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# 1

# PRIMITIVES

In this chapter we review elementary concepts that are used to describe Nature. These concepts are so basic that we call them *primitives*, for everything in later chapters builds on these ideas. You have probably encountered this material before, but our presentation may be new to you. The chapter is divided into primitive things (§ 1.1), primitive quantities (§ 1.2), primitive changes (§ 1.3), and primitive analyses (§ 1.4).

## 1.1 PRIMITIVE THINGS

Every thermodynamic analysis focuses on a *system*—what you're talking about. The system occupies a definite region in space: it may be composed of one homogeneous phase or many disparate parts. When we start an analysis, we must properly and explicitly identify the system; otherwise, our analysis will be vague and perhaps misleading. In some situations there is only one correct identification of the system; in other situations, several correct choices are possible, but some may simplify an analysis more than others.

A system can be described at either of two levels: a *macroscopic* description pertains to a system sufficiently large to be perceived by human senses; a *microscopic* description pertains to individual molecules and how those molecules interact with one another. Thermodynamics applies to macroscopic entities; nevertheless, we will occasionally appeal to microscopic descriptions to interpret macroscopic phenomena. Both levels contain primitive things.

### 1.1.1 Macroscopic Things

Beyond the system lies the rest of the universe, which we call the *surroundings*. Actually, the surroundings include only that part of the universe close enough to affect the system in some way. For example, in studying how air in a balloon responds to being moved from a cool room to a warm one, we might choose the air in the balloon to be the system and choose the air in the warmer room to be the surroundings. If the universe beyond the room does not affect the balloon, then objects and events outside the room can be ignored.

An *interaction* is a means by which we can cause a change in the system while we remain in the surroundings; that is, an action in the surroundings will cause a response in the system only if the proper interaction exists. Interactions are of two types: thermal and nonthermal. A *nonthermal* interaction connects some variable $x$ in the system to a variable $y$ in the surroundings. This means that $x$ and $y$ are not independent; instead, they are coupled by a relation of the form

$$F(x, y) = 0 \tag{1.1.1}$$

Each nonthermal interaction involves a force that tends to change something about the system. Of most concern to us will be the nonthermal interaction in which a mechanical force deforms the system volume. In this case, the system volume is $x$ in (1.1.1) and the surroundings have volume $y$. When the system volume increases, the volume of the surroundings necessarily decreases, and vice versa. One of these variables, typically the system variable $x$, is chosen to measure the extent of the interaction; this variable is called the *interaction coordinate*.

When two or more nonthermal interactions are established, the choice of interaction coordinates must be done carefully, to ensure that the coordinates are mutually independent. That is, each interaction coordinate must be capable of being manipulated while all others are held fixed. Such coordinates are called *generalized coordinates*, the interaction corresponding to a generalized coordinate is said to be *conjugate* to its coordinate, and each conjugate interaction is said to be *orthogonal* to every other interaction [1–3]. As suggested by Figure 1.1, many orthogonal interactions are possible; examples (with their conjugate coordinates) are mechanical interactions (volume), chemical interactions (composition), gravitational interactions (position relative to a mass), and electrical interactions (position relative to a charge).

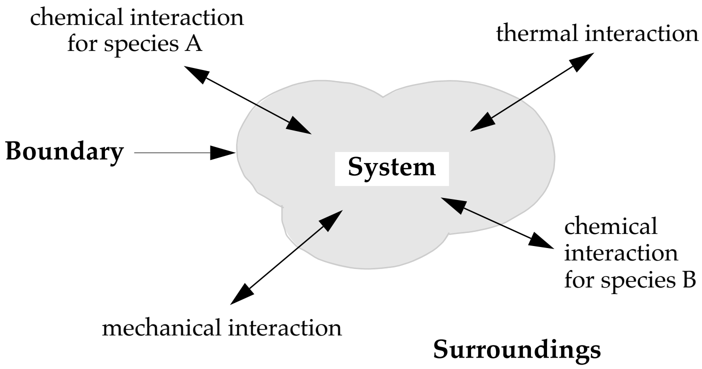

**Figure 1.1** A system may engage in several kinds of orthogonal interactions with its surroundings. Examples include mechanical interactions, by which a force acts to change some coordinate of the system; chemical interactions, by which amounts of species change either by chemical reaction or by diffusion across boundaries; and thermal interactions, by which the system responds to a temperature difference across the boundary.

