thermodynamics
second edition

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preface

This book is intended for use in the first course in thermodynamics taken by students in engineering. Naturally, not all the material presented can be covered in one semester, and different courses may demand different emphases. For those programs which require it, the text contains sufficient material for a two-semester sequence.

Considerable difference of opinion exists as to the subjects to be covered in a first course in engineering thermodynamics. Some instructors prefer a strictly classical, or macroscopic, approach, while others advocate a strong input of microscopic thermodynamics. Both schools would agree that the course content should be matched to overall program objectives, and that a text for such a first course must address itself to both the macro and micro applications. The student interested in solid-state electronics will find the sections on applications of statistical thermodynamics useful in later work but, hopefully, will also recognize the importance of classical thermodynamics in developing a proper foundation for the microscopic models of substances. The student interested in power cycles and energy conversion will profit most from the macroscopic thermodynamics.

In this second edition the addition of new materials has been concentrated in the chapters dealing with macroscopic thermodynamics because of the continuing interest in such applications and increasing severity of problems associated with economical and pollution-free production of power.

Some discussion of the chapter sequence is in order at this point. Chapters 1 to 4 present a classical development of the first law of thermodynamics, properties of pure substances, and energy analysis of open systems. Chapter 5 introduces the subject of statistical thermodynamics and can be omitted in a course primarily concerned with macroscopic applications or deferred until the end of the course. Chapter 6 presents the second law of thermodynamics and the concept of available energy from a macroscopic viewpoint. Chapter 7 gives a classical presentation of equations of state and generalized compressibility relations. Chapter 8 illustrates the applicability of statistical thermodynamics to the calculation of properties of gaseous and solid materials, while Chapter 9 develops the basic molecular model for kinetic theory of gases and transport phenomena. Both Chapters 8 and 9 can be omitted in a course devoted strictly to macroscopic thermodynamics.

Chapter 10 considers gaseous mixtures from the macroscopic viewpoint, with substantial emphasis placed on air conditioning applications. The calculation of properties of real-gas mixtures is also discussed but can be omitted if sufficient time is not available to cover this material. Chapter 11 gives a classical development of chemical thermodynamics and equilibrium, including energy analyses of such systems. Chapter 12 discusses a broad variety of power cycles, with strong emphasis given to the limitations imposed on efficiency by the second law. Chapter 13 gives an abbreviated treatment of the thermodynamics of compressible flow, while Chapters 14 and 15 consider some specialized applications of irreversible thermodynamics and direct energy conversion.

While the text allows for considerable flexibility in topic coverage, one must insist upon the inclusion of the materials in Chapters 1 to 4 and 6 in order to provide a proper basis for further study. The course, with these materials as a base, can then move in the direction of applications most appropriate to those students enrolled.

Additional mention should be made of the material which has been added in this edition. Supplementary motivational remarks have been added to Chapter 1 to stress the importance of thermodynamic analysis in the production of power and the efficient use of energy resources. More emphasis has been given to SI units in the basic discussion of Chapter 1 and throughout the text. Additional examples and discussion on first law analysis have been added in both Chapters 2 and 4 with an expanded list of problems. Useful relations for calculation of solid and vapor properties of water down to −40°F have been added to Chapter 3 along with expanded discussions and examples. Chapter 6 has been enlarged to include discussions of available energy and availability in steady flow, along with additional examples. Chapter 7 has some new examples and a modified presentation in some sections. Chapter 10 includes new information on the calculation of air-water vapor mixtures, including frost, at low temperatures. The chapter has been expanded in the latter sections to include calculations of the properties of real-gas mixtures. Chapter 11 has new sections and examples dealing with equilibrium in multiple reactions, effects of nonreacting gases on equilibrium concentrations, the van't Hoff isobar equation, phase equilibrium, and the Gibbs phase rule. Chapter 12 has been expanded to include more examples, a discussion of the Wankel engine, the practical LiBr absorption cycle, and closed gas-turbine cycles. Chapter 13 is new and presents the thermodynamics of compressible flow in a manner which is easily adaptable to most engineering curricula. A background in fluid mechanics is not required for understanding this material.

