** can exchange energy but not matter with its surroundings. An ***isolated system*** can exchange neither matter nor energy.

Together, system and surroundings comprise the ***universe***, thermodynamic.

If we are too literal-minded, this reference to "the universe" can start us off on unnecessary ruminations about cosmological implications. All we really have in mind is an energy-accounting scheme, much like the accountants' system of double-entry bookkeeping, in which every debit to one account is a credit to another. When we talk about "the universe," we are really just calling attention to the fact that our scheme involves only two accounts. One is labeled "system," and the other is labeled "surroundings." Since we do our bookkeeping one system at a time, the combination of system and surroundings encompasses the universe of things affected by the change.

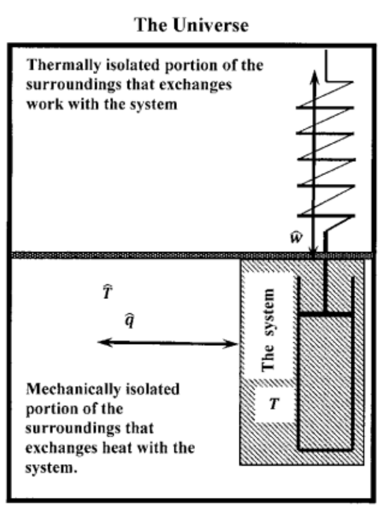

Figure 2. Transferring heat and work in a thermodynamic universe.

Figure 2 schematically depicts a closed system that can exchange heat and work with its surroundings. The surroundings comprise a heat reservoir and a device that can convert potential energy in the surroundings into work exchanged with the system. The heat reservoir can exchange heat but not work with the system. In this sketch, the heat reservoir is at a constant temperature, $\widehat{T}\ (=T_{surroundings})$. It might comprise, for example, a large quantity of ice and water in phase equilibrium. The work-generating device cannot exchange heat, but it can exchange work with the system. A partially extended spring represents the potential energy available in the surroundings. The system can do work on the device and increase the potential energy of the spring. Alternatively, the surroundings can transfer energy to the system at the expense of the potential energy of the spring. Since nothing else in the rest of the universe is affected by these exchanges, our sketch encompasses the entire universe insofar as these changes are concerned. A system that cannot interact with anything external to itself is isolated. The combination of system and surroundings depicted in Figure 2 is itself an isolated system.

When we deal with the entropy change that accompanies some change in the state of the system, the properties of the surroundings become important. We develop the reason for this in Chapter 9. It is useful to introduce notation to distinguish properties of the surroundings from properties of the system. In Figure 2, we indicate the temperatures of system and surroundings by T and $\hat{T}$, respectively. We adopt this general rule:

When a thermodynamic quantity appears with a superscripted caret, the quantity is that of the surroundings. If there is no superscripted caret, the quantity is that of the system.

Thus, $\hat{T}$, $\hat{E}$, and $\hat{S}$ are the temperature, the energy, and the entropy of the surroundings, respectively, whereas T, E, and S are the corresponding quantities for the system.

We develop thermodynamics by reasoning about closed chemical systems that consist of one or more ***homogeneous phases***. A phase can be a solid, a liquid, or a gas. A phase can consist of a single chemical substance, or it can be a homogeneous solution containing two or more chemical substances. When we say that a phase is homogeneous, we mean that the pressure, temperature, and composition of the phase are the same in every part of the phase. Since gases are always miscible, a system cannot contain two gas phases that are in contact with one another. However, multiple solid and immiscible-liquid phases can coexist.

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