**Table 1.1** Examples of boundaries between systems and surroundings

| Boundary | Constraints on interactions |
|---|---|
| Open | Any interaction is possible |
| Closed | Impenetrable by matter, but other kinds of interactions can occur |
| Semipermeable | Penetrable by some chemical species, but not by others; all other interactions are possible |
| Insulated | Thermal interactions are not possible, but nonthermal interactions can occur |
| Rigid | Boundary cannot be mechanically deformed |
| Isolated | No interactions can occur |

Besides nonthermal interactions, the system and surroundings may be connected through a *thermal* interaction. The thermal interaction causes a change in the system by means of a difference in hotness and coldness, which is measured by a temperature difference between system and surroundings. The thermal interaction distinguishes thermodynamics from other branches of science: when the thermal interaction is unimportant or irrelevant, some other branch of knowledge can be applied. For example, in predicting the motions of bodies in the solar system, the interactions are gravitational and classical mechanics describes the motion. For the behavior of electrons in molecules, the interactions are electromagnetic and quantum mechanics applies.

*Boundaries* separate a system from its surroundings, and the nature of the boundary may limit how the system interacts with its surroundings. Therefore the location and nature of the boundary must be carefully and completely articulated to successfully analyze a system. Boundaries are usually physical entities, such as walls, but they can be chosen to be imaginary. Common boundaries are listed in Table 1.1.

### 1.1.2 Microscopic Things

Molecular theory asserts that all matter is composed of molecules, with molecules made up of one or more atoms. What evidence do we have for the existence of molecules? That is, why do we believe that matter is ultimately composed of lumps, rather than being continuous on all scales? (For a review of the nineteenth-century debate on the discrete vs. continuous universe, see Nye [4].) One piece of evidence is the law of definite proportions: the elements of the periodic table combine in discrete amounts to form compounds. Another piece of evidence is obtained by shining X rays on a crystalline solid: the resulting diffraction pattern is an array of discrete points, not a continuous spectrum. More evidence is provided by Brownian motion; see Figure 1.2.

Molecules themselves exhibit certain primitive characteristics: (a) they have size and shape, (b) they exert forces on one another, and (c) they are in constant motion at high velocities. Molecules vary in size according to the number and kind of constituent atoms: an argon atom has a "diameter" of about $3.4(10^{-10})$ m; a fully extended octane chain ($C_8H_{18}$) is about $10(10^{-10})$ m long; the double helix of human DNA (a polymer) is about $20(10^{-10})$ m thick and, when extended, is about 0.04 m long [5].

These microscopic sizes imply that huge numbers of molecules make up a macroscopic chunk of matter: there are about as many molecules in one living cell as there are cells in one common domestic cat [6].

The size and shape of a molecule constitute its *molecular structure*, which is a primary aspect of molecular identity. But identity may not be conserved: in the absence of chemical reactions, identity is preserved at the molecular level, but when reactions do occur, identity is preserved only at the atomic level. Molecular structure results from forces acting among constituent atoms. These forces are of two types: (a) chemical forces, which are caused by sharing of electrons and are the primary determinants of structure, and (b) physical forces, which are mainly electrostatic. Molecular structure is dynamic, not static, because the atoms in a molecule are continually moving about stable positions: the structure ascribed to a molecule is really a time-average over a distribution. In large molecules the structure may be an average over several different "sub-structures" that are formed when groups of atoms rearrange themselves relative to other parts of the molecule. Such rearrangements occur, for example, as internal rotations in alkanes and folding motions in proteins. Molecular structure and its distribution can be distorted by changes in temperature and pressure.

