

## CHAPTER 1

### A OVERVIEW OF THERMODYNAMICS

Here an overview of thermodynamics will be presented with the intent of defining and describing it in rather broad terms. Some topics that are lightly covered here will be developed in more detail in later chapters. The intent of this chapter is to provide the context for these later explorations. Many modern-day textbook authors take statistical mechanics to be an integral part of thermodynamics, but here the term thermodynamics will refer to classical or phenomenological thermodynamics. One of the objectives of this work is to examine thermodynamics and its relationship to statistical mechanics.

#### **1.1 The Strangeness of Thermodynamics.**

Among those formally exposed to thermodynamics, few would disagree that while there is no doubt of its usefulness, there is also no doubt of its strangeness. Lest this be taken as a defect in our intellectual powers, it is both appropriate and comforting to quote two Nobel laureates in physics who have publicly acknowledged their discomfort with the subject. Max Born, one of the founders of quantum mechanics, freely admits his mystification<sup>1</sup>

"I tried hard to understand the classical foundations of the two theorems, as given by Clausius and Kelvin; they seemed to me wonderful, like a miracle produced by a magician's wand, but I could not find the logical and mathematical root of these marvelous results."

And Percy Bridgman, a respected thermodynamicist, is bothered by the strange human-scented quality permeating thermodynamics<sup>2</sup>

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<sup>1</sup> Max Born, *My Life: Recollections of a Nobel Laureate*, Taylor and Francis Ltd., London, 1978, p. 119.

<sup>2</sup> P.W. Bridgman, *The Nature of Thermodynamics*, Harper & Brothers, New York, 1961, p. 3.

"It must be admitted, I think, that the laws of thermodynamics have a different feel from most of the other laws of the physicist. There is something more palpably verbal about them — they smell more of their human origin. The guiding motif is strange to most of physics: namely, a capitalizing of the universal failure of human beings to construct perpetual motion machines of either the first or second kind. Why should we expect Nature to be interested either positively or negatively in the purposes of human beings, particularly purposes of such an unblushingly economic tinge?"

The most notable aspect of this strangeness is the mathematics employed by thermodynamics. While many thermodynamic quantities are expressed as partial derivatives, many of the equations relating these quantities are algebraic and bear little resemblance to the differential equations of classical physics. Also, the partial derivatives of thermodynamics are different in that they are adorned with subscripted variables. The reason for this is that there is an excess of variables in thermodynamics. A simple system is defined when two variables are determined, but thermodynamics does not specify which two among the many variables should be chosen. Thus, if the system were a quantity of gas, the two variables could be chosen from among temperature,  $T$ , pressure,  $P$ , volume,  $V$ , internal energy,  $U$ , enthalpy,  $H$ , or entropy,  $S$ . The choice of variables is indicated from the appearance of the partial derivative. For example, the partial derivative  $(\partial V/\partial T)_P$  indicates that  $T$  and  $P$  were chosen to represent the volume while  $(\partial V/\partial T)_S$  indicates that  $T$  and  $S$  were chosen. The simple notation  $\partial V/\partial T$  would be ambiguous.

On the other hand, the other laws of classical physics are expressed in terms of differential equations which, when integrated for a given set of boundary conditions, yield algebraic equations with time and position coordinates as the independent variables. These laws specify the independent variables and there is no need to subscript partial derivatives. For example, the equation of continuity of fluid mechanics is a partial differential equation expressing fluid density,  $\rho$ , as a function of time,  $t$ , and position coordinates and there is no doubt as to the identity of the independent variables held constant when the partial derivative  $\partial\rho/\partial t$  is written. Again, contrasting the mathematics of thermodynamics with that of classical physics, we note that the defined thermodynamic variables  $U$ ,  $H$ ,

and  $S$  cannot be expressed as absolute values<sup>3</sup> and are always written as changes between two states:  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$ . This feature derives from the central idea of thermodynamics — the concept of a state and a state variable. With the exception of heat and work, all thermodynamic variables are state variables.<sup>4</sup> To improve our understanding of a system we would like to know how the system moved between initial and a final states, but thermodynamics does not provide that information. Also, thermodynamics has nothing at all to say about the time required for the system to move between the two states; time is not a thermodynamic variable. While the silence of thermodynamics on these points is an obvious disadvantage to the state approach, there are compensations — namely, flexibility and economy of description.