The author is grateful for the comments and suggestions received from individuals who have used the first edition, and most grateful for those penetrating questions of students that strike at the heart of a subject and demand clarification and explanation. It is hoped that the new materials have answered at least some of their questions and will serve, most importantly, to stimulate further inquiry.

J. P. Holman

contents

1 introduction

1-1 the nature of thermodynamics

Energy propels society. The matchless economic and technological advances of the civilized world are traceable directly to an increasing amount of energy available to perform the tasks previously performed through human muscular effort. The availability of goods and services, and industrial productivity in general, are directly related to per capita energy consumption.

Thermodynamics is the study of energy and its transformation. This statement may seem rather aspiring, because it could be interpreted to mean that thermodynamics is the one science that is most strongly related to man's societal needs because of his increasing consumption of energy to produce goods and services. There are many different types of energy: the frictional work of a block sliding on a plane, electric energy, magnetic energy, nuclear energy, the energy stored in a quantum of light, the chemical energy of a petroleum fuel, and others. All of these types of energy can fall in the province of thermodynamic analysis and we shall examine a variety of applications as the subject develops. As we shall see later, the laws of thermodynamics limit the amount of energy which is available to us for performing useful work.

In the early beginnings of civilization man was dependent upon his own muscular effort to hunt and perform whatever farming tasks were necessary to his survival. With the invention of the wheel he was able to expand his sources of energy to include the muscular effort of work animals and with the invention of fire he had a source of energy to forge new instruments and machines of iron and other materials. All the while man's standard of living was steadily rising as more and more energy became available to him to heat his home, form materials of construction, and expand his communication through better modes of transportation. With the invention of the steam engine in the 1700s a new source of power was available to drive machines which could be controlled at will, independent of the wind, the course of a stream, or the whims and limitations of an animal. Later in the 1800s and 1900s came the internal combustion engine, steam turbine, gas turbine, and nuclear power. And with each new source of energy man's standard of living has taken a substantial upswing.

Today the total production of goods and services of a nation, the gross national product (GNP), is directly related to the energy available to produce the goods. We find that the gross national product per capita is strongly related to the energy consumption per capita as illustrated in Fig. 1-1. The data for this figure are for 1961 and by 1970 the GNP for the United States was $5000 per capita and energy consumption had risen to 330 million Btu per capita. At that time the United States had 6 percent of the world's population and consumed 35 percent of the energy. So-called underdeveloped nations are clearly those with less energy per capita and less GNP. In Fig. 1-2 we see the long-term trends of energy use in the United States, with several clearly evident conclusions. Both the population and per capita energy consumption are growing, producing a rapid exponential rise in total energy consumption. The rise has been so rapid in fact that a long-term drop in energy required to produce a unit increase in GNP is now sharply reversed, reflecting the impact of inflation, the increased costs of environmental protection equipment associated with power generation, and the mature status of current energy-conversion technology.

The long-term implications of the above data are unmistakable. The standard of living of a heavily industrialized nation depends on the supply of energy available to the nation and the efficiency with which it is utilized.

We may remark that the overall quality of life depends on many factors. Clean air and water, spacious green areas for recreation, and the availability of goods and services all contribute to human satisfaction. Energy must be consumed to farm the land and transport people and goods from home to place of employment, and in each of these cases some pollution of the environment will occur. The important point is that a proper balance must be drawn between uncontrolled energy consumption and pollution and the equally undesirable goal of severely restricted energy use to the point that man's standard of living is lowered substantially.

