Thermodynamics and its Applications

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Preface

As long as we can remember, our department has offered a one-semester, graduate level subject in classical thermodynamics. Traditionally, it has been applications-oriented; one of its primary objectives has been to develop competence and self-confidence in handling challenging applications in new and sometimes unusual situations. Half to two-thirds of the contact hours are usually devoted to problem-solving. Over the years, there accumulated many interesting, challenging problems—most of which originated from our consulting practice.

We have used a number of texts in conjunction with our graduate subject. None were completely satisfactory. We are convinced that a firm foundation in theory is essential for students who will be asked to fulfill the needs of tomorrow with an increasing demand for talents which are flexible and adaptable. On the other hand, the theory is useless unless the student can effectively bridge the gap between theory and application. Thus, we have attempted to develop a text with a rigorous theoretical and conceptual basis, interspersed with a relatively large number of examples and solutions. We have stressed to our students the desirability of working these examples before reviewing the solutions.

This text is intended to be a *learning text* rather than a teaching text. We have attempted to be thorough; but as a consequence of limited space and the short time a student spends in formal education, it is unreasonable to expect the student to appreciate all of the subtleties that will be apparent to the experienced reader. It is our hope that students will attain a basic level of understanding of theory and rationale of applications in their formal use of this text such that deeper insights can be gained in a self-instructional mode throughout their professional careers, as the need arises.

Following this philosophy, the text contains more material than one could hope to cover in one term—nor do we recommend a two-term sequence at the expense of the students' flexibility to shape their graduate curriculum to meet their individual needs. In three contact hours per week in a term, we have covered at a fairly rapid pace, all the chapters except for parts of Chapter 7 and Chapters 11 and 12; with four contact hours per week, we have covered thoroughly and at a more acceptable pace, ten chapters (excluding Chapters 12 and 7 or 11).

The theoretical basis of classical thermodynamics is developed in the first five chapters; that can be covered in one-third to one-half of a term. The flow of concepts is illustrated schematically in Figure P.1. The developments up to the introduction of the Fundamental Equation parallels the historical evolution of the classical body of knowledge (see Chapter 1).

The introduction of the formalism of the Fundamental Equation and Legendre transforms is a departure from traditional chemical engineering texts. (This route is becoming commonplace in physics and some other engineering fields, but these are often devoid of practical applications.) The Fundamental Equation is introduced because we believe it is of significant conceptual value in treating one of the central problems in engineering applications, namely, what are the minimum data required to reach a given objective and how does one manipulate available data to forms that are more appropriate to the problem at hand.

The Fundamental Equation in the energy representation, i.e., $U = f(S, V, N_1, \ldots, N_n)$, contains all thermodynamic information for a given single-phase, simple system. All other thermodynamic properties can be derived from it. Although we do not have available the Fundamental Equation for many materials, we can determine what other data sets have equivalent information content. Using Legendre transformations to preserve the information content, it is shown that, e.g., $H = f(S, P, N_1, \ldots, N_n)$ is also a Fundamental Equation and, thus, a Mollier diagram contains all thermodynamic information. Similarly, the Fundamental Equation of a pure material can be reconstructed from the equation of state and the heat capacity. Thus, any problem can be solved using P-V-T and C_p data; if these data are available, we need not search for any other data.

The last half of the text covers systems of increasing complexity. Following a discussion of single-phase systems of pure materials (Chapter 6), the criteria of equilibrium and stability are introduced (Chapter 7) so as to set the stage for treating mixtures and phase equilibrium.

Single-phase mixtures are synthesiezd from pure materials using the criteria of equilibrium to mix reversibly. Paralleling the pure material development, the type of data necessary to describe a mixture is discussed. The concept of ideal mixing is then appreciated as an idealization for which mixture properties can be synthesized from pure component data. Many common mixture properties (e.g., chemical potential, fugacity, activity coefficient) are explored as alternative methods of presenting similar information.

Phase equilibrium and chemical equilibrium are treated as progressively more complex applications of the building blocks covered previously. In these areas especially, it is stressed that thermodynamics is of little practical utility without sound engineering judgment. A phase diagram can only be constructed when there is prior knowledge of what phases do in fact exist and what properties (e.g., information equivalent to the Fundamental Equation) each phase exhibits. Similarly, the concept of chemical equilibria is of little use in the complex systems engineers generally face until there are data or insight into the kinetically feasible routes.

The last two chapters of the book deal with the thermodynamics of surfaces and nucleation (Chapter 11) and the thermodynamics of systems in electric, magnetic, stress, or other potential fields (Chapter 12). The approach used is parallel to that developed earlier, i.e., the applicable Fundamental Equation is found and Legendre transforms employed to relate the variables of interest in any real application.