The state of a gas is defined when any two of the state variables  $T$ ,  $P$ ,  $V$ ,  $U$ ,  $H$ , or  $S$  are specified. This means that the values of all of the other state variables are fixed and that between any two such specified states the changes in these variables are fixed regardless of the actual path taken by the system. Because of this, changes in state variables can be evaluated by any convenient path. Thus, we can choose variables that are convenient and we need not be concerned with mechanistic particulars when applying thermodynamics. Unfortunately, these advantages often cause discomfort for the neophyte or casual observer, for it would seem that thermodynamics revels in indifference and arbitrariness.

There are two other factors that contribute to the aura of strangeness surrounding thermodynamics — the reversible process and the standard state. The reversible process is an idealization necessary for the development and implementation of thermodynamics, and it imposes conditions that can be approached in practice. While one can usually visualize the physical conditions required to approach reversibility, the concept of a standard state, so useful in dealing with chemical reactions, often involves conditions that can not be physically realized. Both of these concepts impart a certain amount of artificiality and remoteness to thermodynamics.

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<sup>3</sup> The case of the third law and absolute entropy will be discussed in Chap. 3.

<sup>4</sup> The state approach, first applied to thermodynamics by Gibbs, is also used in quantum mechanics with considerable success.

## 1.2 The Method of Thermodynamics.

There are three major applications of thermodynamics:

1. The first and second laws can be applied to the calculation of heat and work effects associated with processes. This would include finding the maximum work obtainable from a process, the minimum work to drive the process, or whether a proposed process is possible. The answer to the last question is a permissive yes if neither law is violated, but an emphatic no for any violation.
2. The established network of thermodynamic equations can be used to determine relationships among the state variables of a system. These relationships can be used to calculate values of variables that are difficult to measure from values of variables that are easier to measure.
3. Special functions defined by thermodynamics can be used to make calculations involving phase and chemical equilibrium.

Actually, the property changes needed for the first application must be calculated from experimental data via the thermodynamic network. Therefore, in all its applications thermodynamics requires experimental information. Often it is easy to miss this intimate experimental dependence when solving textbook problems in which the steam tables are used or where the substance is conveniently specified as an ideal gas with a specified heat capacity. When the origin of the data is not recognized, thermodynamics is disassociated from its experimental context and rendered a lifeless and meaningless set of equations.

The experimental context suggests the following definition. It is intended to be heuristic rather than rigorous and should be suitable for the discussion which follows.

*Thermodynamics may be broadly defined as a means of extending our experimentally gained knowledge of a system or as a framework for viewing and correlating the behavior of the system.*

Accordingly, it would be better to speak of the thermodynamic method rather

than thermodynamics as an area of science; the adjective *thermodynamic* is preferable to the noun *thermodynamics*. One is certainly justified in protesting that this definition is so general that it could be applied to almost any area of science or to science in general. Nevertheless, because it will aid our understanding of thermodynamics, this non-exclusive definition will be useful.

The thermodynamic method is quite general and is capable of treating any system which can exist in an observable and reproducible equilibrium state and which can exchange heat and work with the surroundings. In addition to fluids, chemically reacting systems, and systems in phase equilibrium, thermodynamics has also been successfully applied to stressed solids, systems with surface effects, and substances subjected to gravitational, centrifugal, magnetic, and electric fields.<sup>5</sup>

A diagram illustrating the development of the thermodynamic network and the application of the thermodynamic method is shown on Fig. 1-1. The sequence of rectangles connected by heavy arrows traces the development of the laws, functions, and relationships that constitute the thermodynamic network — the tools of thermodynamics. The sequence of circles connected by light arrows shows the steps in applying thermodynamics to the solution of practical problems, and the dashed arrows indicate where the various thermodynamic tools are employed in the problem-solving process.

The first and second laws have been fashioned in mathematical language from statements of experience and have defined the functions  $U$  and  $S$ . These functions, previously unknown, were shown to be state functions. By way of the Clausius inequality, the combination of these two laws leads to the fundamental equation of thermodynamics. And application of the methods of the calculus to this equation yields the network of relationships among the state properties. Thus, the laws which define  $U$  and  $S$  lead eventually to the prescriptions for their evaluation from experimental data.

