

2.1: The System, Surroundings, and Boundary

Chemists are interested in systems containing matter—that which has mass and occupies physical space. Classical thermodynamics looks at *macroscopic* aspects of matter. It deals with the properties of aggregates of vast numbers of microscopic particles (molecules, atoms, and ions). The macroscopic viewpoint, in fact, treats matter as a *continuous* material medium rather than as the collection of discrete microscopic particles we know are actually present. Although this e-book is an exposition of classical thermodynamics, at times it will point out connections between macroscopic properties and molecular structure and behavior.

A thermodynamic **system** is any three-dimensional region of physical space on which we wish to focus our attention. Usually we consider only one system at a time and call it simply “the system.” The rest of the physical universe constitutes the **surroundings** of the system.

The **boundary** is the closed three-dimensional surface that encloses the system and separates it from the surroundings. The boundary may (and usually does) coincide with real physical surfaces: the interface between two phases, the inner or outer surface of the wall of a flask or other vessel, and so on. Alternatively, part or all of the boundary may be an imagined intangible surface in space, unrelated to any physical structure. The size and shape of the system, as defined by its boundary, may change in time. In short, our choice of the three-dimensional region that constitutes the system is arbitrary—but it is essential that we know exactly what this choice is.

We usually think of the system as a part of the physical universe that we are able to influence only indirectly through its interaction with the surroundings, and the surroundings as the part of the universe that we are able to directly manipulate with various physical devices under our control. That is, we (the experimenters) are part of the surroundings, not the system.

For some purposes we may wish to treat the system as being divided into *subsystems*, or to treat the combination of two or more systems as a *supersystem*.

If over the course of time matter is transferred in either direction across the boundary, the system is **open**; otherwise it is **closed**. If the system is open, matter may pass through a stationary boundary, or the boundary may move through matter that is fixed in space.

If the boundary allows heat transfer between the system and surroundings, the boundary is **diathermal**. An **adiabatic** (Greek: *impassable*) boundary, on the other hand, is a boundary that does not allow heat transfer. We can, in principle, ensure that the boundary is adiabatic by surrounding the system with an adiabatic wall—one with perfect thermal insulation and a perfect radiation shield.

An **isolated** system is one that exchanges no matter, heat, or work with the surroundings, so that the mass and total energy of the system remain constant over time. (The energy in this definition of an isolated system is measured in a local reference frame, as will be explained in Sec. 2.6.2.) A closed system with an adiabatic boundary, constrained to do no work and to have no work done on it, is an isolated system.

The constraints required to prevent work usually involve forces between the system and surroundings. In that sense a system may interact with the surroundings even though it is isolated. For instance, a gas contained within rigid, thermally-insulated walls is an isolated system; the gas exerts a force on each wall, and the wall exerts an equal and opposite force on the gas. An isolated system may also experience a constant external field, such as a gravitational field.

The term **body** usually implies a system, or part of a system, whose mass and chemical composition are constant over time.

2.1.1 Extensive and intensive properties

A quantitative *property* of a system describes some macroscopic feature that, although it may vary with time, has a particular value at any given instant of time.

Table 2.1 lists the symbols of some of the properties discussed in this chapter and the SI units in which they may be expressed. A much more complete table is found in Appendix C.

Most of the properties studied by thermodynamics may be classified as either extensive or intensive. We can distinguish these two types of properties by the following considerations.

If we imagine the system to be divided by an imaginary surface into two parts, any property of the system that is the sum of the property for the two parts is an **extensive property**. That is, an additive property is extensive. Examples are mass, volume, amount,

energy, and the surface area of a solid.

Sometimes a more restricted definition of an extensive property is used: The property must be not only additive, but also proportional to the mass or the amount when intensive properties remain constant. According to this definition, mass, volume, amount, and energy are extensive, but surface area is not.

If we imagine a homogeneous region of space to be divided into two or more parts of arbitrary size, any property that has the same value in each part and the whole is an **intensive property**; for example density, concentration, pressure (in a fluid), and temperature. The value of an intensive property is the same everywhere in a homogeneous region, but may vary from point to point in a heterogeneous region—it is a *local* property.

Since classical thermodynamics treats matter as a continuous medium, whereas matter actually contains discrete microscopic particles, the value of an intensive property at a point is a statistical average of the behavior of many particles. For instance, the density of a gas at one point in space is the average mass of a small volume element at that point, large enough to contain many molecules, divided by the volume of that element.

Some properties are defined as the ratio of two extensive quantities. If both extensive quantities refer to a homogeneous region of the system or to a small volume element, the ratio is an *intensive* property. For example concentration, defined as the ratio amount/volume, is intensive. A mathematical derivative of one such extensive quantity with respect to another is also intensive.

A special case is an extensive quantity divided by the mass, giving an intensive **specific quantity**; for example

$$\text{Specific volume} = \frac{V}{m} = \frac{1}{\rho} \quad (2.1.1)$$

If the symbol for the extensive quantity is a capital letter, it is customary to use the corresponding lower-case letter as the symbol for the specific quantity. Thus the symbol for specific volume is v .

Another special case encountered frequently in this e-book is an extensive property for a pure, homogeneous substance divided by the amount n . The resulting intensive property is called, in general, a **molar quantity** or molar property. To symbolize a molar quantity, this e-book follows the recommendation of the IUPAC: The symbol of the extensive quantity is followed by subscript m, and optionally the identity of the substance is indicated either by a subscript or a formula in parentheses. Examples are

$$\text{Molar volume} = \frac{V}{n} = V_m \quad (2.1.2)$$

$$\text{Molar volume of substance } i = \frac{V}{n_i} = V_{m,i} \quad (2.1.3)$$

$$\text{Molar volume of H}_2\text{O} = V_m(\text{H}_2\text{O}) \quad (2.1.4)$$

In the past, especially in the United States, molar quantities were commonly denoted with an overbar (e.g., \bar{V}_i).

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