It is impossible to acknowledge all who made this book a reality. We have been influenced by authors of previous articles and texts in thermodynamics and by our teachers. Professors J.M. Smith and H.P. Meissner excited our interest in this field and illustrated its power to attack and solve real and significant problems. Our students were critical and demanding and therefore a real delight. Sanjay Amin and Margaret Nemet provided significant comments as we approached completion. The typing was done in a superb manner by Ms. Judith Hawkins and Ms. Maria Tseng. To our wives and children, we are deeply indebted and grateful for their encouragement, understanding, and patience. Their confidence in this joint venture was a constant source of inspiration.

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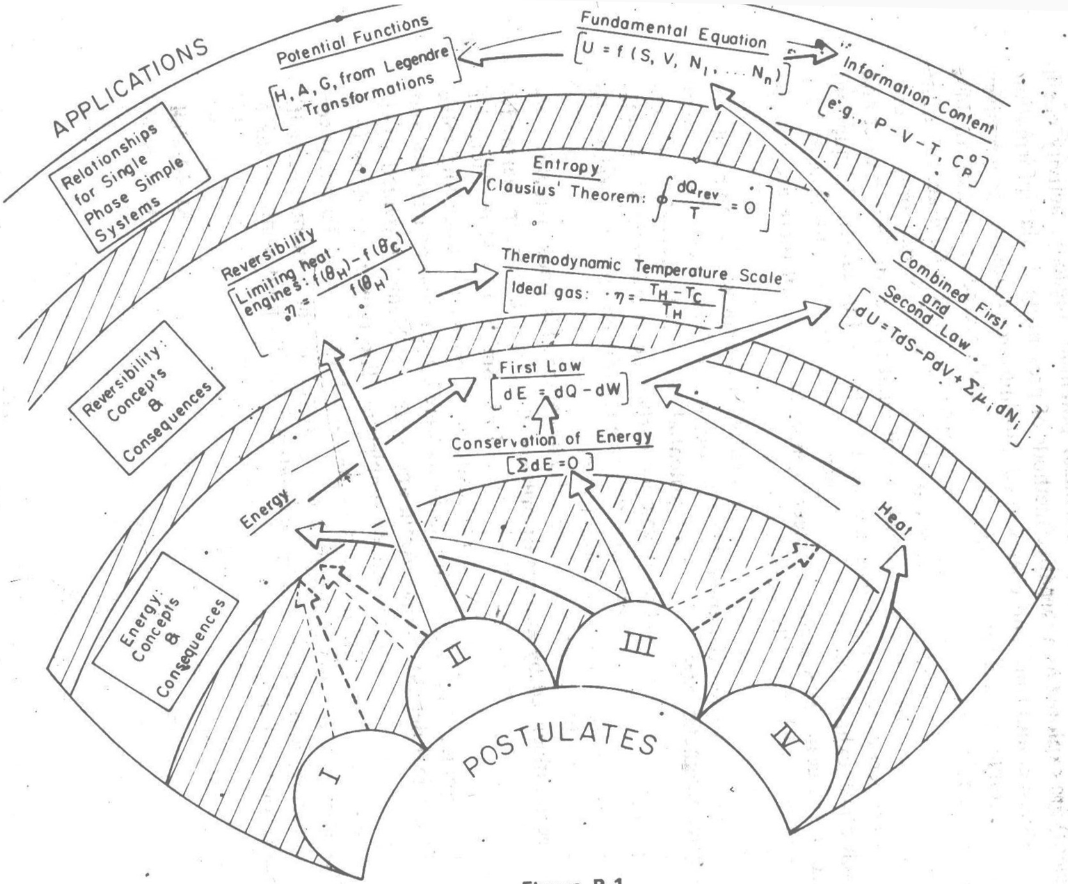
APPLICATIONS
Relationships for Single Phase Simple Systems
Potential Functions
[H, A, G, from Legendre Transformations]
Fundamental Equation
[U = f (S, V, N1, ... Nn)]
Information Content
[e.g., P-V-T, C°P]
Entropy
[Clausius' Theorem: ∮ dQrev/T = 0]
Reversibility
[Limiting heat engines: η = (f(θH) - f(θC))/f(θH)]
Thermodynamic Temperature Scale
[Ideal gas: η = (TH - TC)/TH]
Combined First and Second Law
[dU = TdS - PdV + Σμi dNi]
Reversibility: Concepts & Consequences
First Law
[dE = dQ - dW]
Conservation of Energy
[ΣdE = 0]
Energy
Heat
Energy: Concepts & Consequences
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III
IV
POSTULATES

Figure P-1

Thermodynamics
and its
Applications

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Introduction

1

1.1 The Scope of Classical Thermodynamics

To the scientist, classical thermodynamics is one of a few mature fields epitomized by a rather well-defined, self-consistent body of knowledge. The essence of the theoretical structure of classical thermodynamics is a set of natural laws governing the behavior of macroscopic systems. The laws are derived from generalizations of observations and are largely independent of any hypothesis concerning the microscopic nature of matter. From these laws, a large number of corollaries and axioms are derivable by proofs based entirely on logic.

