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Introduction and synopsis

1.1 SCOPE AND IMPORTANCE OF THERMODYNAMICS

Thermodynamics is a sub-area of physics, of chemistry, and of most engineering disciplines. Unlike mechanics, in which only work and mechanical energy are defined, thermodynamics deals with all forms of energy and energy transfer, including thermal energy and heat. Therefore, thermodynamics is a continuation of mechanics. Together, mechanics and thermodynamics provide a much more comprehensive, detailed, and quantitative description of our physical world, and of actual physical and chemical processes.

The two major “laws,” or “hypotheses,” or “postulates,” of mechanics (see Chapter 2) and six new principles of thermodynamics, which are covered in detail in this book (see Section 1.7.1), provide highly important predictions as to what processes are physically possible, or feasible, and what processes are not possible. Consequently, these eight principles act as the “constitution” of the physical, chemical, biological, and engineering sciences. This “constitution” has many secondary consequences, or implications, that are important in all these areas, and are discussed in various books on thermodynamics, physical chemistry, materials science, and related areas. Therefore, technical professionals should learn and understand at least the key principles and ideas of thermodynamics.

Thermodynamics is important in everyday life. The general public should be informed about what processes are possible in energy production and use, materials production and use, food production and use, and waste generation and treatment. The availability of energy sources, especially renewable and sustainable energy, is essential for the quality of life of all human beings. Biological and physiological processes should also follow the thermodynamic principles. Thus, medical professionals, business people, attorneys, and other non-technical people should have some appreciation of what processes make physical and thermodynamic sense, so that they can make informed decisions.

1.2 BASES AND VALIDITY OF THERMODYNAMICS

Thermodynamics is based on observations, experiments, hypotheses, and theoretical tests of such hypotheses with rational experiments and rational, mathematically based, physical arguments. The eight principles or hypotheses reviewed in Section 1.5, and throughout this book, have been scientifically validated numerous times, and have never been disproven. For
example, no exceptions have been found to the principles of mass conservation and energy conservation (in non-relativistic, or low-velocity, systems). Hence, there exists a general scientific consensus that they are universally valid. In fact, when certain controversies have arisen regarding their validity, alternative explanations have been found, to further the conviction of scientists about their validity.

As physics and physical chemistry progressed over the past 200 years, the molecular theory of matter was developed and established further, primarily within the areas of chemistry, quantum mechanics, statistical mechanics, and statistical thermodynamics. These areas provided an extension of our knowledge of classical mechanics and thermodynamics, and further confirmed the ideas and principles of thermodynamics (see Chapter 14). They also provided a more detailed and more comprehensive understanding and explanation of the last three key principles of thermodynamics. Thus, thermodynamics is now considered to be a well-established area of science, with applications to most physical and chemical processes and products.

1.3 GOALS OF THE BOOK

The primary goal of this book is to serve as a textbook for undergraduate students in chemical engineering, or other engineering disciplines, such as mechanical or material engineers, at least for the development of the basic principles, which are the same for all disciplines. Students in other science disciplines, chemistry, physics, biochemistry, etc., may also find some value in this book. Another goal of this book is to provide sufficient qualitative information and discussion, so that even a “layman” (a non-technical person) can understand many of the key ideas of thermodynamics. A third goal of this book is to serve as self-study reading material for professionals who need to refresh their memory some time after they have finished their course work or training.

In my experience I have found that students and readers have more difficulties in understanding the physical origins and significance of the key concepts and principles of thermodynamics than in learning how to solve problems that require numerical answers. To address this problem, I have included detailed qualitative and quantitative explanations and definitions, to make it easier to overcome this hurdle. For example, the key concepts of internal energy, enthalpy, entropy, Gibbs free energy, chemical potential, fugacity, and several others, are covered in detail. To further emphasize this approach, I have included a long list of study questions, to help readers test and challenge their understanding. In Section 1.7, I have added some detailed guidelines on how to cover the key points of each chapter. In Section 1.8 I have also included a set of detailed metrics, which, in my opinion, can provide a certain measure of the level of accomplishment by a student of thermodynamics.