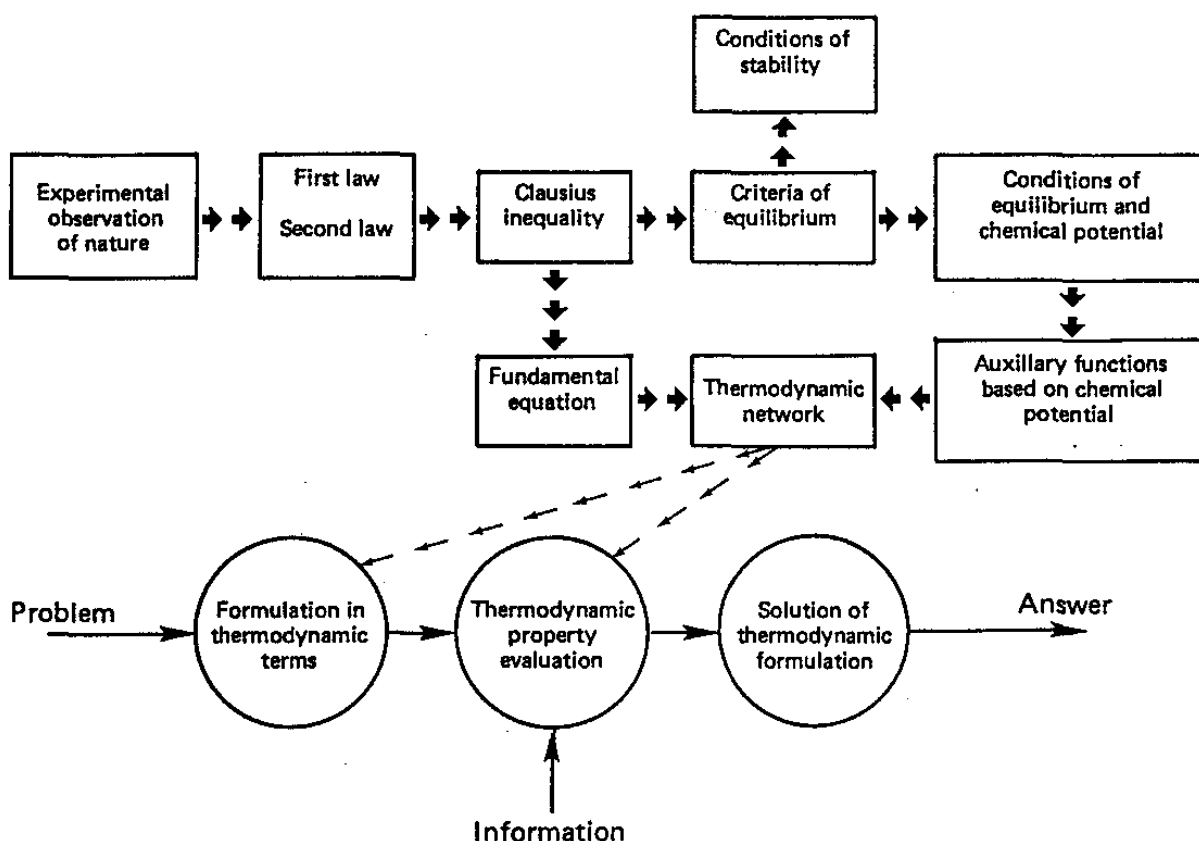
A new and useful state variable, the chemical potential, can be identified when the fundamental equation is extended to include mixtures. The application of this new fundamental equation leads to the specification of the conditions of equilibrium, which require that the temperature, pressure, and chemical

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<sup>5</sup> For a generalization of the thermodynamic method see Sec. 5-9 of this textbook.

potential be uniform throughout the system. The chemical potential and other functions derived from it form the basis of the thermodynamic treatment of phase and chemical equilibrium and the equations relating these functions are also a part of the thermodynamic network.

As we have seen, the entire thermodynamic network derives from the first and second laws. The laws are unquestioned, but their acceptance rests mainly on the successful application of the network they support; the experimental evidence for the laws *per se* is not overwhelming. The application of thermodynamics is represented in Fig. 1-1 as a three-step process requiring the input of experimental information. While the problem-solving process shown in Fig. 1-1 is certainly not unique to thermodynamics, there are certain features that distinguish thermodynamic problems. The most obvious feature is that the defined thermodynamic variables (e.g.,  $U$ ,  $H$ ,  $S$ , and chemical potential) do not



**Figure 1-1.** Road map for the conceptual development and application of thermodynamics.

appear in either the problem statement or the solution. These variables are simply used to solve the problem and therefore have no ultimate value beyond this application; in a sense they are dummy variables. Contrast this situation with that of fluid mechanics, for example, where the variables velocity, time, and position are part of the problem statement, are the variables in which the theory is formulated, and are the variables in which the solution is expressed. In addition to not being intrinsic to the problem statement or solution, the defined thermodynamic variables often require complicated, multi-step paths for their evaluation. Sometimes the path includes hypothetical steps and requires several types of experimental data. The thermodynamic method is thus characterized by an emphasis on information processing.