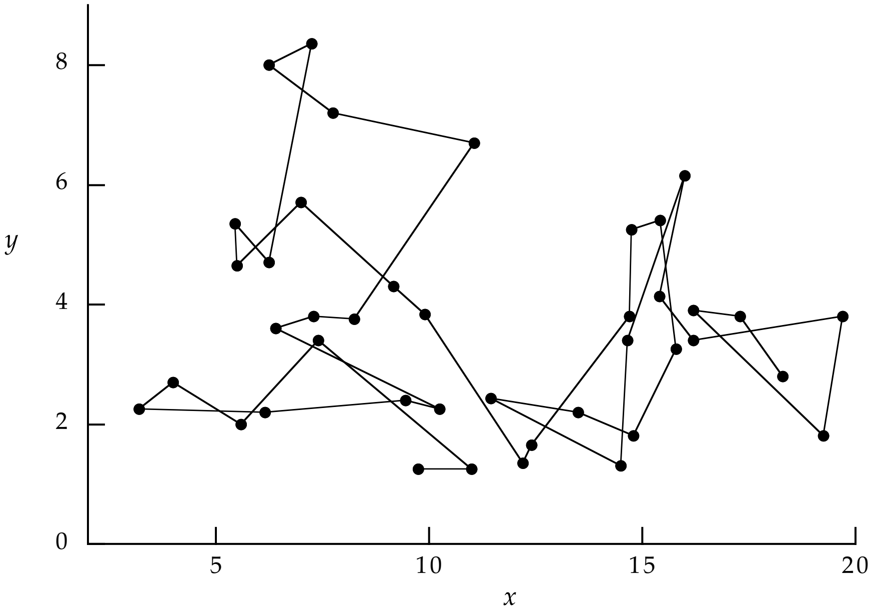

**Figure 1.2** One piece of evidence for the existence of molecules is Brownian motion: a small macroscopic particle suspended in a medium will exhibit irregular trajectories caused by the particle colliding with molecules of the medium. The trajectories shown here are from Perrin [7], in which a mastic grain of $1.06(10^{-6})$ m diameter was suspended in a liquid. The dots represent positions of the grain observed at intervals of 30 seconds, with the positions projected onto a horizontal plane (orthogonal to the force of gravity). The straight lines indicate the order of observations; but otherwise, they have no physical significance. (Units on the axes are arbitrary.) Note that this image is incomplete because it is a two-dimensional projection from a three-dimensional phenomenon.

Besides forces acting among atoms on one molecule (*intramolecular forces*), there are also *intermolecular forces* acting between molecules. Such forces depend on distances between molecular centers and, in nonspherical molecules, on the relative orientations of the molecules. When molecules are widely separated, as in a gas, intermolecular forces are small; see Figure 1.3. If we squeeze the gas, it may condense to form a liquid; evidently, when molecules are pushed moderately close together they attract one another. But if we squeeze on the condensate, the liquid resists strongly: when molecules are close together they repel one another. This behavior is typical.

Even a superficial knowledge of molecular structure and intermolecular forces may help us explain why some substances behave as they do. For example, at ambient conditions the chain molecule n-decane $C_{10}H_{22}$ is a liquid, while the double-ring molecule naphthalene $C_{10}H_8$ is solid. This difference is not caused by the small difference in molecular masses—these substances have similar boiling points and critical points. Rather, it is caused by the difference in molecular structure. Differences in structure cause differences in molecular flexibility and in the ability of molecules to pack. Such differences lead to different temperatures at which molecular kinetic energies overcome intermolecular potential energies thereby allowing molecular centers to move enough to produce phase changes; for example, solids melt and liquids vaporize.