I have included a large number of problems in many chapters, for further practice of the reader’s understanding. In Chapter 2, and especially in Chapter 6, general methods of problem formulation and problem solving have been emphasized. The reader is shown how to develop mathematical models of phenomena and processes, starting from the simplest and least accurate models, and progressing to the more accurate and more complex models.
Many practical applications are covered in most of the chapters, usually in engineering and science. Many applications in energy are covered in Chapters 4 and 6–8. Applications to chemical separations, distillation, gas absorption, liquid–liquid extraction, and reverse osmosis, are covered in Chapters 10–13. Several environmental applications, with a more limited scope than those in energy, are covered in various chapters, and summarized in Chapter 18. This book is not a substitute for more extensive books on energy and environmental engineering. One of its goals is to cover briefly how the key principles of the mass and energy balances, of the Second Law, and of reaction equilibria can be used to analyze problems of energy efficiency and climate change.

1.4 Macroscopic, microscopic, and molecular aspects

The area of “classical thermodynamics,” or simply “thermodynamics,” covers “macroscopic systems.” Such systems consist of large numbers of molecules, in three dimensions, as in bulk systems or phases (see Chapter 3), in two dimensions, as at interfaces between two phases, or in one dimension, as in “contact lines” between three phases. Classical thermodynamics covers physical laws resulting from the collective behavior of large numbers of molecules. Even though it is well established that molecules exist, the behavior of individual molecules is not considered in detail by classical thermodynamics. This approach to system description is called a “continuum” description, since the discrete nature of molecules is not considered. It is also called a “phenomenological” approach, indicating that one considers how the processes appear to be happening on a large scale, and not why they are happening on a molecular scale. In this approach, the average properties of the molecules, for example their average pressure and their average energy, are considered. Finally, the length scale $\ell$ of the systems studied is much larger than the size of the molecules ($\ell \gg 10^{-9}$ m), and usually also much larger than the average separations among the molecules.

When one considers explicitly the behavior of individual molecules, or small numbers of molecules, one uses a “microscopic” approach, or a “molecular theory.” When some molecular theory or information is used along with a macroscopic approach, one deals with “molecular thermodynamics.” Prominent books in this field may include many books in physical chemistry (e.g. Atkins (1994), Adamson (1986), etc.) or the book by Prausnitz et al., *Molecular Thermodynamics of Fluid-Phase Equilibria* (1999).

The behavior of individual molecules is studied more simply in the “kinetic theory of gases,” and most generally in statistical and quantum mechanics. Quantum mechanics is used to help predict the values of macroscopic thermodynamic properties, such as the pressure and the energy. Statistical mechanics and thermodynamics, either classical or quantum, are used for studying the behavior of systems of large numbers of molecules from a more general perspective than that of classical thermodynamics, and help predict various measurable thermodynamic laws (see Chapter 14). Even though these areas require a specialized and strong mathematical and physical background to be fully covered and appreciated, some of their simpler ideas can be understood by a beginning student.
Nonetheless, the thermodynamic laws can be developed, explained, and understood, without a significant level of understanding of their molecular origins. Moreover, the mathematical background needed in classical thermodynamics is less demanding than the background needed for understanding quantum and statistical mechanics, or for learning fluid dynamics. Some knowledge of calculus and differential equations is, of course, required for understanding thermodynamics, since several of the thermodynamic laws are expressed not only qualitatively and conceptually but also by the use of essential mathematical principles, equations, and inequalities.

1.5 SUMMARY OF THE KEY PRINCIPLES OF THERMODYNAMICS

The first two key principles of thermodynamics are borrowed from mechanics. They are (a) Newton’s Second Law of Motion, that the net external force acting on a body is equal to the mass times the acceleration (see Chapter 2), and (b) the principle that mass is conserved (see Chapters 2 and 4). These principles are based on the purely mechanical concepts of length, time, mass, force, velocity, acceleration, pressure, etc.