The scientist is sometimes at a loss to understand why the engineer has so much difficulty applying thermodynamics; after all, the theoretical development is rather straightforward. From the engineer's point of view, understanding the theory as developed by the chemist or physicist is not particularly difficult; however, the neat, self-contained presentation of the subject by the scientist is not necessarily amenable to practical application. Real-world processes are usually far from reversible, adiabatic, or well-mixed; very rarely are they isothermal or at equilibrium; few mixtures of industrial importance are ideal. Thus, the engineer must take a pragmatic approach to the application of thermodynamics to real systems. One of his major concerns is to redefine the real problem in terms of idealizations to which thermodynamics can be applied.

In the engineering context, almost all problems of thermodynamic importance can be classified into one of three types:

1. For a given process with prescribed (or idealized) internal constraints and boundary conditions, how do the properties of the system vary?
2. To effect given changes in system properties, what external interactions must be imposed? (The inverse of 1.)
3. Of the many alternative processes to effect a given change in a system, what are the efficiencies of each with respect to the resources at our disposal?

Problems of the first two classes require application of the First Law, which is developed in Chapter 3:

$$\Delta E = Q - W \tag{1-1}$$

where E is energy and Q and W are the heat and work interactions, respectively. The First Law may also be viewed as:

$$\text{internal changes} = \sum \text{interactions occurring at boundaries}$$

The change in energy can be related to variations of other internal properties of interest (e.g., T, P, V, etc.).

The third class of problems requires application of the Second Law, for which an idealization — the reversible process — is introduced as a standard for comparison.

There are basically only three steps required to develop a solution to any thermodynamic problem:

1. *Definition of the problem.* The real-world situation must be modelled by specifying the internal constraints and boundary conditions. For example, is a boundary permeable, semipermeable, or impermeable? Is heat transfer fast or slow relative to the time span of interest? Which chemical reactions are known to occur under the conditions of interest?
2. *Application of thermodynamic laws.* As described above, these either relate effects internal to the system with external interactions (the First Law) or they set limits on the extent of internal variations (the Second Law). The combined laws prescribe in part the relationships between property variations, but they do not uniquely specify the magnitude of the change in properties. For example, for a simple system undergoing a process in which the temperature and pressure are observed to change from T_1, P_1 to T_2, P_2, we might wish to calculate the energy change in order to specify the necessary heat and work interactions. We might employ the following analysis:
   a. From *thermodynamic reasoning*, ΔE is a unique function of T_1, P_1 and T_2, P_2 because E is a state function. Therefore, ΔE can be evaluated over any path between these end states.

b. From *mathematical reasoning*, over any path for which E is defined, dE may be expressed as an exact differential such as:

$$\Delta E = \int dE = \int_{T_1}^{T_2} \left(\frac{\partial E}{\partial T}\right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial E}{\partial P}\right)_{T_2} dP \tag{1-2}$$

Note that $(\partial E/\partial T)_P$ and $(\partial E/\partial P)_T$ must be expressed as functions of T and P before Eq. (1-2) can be integrated.

c. Applying *thermodynamic reasoning*, E is defined as a function of T and P over a reversible path and, thus, $(\partial E/\partial T)_P$ and $(\partial E/\partial P)_T$ can be reduced to other variable sets that are more readily quantified:

$$\Delta E = \int_{T_1}^{T_2}\left[C_p - P\left(\frac{\partial V}{\partial T}\right)_P\right] dT - \int_{P_1}^{P_2}\left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP \tag{1-3}$$

where C_p is the constant-pressure heat capacity. Note that Eq. (1-3) is a *general result;* it must be satisfied by any material undergoing a change from T_1, P_1 to T_2, P_2. However, the value of ΔE is not unique; it differs from one material to the next, which leads us to the third and final step.

3. *Evaluation of property data*. There are property relationships that are unique characteristics of matter. For example, in Eq. (1-3), thermodynamics does not dictate the functions,

$$C_p = f_1(T, P); \qquad V = f_2(T, P) \tag{1-4}$$

required for the integration. Evaluation of these property data lie outside of the scope of classical thermodynamics. However, they are essential to the solution of real problems and, hence, are within the scope of this text. The engineer must make recourse to a variety of methods (e.g., literature, experiments, correlations, or microscopic theories as developed with statistical mechanics) in order to determine or approximate these property relationships.

Before discussing the approach to classical thermodynamics (Section 1.3) used herein, it is instructive to review the historical evolution of this body of knowledge.

1.2 Preclassical Thermodynamics

The origin of classical thermodynamics can be traced back to the early 1600's. The laws, as we know them today, were not formalized until the late 1800's. The interim 250 to 300 years are called the *preclassical* period, during which many of our current concepts were developed.

The chronological development is a fascinating example of the application of scientific methodology. Experimentation (e.g., thermometry) led