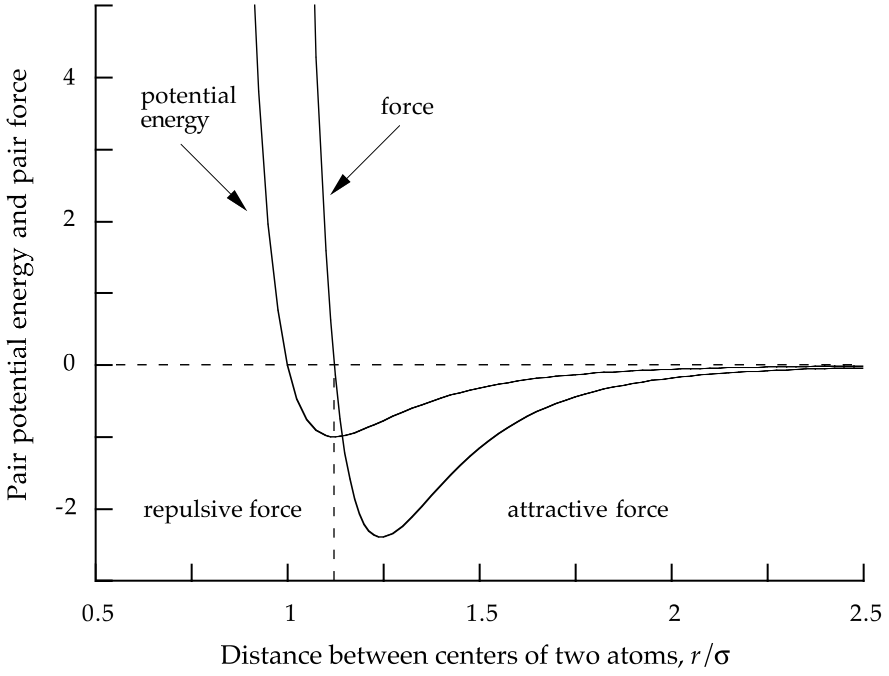

**Figure 1.3** Schematic of the potential energy and force acting between two spherical molecules, such as those of argon. When two molecules are far apart, they do not interact, so both the force and the potential energy are zero. When the molecules are close together, their electron clouds are distorted, causing a strong repulsive force. At intermediate separations, the molecules attract one another. Here the scales on ordinate and abscissa are dimensionless. On the abscissa, distances have been divided by $\sigma$, which is related to the atomic diameter. On the ordinate, energies were divided by the magnitude of the minimum energy $u_{min}$, while dimensionless forces were computed as $F\sigma/u_{min}$.

According to kinetic theory, molecules in liquids and gases are continually moving. We see this in Brownian motion, and in some cases, we can sense molecular diffusion: when a bottle is opened, we can soon decide whether it contained ammonia or perfume. Further, molecular motion serves as the mechanism for the thermal interaction.

## 1.2 PRIMITIVE QUANTITIES

Once we have identified the system, its boundaries, and its interactions with the surroundings, we must describe the condition of the system. This description involves certain quantities, called *properties*, whose values depend only on the current condition. We take properties to be macroscopic concepts; microscopically, there are additional quantities, such as bond lengths, force constants, and multipole moments, that describe molecular structure and define intermolecular forces. These microscopic quantities are not properties, but they contribute to the values taken by properties.

In thermodynamics, we assume properties are continuous and differentiable. These assumptions cannot be rigorously confirmed because sufficient experiments cannot be done to verify them; nevertheless, they allow us to invoke the mathematical limit for transforming discretely distributed data into continuous functions. They seem to fail only in special cases, such as at critical points. These mathematical assumptions are so significant that they could be considered fundamental laws.

### 1.2.1 Generalized Forces

Recall from § 1.1.1 that we impose changes on a system via thermal and nonthermal interactions. In the case of nonthermal interactions, changes are caused by forces. Common forces and their conjugate nonthermal interactions are listed in Table 1.2. A force has the following characteristics:

(a) It causes or can cause a change in the condition of a system; the change results in a modification of the value of a generalized coordinate.

(b) It can be measured by a balancing procedure; that is, an unknown force is measurable by finding a calibrated standard that stops the action of the unknown force.

**Table 1.2** Common macroscopic interactions

| Interaction | Generalized coordinate | Conjugate force |
|---|---|---|
| Mechanical | System volume | Pressure |
| Gravitational | Position of a mass | Gravitational field |
| Interfacial | Area of boundary | Interfacial tension |
| Chemical | Species mole number | Chemical potential |
| Electrical | Position of electric charge | Electric field |

In classical mechanics forces are said to be *conservative* if they can be written as the negative gradient of some potential energy function. An example is the force $F_g$ exerted on an object in a gravitational field of potential energy $E_p$,

$$F_g = -\frac{dE_p}{dz} = -\frac{d(mgz)}{dz} = -mg \tag{1.2.1}$$

Here $m$ is the mass of the object, $g$ is the gravitational acceleration, and $z$ is the distance the object's center lies from the center of the field. The negative sign indicates an attractive force and we recognize the result as Newton's second law.

We can extend this idea to thermodynamics by defining any force to be conservative if it is proportional to some thermodynamic potential function differentiated with respect to a generalized coordinate. Under this definition, the forces cited in Table 1.2 are all conservative. A particular example is the pressure involved in the mechanical interaction; in Chapter 2 we will find that

$$P = -\left(\frac{\partial U}{\partial V}\right)_{NS} \tag{1.2.2}$$

where $S$ is the entropy. Here the internal energy $U$ serves as the thermodynamic potential function that connects the generalized coordinate $V$ to its conjugate force $P$. One of our goals is to identify thermodynamic potential functions for computationally convenient choices of generalized coordinates and their conjugate forces.

Besides conservative forces, there are other forces that are not conjugate to a generalized coordinate through a derivative of some potential function. All such forces are said to be *dissipative*, because they add to the amount of energy needed to change a state; ultimately, that extra energy is dissipated as heat. Common examples are frictional forces that must be overcome whenever one part of a system moves relative to other parts. All real macroscopic forces have dissipative components, and one of the goals of thermodynamics is to account for any energy dissipated as heat.