Then thermodynamics starts with the concept of an equilibrium phase (and a non-equilibrium phase later). The thermodynamic state of a phase (which includes all physical properties, such as density, pressure, etc.) is postulated to exist. This first new idea and principle is called in this book the “Minus Second Law” of thermodynamics, and, even though it is a qualitative idea or principle, it is still a key principle and a precursor to the Second Law. The second postulate is that the full thermodynamic state at equilibrium can be fully described by a small number of variables, the number of which most often is \( n = 2 \), for example the pressure and the density. Then the values of all other properties of this equilibrium phase are fixed. This postulate is called in this book the “Minus First Law,” and is the basis of subsequent equations of state and thermal equations of state. It is also one of the origins of the Gibbs phase rule. The third postulate of thermodynamics is that there exists another quantitative parameter, which is a function of the state of an equilibrium phase, and is called the “empirical” or common temperature \( \theta \) (in degrees Centigrade, or Fahrenheit, or other units). This postulate is called the “Zeroth Law” of thermodynamics. The first three postulates are described in Chapter 3.

I should provide an explanation for the strange numbering system of the first three laws of thermodynamics as I formulated them in this book. I have chosen to present and explain these laws with such a system, unlike what is done in many other textbooks, for the following reasons. First, the ideas in these laws or hypotheses are not in any dispute. In fact, the ideas of the Minus Second Law and the Minus Second Law are covered in most books on thermodynamics, but most often without naming or acknowledging them explicitly. I am grateful and would like to give credit for the idea of presenting the Minus Second and Minus First Laws explicitly to one my mentors, the late Professor L. E. Scriven of the University of Minnesota. The Zeroth Law, which deals with the existence of the empirical temperature \( \theta \), is presented in several books. The general energy conservation principle in thermodynamics was named historically the “First Law” (see Chapter 4). Since the other three principles discussed above belong logically before this First Law, as will become apparent in Chapters 3 and 4, the
numbering system of $-2$, $-1$, and $0$ was chosen in this book, to avoid any confusion that may result from changing the numbers of the generally used First and Second Laws.

In the context of the First Law (which is actually the fourth postulate presented in this book), two new fundamental thermodynamic quantities are postulated to exist, the internal energy, $U$, and the heat, $Q$ (see Chapter 4). Then in Chapter 7 we introduce a new principle that covers the direction in which a process can occur. A well-known example is that heat can be transferred from a hot body to a colder body, but not in the opposite direction. The Second Law (the fifth postulate here) was discovered after extensive research in the middle of the nineteenth century. The Second Law was the basis of predicting and discovering the existence of two new quantities that can be measured: (a) the absolute thermodynamic temperature $T$, which depends on the empirical temperature $\theta$, and (b) the entropy $S$, which can be defined from the absolute temperature $T$ and the heat $Q$. The combination of the two postulates of mechanics, the first three thermodynamic postulates discussed above, the First Law, and the Second Law provides a complete set of principles, which can be applied to determine whether a process being considered has a chance of happening or not.

Finally, the Third Law (the sixth postulate here) covers a special property of the entropy $S$ (see Chapter 14), namely that it can be defined on an absolute basis. All six postulates of thermodynamics were conceived after extensive research in the middle of the nineteenth century. The first five laws can be explained and justified (but not proven, since they are postulates) on the basis of common everyday observations, as will be detailed later (Chapters 3, 4, and 7). The Third Law is based, to an extent, on specialized scientific knowledge of the behavior of matter at very cold temperatures, so cold that they could not be realized in the laboratory until the late nineteenth century. Moreover, the molecular explanation of these laws did not become available until the twentieth century. A combination of actual experimental evidence and theoretical arguments based on thermodynamic theory and molecular theory led to the conception of the Third Law postulate, as detailed in Chapter 14.

### 1.6 EQUILIBRIUM AND NON-EQUILIBRIUM EFFECTS IN THERMODYNAMIC ANALYSIS

Some authors have argued that thermodynamics covers only effects related to properties of phases at equilibrium, at which there are no pressure, temperature, or composition variations with position. Some authors have even suggested the use of the term “thermostatics” instead of thermodynamics.