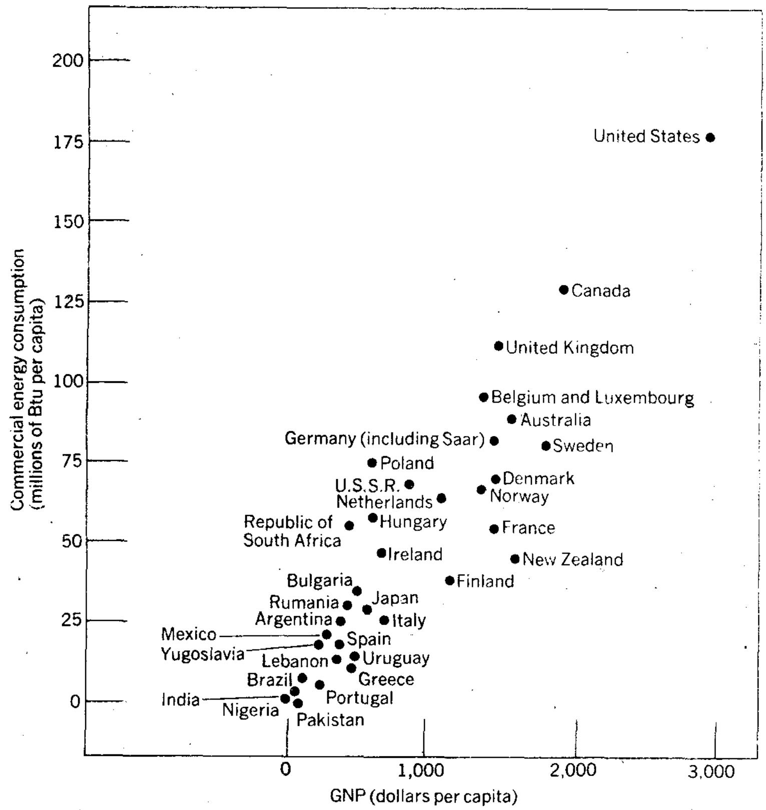

figure 1-1 *Relationship between per capita energy consumption and gross national product (1961).*

Various sources of energy are becoming increasingly expensive to produce and one must be concerned with environmental factors involved in all conversion schemes. For these reasons, more and more attention must be focused on the efficiency of energy utilization. Thermodynamics furnishes the scientific basis for analysis of energy-conversion schemes and thus is central to an understanding of future energy-consumption trends and their social and economic impact.

Generally speaking, most studies of thermodynamics are primarily concerned with two forms of energy: heat and work. The principal objectives of the study are to develop basic principles describing these types of energy and to become conversant with the language surrounding these basic principles. As in all such studies the first step is to build a vocabulary of definitions and terms which may be used to conserve thought as the development becomes more complex. To define rigorously the various concepts of thermodynamics requires considerable space and effort, and will, of course, form a large part of the discus-