For the thermal interaction, the force is sometimes identified as the temperature with its generalized coordinate being the entropy [8]. Such an identification provides an obvious and appealing symmetry because it makes thermal interactions appear to be structurally analogous to nonthermal interactions; however, we prefer not to make such an identification because for all known nonthermal interactions the generalized coordinate can be measured, whereas entropy cannot. In this book we will consider only mechanical, gravitational, interfacial, and chemical forces plus the thermal interactions; others will not be used.

### 1.2.2 Equilibrium and State

The condition of a system is said to be an *equilibrium* one when all forces are in balance and the thermal interaction is not acting, either because it is blocked or because temperatures are the same on both sides of the boundary. These restrictions apply not only to interactions across system boundaries, but also to interactions between system parts. At equilibrium, macroscopic properties do not change with time nor with macroscopic position within a uniform portion of the system. Equilibrium conditions differ from *steady state* conditions. During steady states, net interactions are constant with time, while at equilibrium net interactions are not merely constant, but zero. Moreover, when equilibrium conditions are disturbed by a small interaction, the system tends to resist the interaction; that is, a small disturbance from equilibrium causes only a small bounded change in the system's condition. This is called *Le Chatelier's principle*.

Equilibrium is an idealized concept because everything in the universe is apparently changing on some time-scale (the scales range from femtoseconds to eons). The concept is useful when changes occur on time-scales that are unimportant to the observer. For example, a system may have corroding boundaries or its contents may be decomposing because of electromagnetic radiation (visible or ultraviolet light, for example); it may be expanding via chemical explosion or collapsing under glacial weight. In any situation, we must identify those interactions that occur over the time-scale of our application. "Equilibrium" is said to exist when those interactions are brought into balance. If other interactions are long-lived compared to the time-scale of interest and if, during that time-scale, those interactions have little effect on the system's condition, then those interactions can be ignored.

By stipulating values for a certain number of properties, we establish the condition of the system: the thermodynamic *state*. The number of properties needed depends on such things as the number of parts of the system and the number of chemical species in each part. This issue will be addressed in Chapter 3. When only a few properties are sufficient to identify the state, it may be useful to construct a *state diagram* by plotting independent properties on mutually orthogonal coordinate axes. The dimensionality of this diagram equals the number of properties needed to identify the state.

We say a state is *well-defined* when sufficient property values are specified to locate a system on its state diagram. If, in a well-defined state, the system is at equilibrium, then the condition is said to be an *equilibrium state*. Consequently, all equilibrium states are well-defined, but well-defined states need not be equilibrium states. In fact, a well-defined state may not be physically realizable—it may be thermodynamically unstable or hypothetical or an idealization. For example, many well-defined states of an ideal gas cannot be realized in a laboratory; nevertheless, thermodynamic analyses can be performed on such hypothetical systems.

Since by definition properties depend only on the state, properties are called *state functions*. State functions have convenient mathematical attributes. For example, in the calculus they form exact differentials (see Appendix A); this means that if a system is changed from state 1 to state 2, then the change in any state function $F$ is computed merely by forming the difference

$$\Delta F = F_2 - F_1 \tag{1.2.3}$$

For specified initial (1) and final (2) states, the value of the change $\Delta F$ is *always* the same, regardless of how state 2 is produced from state 1. Examples of measurable state functions include temperature, pressure, volume, heat capacity, and number of moles. Properties constitute an important set of primitives, for without state functions, there would be no thermodynamics.

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### 1.2.3 Extensive and Intensive Properties

Thermodynamic properties can be classified in various ways. One classification divides properties into two kinds: extensive and intensive. *Extensive* properties are those whose experimental values *must* be obtained by a measurement that encompasses the entire system, either directly or indirectly. An indirect measurement would apply to systems of disparate parts; measurements would be performed on all the parts and the results added to obtain the total property for the system. Examples include the total volume, the total amount of material, and the total internal energy.

*Intensive* properties are those whose experimental values *can* be obtained either by inserting a probe at discrete points into the system or (equivalently) by extracting a sample from the system. If the system is composed of disparate parts, values for intensive properties may differ in different parts. Examples of intensive properties are the temperature, pressure, density, and internal energy per mole.