I do not agree with the above argument for the following reasons. First, the mass and energy balance equations (see Chapter 4) do apply to systems that are not at equilibrium. Secondly, even though the “equations of state” (see Chapter 5), which relate the specific volume or the density of a phase to its pressure and the temperature, apply strictly to systems of equilibrium, they are still used routinely, and usually do apply, for non-equilibrium systems as well. For example, the fluid mechanical equations which are used for describing flows of a gas or a liquid phase include, along with the other fluid dynamics equations of mass, momentum, and energy balances, the same equations of state, or “constitutive equations,” as determined from
experiments at equilibrium. Moreover, the thermodynamic laws, especially the Second Law, determine the “driving force” for heat transfer, namely the temperature difference (see Section 8.4), for mass transfer, namely the chemical potential or concentration difference (see Section 8.10 and Chapters 11–13), or for the direction of a chemical reaction (see Chapter 16). Hence, thermodynamics is also important for non-equilibrium systems and effects.

It is true that thermodynamics cannot describe or predict the rates, which sometimes are called the “dynamics” or the “kinetics,” of heat transfer, or of fluid deformation, or of mass transfer, or of chemical reactions. The sciences of heat transfer, fluid mechanics, transport phenomena, and reaction kinetics deal with these issues. In these areas one defines some other material properties, such as thermal conductivity, viscosity, and diffusivity, which depend on the temperature, pressure, and composition, just as the common thermodynamic properties do. One can also define concepts such as the heat transfer coefficient (see Chapter 6), or the mass transfer coefficient (see Chapter 12), which depend not only on the intrinsic properties of the materials but also on the details of the flow conditions such as the flow patterns and the velocities.

1.7 OVERVIEW OF THE BOOK

1.7.1 What this book covers

In Chapter 2, we cover, in some detail, the connection of thermodynamics to mechanics. The key concepts in mechanics are reviewed. The pressure, stress, and work are covered rigorously, as is the incomplete principle of the “mechanical energy conservation or balance.” The introduction of the internal energy and the First Law in Chapter 4 are meant to augment, or correct, or complete, the incomplete, and often violated, mechanical energy balance. In addition, several problems involving determining the pressure and temperature distributions in a liquid or in a gas phase in a gravity field are modeled at an increasing mathematical and physical sophistication. The goal is to introduce the reader to the ideas and limitations of various levels of mathematical analysis and modeling of physical phenomena. Such ideas are used throughout the book.

In Chapter 3, we cover the types and precise definitions of various phases, equilibrium and non-equilibrium. We emphasize the general definition of a phase, with and without gravity (or other field) effects, either at equilibrium conditions or in flow conditions, in order to avoid the misconception that a phase must have uniform properties. In addition, we cover the definitions of multiphase systems, interfaces, dispersions, “colloids,” “nanoparticles,” etc., in order to clarify that thermodynamics applies to most types of phases.

Then in Chapter 3 we cover the rationales and statements of the Minus Second Law, the Minus First Law, and the Zeroth Law. With the Zeroth Law, we cover the definition of the empirical temperature \( \theta \) and the experimental ideal gas temperature \( T_{\text{id}} = \theta \degree C + 273.16 \degree C \). We emphasize that the concept of the ideal gas temperature, \( T_{\text{id}} \), is quite different from the concept of the thermodynamic absolute temperature \( T \), even though they may be represented (by convention) by the same number; \( T \) is defined only in the context of the Second Law (see Section 7.6).
In Chapter 4, we cover the definition and significance of the new energy function called internal energy $U$, and a second mode of energy transfer, in addition to work $W$, called heat, $Q$. In a unique feature of this book, the First Law is covered in various versions, starting from the most fundamental versions which are required for an accurate definition of the internal energy and of the heat. Moreover, in a fairly novel feature of Chapter 4, and generally of this book, when a new concept or quantity is introduced, the method of its measurement is described, in order to make it clear that each thermodynamic concept is not just an abstraction but a real and accessible quantity that is amenable to physical understanding. For example, the internal energy change $\Delta U$ is measured from the work $W$ expended. The work is either mechanical (as in Joule’s experiments) or electrical, as done in modern instruments called “calorimeters.” Moreover, the heat $Q$ is measured indirectly from the change in the internal energy $\Delta U$, which is measured from the work $W$. We try to correct the common misconception that the heat $Q$ is measured from the heat capacity $C_p$ or $C_v$ and the temperature difference $\Delta T$. In fact, the opposite is true: the heat capacity $C_p$ or $C_v$ is measured from the heat $Q$ (which is measured from the work $W$) and the temperature difference $\Delta T$. In older books it is often stated that the heat $Q$ is measured separately from the measurement of the work $W$, and that there is a so-called “mechanical equivalent of heat,” or that $Q$ is proportional to $W$. Although it is true that the heat $Q$ is a different form of energy transfer than the work $W$, the units of the two quantities are the same, and the heat is measured from work, as stated above, and as detailed in Section 4.1.4.