In both structure and application, thermodynamics resembles mathematics; both are self-contained and confidently used and both contain much that is never used. Just as much of mathematics has found no application, there are many unused relationships in the thermodynamic network. And when unacceptable results are obtained from the application of either of these tools, and no errors are found in the execution, it is the conceptual description of the system that must accommodate.

To understand this state of affairs it is necessary to distinguish the thermodynamic network, which derives solely from the first and second laws, from the equation of state used to describe the particular system. The equation of state is an algebraic equation that relates the state variables of the system: the ideal gas law or Currie's law for paramagnetic systems. Often the equation of state will have a theoretical basis (e.g., the ideal gas law or the virial equation of state), but its justification or the determination of its parameters is always empirical. When the relationships of the network are used with an equation of state, results specific to that system are obtained. Thus, if the thermodynamic method were applied to a gas with unsatisfactory results, the efficacy of the equation of state would be questioned and a more descriptive, and usually a more complex, equation of state would be employed.

Also, in applying the thermodynamic method it is necessary to know that the system is properly defined in terms of the state variables. The phase rule provides this guidance for conventional applications, but there are some systems that require the specification of additional state variables such as field strength or surface area. When these systems are encountered it is necessary to revise the

fundamental equation to account for the various ways in which the system can exchange work with the surroundings. The details of the thermodynamic network will change as a result of this new formulation, but the basic method for working out the details of the network remains unchanged.

### 1.3 The Nature of Thermodynamics.

The three major areas of classical physics are mechanics, electromagnetic theory, and thermodynamics and it seems to be a source of embarrassment to many physicists that thermodynamics does not fit too well into this triumvirate. The reasons for this lack of fit have already been discussed.

Statistical mechanics began as an effort to bring thermodynamics into closer conformity with the rest of classical physics. Here the methods of mechanics were applied statistically to the astronomically large number of molecules constituting the average thermodynamic system. Quantum mechanics developed somewhat later and was shown to subsume statistical mechanics. This new field, now known as quantum statistical mechanics, has proven to be a valuable adjunct to thermodynamics by allowing the evaluation of thermodynamic properties from molecular parameters. However, despite this practical success, there is still some uncertainty in explaining entropy in molecular terms. The two most common formulations

$$S = k \ln \Omega \quad (1-1)$$

and

$$S = - \sum P_i \ln P_i \quad (1-2)$$

relate entropy to the number of accessible quantum states of an isolated system,  $\Omega$ , or the probabilities,  $P_i$ 's, of the various quantum states in an isothermal system. If the entropy were an intrinsic property of matter, and not just a defined state function, one would expect a microscopic formulation to be expressed in terms of *physical* quantities. Instead it is related to the *logical* quantities  $\Omega$  and  $P_i$ 's which do not refer to any physical aspect of the system, but to the manner in which we choose to represent the system. Early workers in statistical mechanics referred to the expressions on the right-hand side of Eqs. (1-1) and (1-2) as entropy analogues; now, they are called statistical entropy, or often, they are



simply called entropy. They provide the basis for the putative interpretation of entropy as a measure of disorder.

The situation in regard to entropy became more confusing when a term arising from communication theory and resembling the right-hand side of Eq. (1-2) was also given the name of entropy. Because it defines the information content of a message, it is usually referred to as information entropy, however, the unmodified term entropy is often used. More recently, the confusion has increased with the assertion that there is an entropy change associated with memory erasure in computers — a computing entropy. In chapters 4 and 5 an attempt will be made to clarify this situation.

The impressive success of quantum statistical mechanics has prompted many scientists to state that the second law is statistical in nature. Some even go so far as to suggest that statistical mechanics subsumes thermodynamics. This undoubtedly holds great appeal to those who are uncomfortable with the lack of fit in the triumvirate of classical physics. These questions will be explored in chapter 9.

#### **1.4 A Chemical Engineering Perspective.**

Those who deal only with the familiar applications of the first and second laws might be inclined to describe thermodynamics as a consistent, self-standing system of laws and relations which govern processes or transitions where energy is transformed. They may go so far as to visualize the laws of thermodynamics in a Platonic sense as eternal and immutable laws of the universe which were discovered by human inquiry. This Platonic view, however, may not be so congenial to those who apply thermodynamics to chemical and phase equilibrium. These applications clearly involve contrived functions (activity coefficients) and artificial conditions (standard states) whose sole purpose is to facilitate a desired calculation. When one has worked with these obvious contrivances, it seems natural to regard the whole of thermodynamics in this light. From this perspective thermodynamics seems to be an information processing system— an invention of the human mind serving a human need to economize on the experimental description of physical systems. This view is inclusive enough to include all applications of thermodynamics; it is clearly utilitarian in nature.