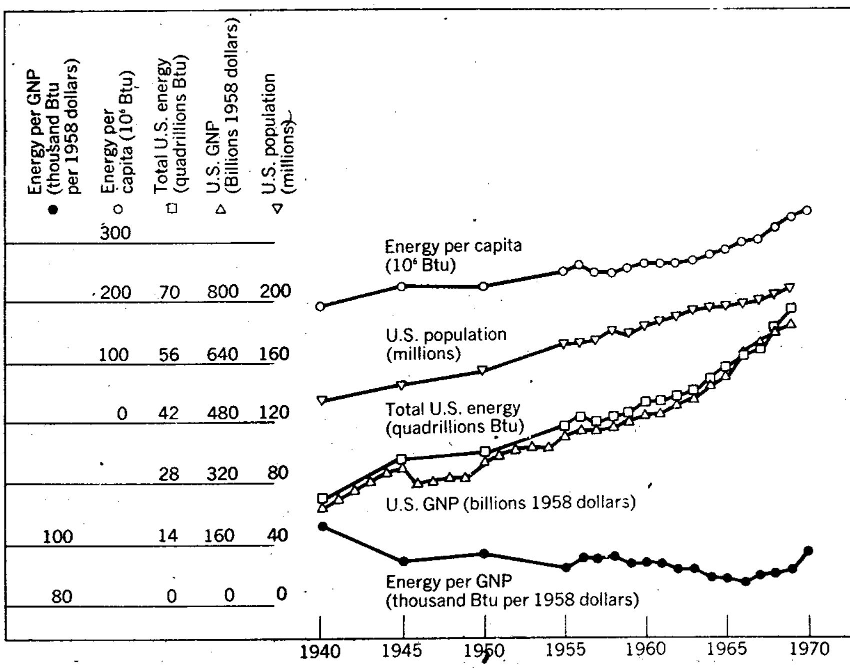

figure 1-2 *Energy consumption rates in the United States.*

sion in this book. In this introductory chapter we seek to give a brief qualitative picture of the broad subject of thermodynamics to achieve a perspective for detailed studies in subsequent chapters. In this respect it is well to note that many of the qualitative discussions are offered on the basis of physical reasonableness and should be accepted with the view that more rigorous definitions and developments will be presented later. The objective of this chapter is to achieve an overall picture of the scope of thermodynamics.

1-2 relation between classical mechanics and thermodynamics

The study of classical mechanics involves concepts of force, mass, distance, and time. A force has a physical meaning of a "push or pull" which may be represented mathematically as a vector with a point of application. Mechanics is developed through the application of Newton's laws of motion and, particularly, the second law which states that the summation of forces acting on a particle is proportional to the time rate of change of momentum,

$$\Sigma F = \frac{d}{d\tau}(mv)$$

For purposes of analyzing mechanical systems a *free body* is used whereby a definite portion of a mechanism is broken away and all forces acting on this mechanism are specified for use with Newton's second law. It is important to realize that the mechanical *system* is specified in terms of its coordinates of space and velocity. The behavior of the mechanical system is further described in terms of its interaction with its surroundings through the application of various forces. We say that the *state* of the system may be specified with its space and velocity coordinates and its *behavior;* i.e., its change from one state to another is described in terms of its interactions with adjoining mechanisms or surroundings. It may be observed that the mechanical system will not change its state, i.e., its position in space and/or its velocity, unless it is acted upon by some net external force. The important point of this brief reference to classical mechanics is that the concept of a system (free body) and specification of the *state* of a system through the use of space or velocity coordinates are already familiar to those readers with experience in classical mechanics.

system

state

Although we are concerned with dynamical quantities in mechanics, the analysis of thermodynamic systems is concerned with energy quantities. A system is described in thermodynamics by breaking away a certain quantity of matter similar to the free-body technique in mechanics. The matter outside this system is termed the *surroundings* and the separation between the system and surroundings is called the *boundary* of the system. As an example of a thermodynamic system consider a mass of air contained under pressure in a steel tank. The boundary of the system would be the inside surface of the tank and the surroundings would consist of the tank and the medium outside the tank. It is well to mention that the boundary of a system may be either a real or imaginary surface. The air-tank system is shown in Fig. 1-3.

surroundings

system boundary

In mechanics the state of a system is specified by its space and velocity coordinates. The state of a thermodynamic system is described by specifying its thermodynamic coordinates. We cannot describe all thermodynamic coordinates at this point but may note that temperature, pressure, chemical energy content, etc., are typical examples. These coordinates are usually denoted as *properties* of the system. In mechanics we noted that a system will not change its state unless there is some interaction with its surroundings to change its spatial position and/or velocity. This interaction usually takes the form of an energy transfer into or out of the system.

properties

When a thermodynamic system changes from one state to another, it is said to execute a *process.*

process

In the study of thermodynamics we are interested in the changes which a system may undergo as it executes various processes. Clearly, we must be able to define the state of the system or its thermodynamic coordinates if we are to meet with success in describing processes which the system may undergo. For, if we are to describe the process, we must