In Chapter 4, we also cover the general mass and energy balance equations which are important in solving many thermodynamics problems. We discuss the first definition of the heat capacity $C$, which generally is not entirely a material property but is path-dependent. We emphasize that the concept of heat capacity can be a state function, or a material property, or path-independent, only when the path of the heating process is specified. The most common examples are the heat capacity $C_v$ at fixed volume and the heat capacity $C_p$ at constant pressure. In certain analyses we may use the term “heat capacity $C$ of liquid water or other liquids or solids” without explicitly specifying the heating path. In such examples the implication is that there is little effect of the path because the quantities $C_p$ and $C_v$ for liquids and for solids are usually approximately equal to each other. This is nearly true only at low pressures. At very high pressures the path has to be specified for the heat capacities of liquids or solids to be well defined. In Chapter 4 we also introduce the general idea of the “thermal equation of state,” which is a mathematical relationship of how the heat capacity $C_p$ (or $C_v$) depends on the temperature $T$, the total pressure $p$, and, for solutions, on the molar composition as well.

In Chapter 5, we introduce the idea of the “$pV T$” equation of state, which is a “constitutive equation,” or a mathematical relationship of how the specific volume $V$ (in m$^3$/kg), or the molar volume (in m$^3$/mol), or the density $\rho$ (in kg/m$^3$) depends on $T$, $p$, and the molar composition. For “wet steam,” which is a two-phase system consisting of liquid water and vapor (gas) phases at equilibrium, we explain how $V$ depends on $T$ (or $p$) and the “steam quality” $w$, which is the mass fraction of vapor. We also cover how the molar volume of a solution depends on $T$, $p$, and the molar composition. Other important applications covered in this chapter are the vapor pressure of a liquid, the partial pressure in a gas mixture, and the absolute and relative humidity of moist air.
In Chapter 6 we cover the application of the ideas and equations presented in Chapters 4 and 5 to analyzing several classes of thermodynamic problems, such as gas expansion, mixing in vessels, heating and boiling of liquids, heat exchangers, and processes occurring in the flow of fluids through valves or in the emptying or filling of containers with fluids. The general methodology for solving such problems is presented. The mass and energy balance equations are also quite important in evaluating the energy efficiency of processes, and are crucial in modeling of global warming/climate change problems. These problems are discussed further in Chapter 18.