Redlich [2] suggests a simple thought-experiment that allows us to distinguish extensive properties from intensive ones. Let our system be in an equilibrium state, for which values of properties can be assigned, and imagine replicating the system (fancifully, run it through a duplicating machine), while keeping the original state undisturbed. Our new system is now a composite of the original plus the replica. *Extensive* properties are those whose values in the composite *differ* from those in the original system, while *intensive* properties are those whose values are the *same* in both the composite and the original.

These operational distinctions between extensive and intensive avoid ambiguities that can occur in other definitions. Some of those definitions merely say that extensive properties are proportional to the amount of material $N$ in the system, while intensive properties are independent of $N$. Other definitions are more specific by identifying extensive properties to be those that are homogeneous of degree one in $N$, while intensive properties are of degree zero (see Appendix A).

But these definitions can lead to ambiguities, especially when we must interpret certain partial derivatives that often arise in thermodynamics. For example, is the system pressure $P$ extensive? Some definitions suggest that $P$ does not change with $N$, and for a pure substance it is true that

$$\left(\frac{\partial P}{\partial N}\right)_{Tv} = 0 \tag{1.2.4}$$

where $v = V/N$ is the molar volume. That is, here $P = P(T, v)$ does not change when material is added to the system because the container volume $V$ must increase to keep the molar volume $v$ constant. However, it is also true that

$$\left(\frac{\partial P}{\partial N}\right)_{TV} \neq 0 \tag{1.2.5}$$

where the quantity held fixed is the container volume $V$. In fact, for a pure ideal gas,

$$\left(\frac{\partial P}{\partial N}\right)_{TV} = \frac{RT}{V} \neq 0 \tag{1.2.6}$$

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because for an ideal gas $P = NRT/V$. That is, $P$ increases when we increase the amount of an ideal gas while $T$ and container volume $V$ remain fixed. The lesson here is that an intensive property (such as P) may or may not respond to a change in $N$, depending on which quantities are held fixed when $N$ is changed.

Any extensive property can be made intensive by dividing it by the total amount of material in the system; however, not all extensive properties are proportional to the amount of material. For example, the interfacial area between the system and its boundary satisfies our definition of an extensive property, but this area changes not only when we change the amount of material but also when we merely change the shape of the system. Further, although some intensive properties can be made extensive by multiplying by the amount of material, temperature and pressure cannot be made extensive.

In this book we restrict ourselves to extensive properties that are homogeneous of degree one in the amount of material. Specifically, for a multicomponent system containing component mole numbers $N_1$, $N_2$, … , we will use only those extensive properties $F$ that are related to their intensive analogs $f$ by

$$F(p_1, p_2, N_1, N_2, \ldots) = Nf(p_1, p_2, x_1, x_2, \ldots) \tag{1.2.7}$$

Here $p_1$ and $p_2$ are any two independent intensive properties, the $x_i = N_i/N$ are mole fractions, and $N = \Sigma N_i$. Therefore, if we fix values for $p_1$ and $p_2$ while doubling all mole numbers, then values for all extensive properties $F$ double. However, we do not expect that (1.2.7) is either necessary or sufficient for identifying extensive properties.

One motivation for distinguishing extensive from intensive is that the intensive thermodynamic state does not depend on the amount of material. The same intensive state can be attained in a hot toddy the size of a tea cup or the size of a swimming pool. This means we can perform a single analysis using intensive variables, but then apply the results to various systems of different sizes.

### 1.2.4 Measurables and Conceptuals

Thermodynamic analyses are also helped by another classification of properties: one that distinguishes measurables from conceptuals. *Measurables* are properties whose values can be determined directly from an experiment; these are the properties of ultimate interest because they can be monitored and controlled in an industrial setting. Examples are temperature, pressure, total volume, mole fraction, surface area, and electric charge. *Conceptuals* are properties whose values cannot be obtained directly from experiment; their values must be obtained by some mathematical procedure applied to measurables. (In some cases we can contrive special experimental situations so that a *change* in a conceptual can be measured.) Conceptuals simplify thermodynamic analyses; for example, conceptuals often simplify those basic equations that describe Nature's constraints on a system or process. The common conceptuals are energy, entropy, the Gibbs energy, chemical potential, fugacity, and activity coefficient.

Conceptuals play an intermediate role in engineering practice; they are a means to an end. For example, assume we are to diagnose and correct a process (perhaps a distillation column) that is behaving abnormally (improper product concentration in the overhead). To document the abnormality, we collect data on certain measurables (say