In Chapter 7 we cover the experimental basis, the key ideas, and the hypotheses of the Second Law. This chapter is probably the most important and challenging of this book. One must study this chapter several times, in order to understand and appreciate fully the basis for the discovery of the concepts of the absolute temperature and the entropy. Entropy changes of a phase can be measured, indirectly, or calculated, from experimental data of the thermal equation of state, \( C_v(T, p) \), and of the equation of state, \( \bar{V}(T, p) \). It is important that the reader realizes and fully appreciates this point. Then the reader should realize that the entropy is not just an abstract or abstruse quantity, but is an accessible, measurable, and useful concept, just like the internal energy \( U \) or the enthalpy \( H \), which, for a beginning student, appear easier to understand because they are energy functions. In fact, both quantities, the entropy \( S(T, p) \) and the internal energy \( U(T, p) \) are calculated indirectly from the same experimental data, and both are needed for analyzing the feasibility of physical and chemical processes. In this chapter, entropy is introduced simply as the “natural” function which determines the direction in time of a physical process occurring in an isolated system, with a constant mass, volume, and energy. If a certain process would change the state of the system and the surroundings in such a way that the total entropy decreased, then the process could not occur. If the entropy would increase, however, then the process could occur. The process still would not necessarily occur if some conditions restricted the process from happening (see Chapter 16 on reaction equilibria). The Second Law can be used to explain, after some derivations, the direction of heat transfer and of mass transfer, and the conditions for equilibrium in one phase, or between two phases (Chapter 8). Therefore, in addition to the constraints for the overall conservation of mass and energy, thermodynamics prescribes the previously missing condition for a process to be feasible. The only additional principle in thermodynamics is the Third Law (see Chapter 14), which states that the entropy can be defined not only on a relative basis (like the energy) but on an absolute basis, and that the entropy is always positive.

Further research by various prominent physicists, chemists, chemical engineers, and others (Helmholtz, Gibbs, van ’t Hoff, Lewis, Randall, and others) revealed more convenient ways and methods for using the three principles of mass conservation, energy conservation, and the entropy inequality for any isolated system. In one example, covered in Chapter 8, if one would like to determine how a system may change when it is maintained at fixed mass \( m \), volume \( V \), and temperature \( T \) (this set of conditions can be denoted concisely by the symbol \((m, V, T)\)), then the above three principles must be followed. One can test this by considering the sum of the changes of the properties \( m, U, \) and \( S \) for both the system and its surroundings, ensuring that the net mass and energy changes are zero and that the net entropy change is positive. Helmholtz proved that it is equally valid or “equivalent” to these conditions to consider changes
1.7 Overview of the book

of a new energy function of the system only, and avoid having to consider changes of the surroundings. This function is the “Helmholtz free energy,” $A$, which is defined as $A \equiv U - TS$, and involves a combination of energy, $U$, and entropy, $S$. Helmholtz proved that for a process to occur at fixed $(m, V, T)$, consistently with thermodynamics, the Helmholtz free energy $A$ of the system must decrease. Moreover, $A$ must be of a minimum value at equilibrium, beyond which no further changes are possible. This idea of decreasing $A$ at fixed $(m, V, T)$ involves no additional new principle of thermodynamics. Hence, the decreasing trend of the Helmholtz free energy under the above conditions is a “theorem,” not an “axiom.”

Similarly, one can define the “Gibbs free energy” $G$ for a closed system of fixed mass at fixed $(m, T, p)$. Its definition is $G \equiv U + pV - TS$ (see Chapter 8). Under these conditions, $G$ must decrease and reach a minimum value at equilibrium. Similarly, when one considers an “open system,” which does not have a fixed mass, and can exchange mass with the surroundings, an equivalent condition for the three thermodynamic principles has been discovered, with the introduction of yet another concept, that of the “chemical potential” $\mu$. This concept is quite useful in determining a simple rule as to the direction of mass transfer, from one region to another when they are at a fixed temperature and pressure. Mass transfer will occur from high to low chemical potential, and will stop, to have equilibrium, when the chemical potentials are the same. Then the sum of the entropies of the system and surroundings will be at a maximum. The chemical potential is an indirectly measurable quantity, as are the quantities $U, H, S, A$, and $G$.

Instead of using Gibbs free energies or chemical potentials to predict the direction of processes and the conditions of phase equilibrium, one may use yet another abstract but measurable quantity, called “fugacity,” or “fugacity coefficient,” or “activity coefficient.” These quantities allow one to use more convenient expressions to represent the three major thermodynamic principles, as detailed in Chapter 9. There is a whole series of important applications of these principles in separation processes — distillation (Chapter 10), gas absorption, (Chapter 11), liquid–liquid extraction (Chapter 12), and osmosis (Chapter 13). These applications are of primary interest to chemical engineers and chemists, and of some interest to biologists and medical scientists.

In Chapter 14, we discuss the Third Law and the molecular or statistical thermodynamic interpretation of the entropy $S$, of the Second Law, and of the Third Law. The goal is to clarify the often misunderstood statement or inference that “entropy is disorder.” Although this inference has some relation to the actual phenomena, it is not accurate and can lead to confusion, rather than improved understanding. Moreover, justifying such an inference is not easy, and requires some elementary understanding of quantum and statistical mechanics for systems of molecules. It also requires the introduction of two new and quite abstract principles of statistical mechanics. Then one may appreciate the molecular basis of entropy, and realize the solid foundations of the classical thermodynamic principles not only on experimental evidence but also on rigorous molecular theory. This molecular theory is, in fact, not independent of classical thermodynamics, but complements, enhances, or extends the validity of classical thermodynamics. It may be more accurate to state that “increases in entropy are often related to increases in the disorder of the molecular system.”

In Chapter 15, we present some special theoretical implications of the First and Second Laws, first to the formulation of the famous Gibbs–Duhem equation. This equation describes
certain mathematical constraints among certain thermodynamic properties. Such constraints allow us to determine one set of properties from another set obtained from experimental data. Or, they allow the testing of two or more sets of experimental data for internal consistency and accuracy. In Section 15.2.5 we present some elements of “surface thermodynamics,” or “thermodynamics of two-phase systems” with a fluid interface. This interface is characterized by a new measurable thermodynamic property, called “surface tension,” which affects properties of droplets, bubbles, and other systems with curved interfaces. New phenomena arise when a fluid interface and its surface tensions become important. For further information on surface thermodynamics, the reader is referred to the literature (see Section A.2 of Appendix A). We further discuss several important applications of solutions, including the techniques of measurement of vapor pressure lowering, boiling point elevation, or “ebullioscopy,” and freezing point depression, or “cryoscopy.” These three methods can be valuable in determining solution nonidealities of mixing, solute dissociation, and solute aggregation or polymerization. Some limited thermodynamic predictions of solubilities of solids are finally covered in Section 15.7.

In Chapters 16 and 17, we cover in considerable detail chemical reaction equilibria for one reaction, or for several reactions occurring simultaneously. Using mass (or mole) and energy balances, and the First, Second, and Third Laws, we present the equations which allow one to calculate the equilibrium reaction yield, which is the fractional or the percentage conversion of one or more reactions at equilibrium. We also explain the issues related to the direction of a chemical reaction, for example whether the formation of water, H2O, from hydrogen, H2, and oxygen, O2, may occur or, in the opposite direction, the decomposition of H2O to H2 and O2 may occur. These chapters should be of interest to most engineers and scientists. They are important in many energy-related or environment-related applications.

In Chapter 18 we discuss how the thermodynamics concepts and principles can be used to help understand issues related to energy efficiencies of devices, climate change, and some other environmental pollution problems. Several sections of this book contain material that can be helpful in understanding such phenomena. Several examples will be discussed. Finally, in Appendix A we provide in alphabetical order a brief guide to literature data, and a limited bibliography.

For each chapter we provide a set of study questions and several problems. In certain key chapters we provide numerous problems. The questions are meant to test the reader’s understanding of the basic concepts and principles. The problems should be of primary interest to chemical engineers, chemists, and possibly some mechanical or other engineers, and should serve to test the reader’s understanding and help the development of problem-solving skills.

1.7.2 What this book does not cover

The kinetic theory of gases (see Davis (1996)) is not covered, except briefly in Section 5.2, where some ideas for helping understand the molecular basis of the internal energy and the pressure are presented. The molecular thermodynamic and statistical thermodynamic aspects of explaining and predicting data on thermodynamic properties are not covered.

Issues involved in the operation and design of various types of engines, and details on refrigeration and air-conditioning, are not covered here. They are covered in more detail in