Preface

Intended mainly for undergraduate chemistry majors, this book contains most of the topics generally taught in classical thermodynamics courses, yet, frequently supplemented and further interpreted based on elementary statistical thermodynamic theory. We mainly base our choice of topics, their order of appearance and mode of presentation, as well as the solved problems appearing in the main text and at the end of each chapter, on our many years of teaching this beautiful (but hard to grasp) subject to generations of students. While the prevalent tradition prescribes to teach separately and successively classical and statistical thermodynamics, our approach here is far more liberal. Thus, wherever they seem helpful to the student, we integrate or even precede the introduction of the underlying statistical-molecular basis to the macroscopic thermodynamic phenomena. In particular, we have noted that many students (and not only chemistry majors) find it difficult to assimilate the formalism of classical thermodynamics, and hence are unable to appreciate its power and beauty. Introducing concepts such as heat and work, the first law of thermodynamics, the efficiency of heat engines, or the classical formulations of the second law are still rather straightforward. To contrast, introducing a new state function called entropy, S, based on the conclusion that the ratio between the reversible heat increment $đQ_{rev}$ and the absolute temperature, T, i.e., $dS \equiv đQ_{rev}/T$, is an exact differential leaves most students speechless. Adding to this conclusion the common saying that "entropy is a measure of disorder" – without providing its statistical-molecular origin – only adds to the student's confusion. Lacking the molecular-level basis and the statistical interpretation of entropy undermines the ability to appreciate the enormous fundamental importance and elegance of the entropy and related thermodynamic functions and phenomena, such as free energies, phase transitions, and chemical equilibrium.

With these notions in mind, we find it more logical and physically intuitive to introduce the concept of entropy based on its molecular-probabilistic interpretation and definition following the work of Boltzmann, Gibbs, and Maxwell. On this basis we shall follow (i.e., in a reversed chronological order) to derive the Clausius inequality and the classical statements of the second law of thermodynamics as originally formulated by Clausius and Kelvin following Carnot's and their own studies of heat engines. We turn to discuss the statistical and classical properties of entropy and their reflection in the second law of thermodynamics in Chapters 5-7, where we also introduce the Maxwell-Boltzmann probability distribution, the canonical partition function, the notion of fluctuations, and several other elementary statistical thermodynamic concepts. Earlier, in Chapter 4, we present the first law of thermodynamics and the balance of heat and work in various thermodynamic systems and processes (transformations). Chapter 3 provides the basic mathematical constructs of thermodynamic state functions and the physical classifications of systems and processes. Still earlier, in Chapter 2, we discuss the microscopic origin of inter-molecular forces, and demonstrate their thermodynamic consequences as reflected in the equation of state of real gases. Chapters 8-20 are concerned with the traditional subjects discussed in thermodynamic textbooks, such as phase transitions, chemical equilibrium, and the properties of mixtures, but also involve some less traditional topics, such as self-assembly phenomena or liquid crystals' phase transition. In most chapters, statistical interpretations are interwoven with the classical thermodynamic discussion.

Our goal in the opening Chapter 1 is to provide a qualitative glimpse into some of the questions, concepts, and phenomena that will be discussed in more detail in subsequent chapters. In a rather descriptive fashion – using the phase transitions of a binary liquid mixture as an example – we comment on the relationships between inter-molecular interactions and thermodynamic behavior, emphasizing the frequent thermodynamic interplay between energy and entropy. This chapter ends with a brief outline of the contents of each of the following chapters in this book.

Finally, we are of course aware of the existence of many outstanding textbooks of classical thermodynamics, among which are comprehensive and rigorous treatises such as Callen's book, or the shorter and elegant monograph by Fermi. Many other excellent books, such as those by Denbigh, Reiss, and Klotz, as well as many physical chemistry textbooks that focus on chemical thermodynamics, address most of the material discussed in the present book, some of which in greater detail. There are also numerous superb statistical thermodynamics textbooks, varying in their level of rigor and the kind of audience that they address. The scope and depth of many classic treatises of statistical mechanics, such as the monumental books of Tolman, Fowler and Guggenheim, Landau and Lifshitz, Mayer and Mayer, and Hill are obviously well above the needs of chemistry undergraduates, even advanced ones, and hence beyond the scope of this text. On the other hand, we found that many descriptions and analyses that appear in introductory or intermediate level textbooks, such as the excellent books by Hill, Reif, Widom or Chandler, can be understood by undergraduate students and help them appreciate the importance and elegance of thermodynamics. Incorporating ideas from such books into the classical thermodynamic theory has played an important role in the development of our thermodynamics courses, on which we base the present book. The combination we present here of the molecular and statistical interpretations in the classical thermodynamic treatment proved attractive to the majority of our students. Their repeated encouragement to transfer our many lecture notes, numerous homework assignments and (always open books and notes) examination problems, has been the ultimate motivation for writing this book. We wanted to name this book "Molecular Thermodynamics", because as physical chemists, we wished to emphasize the intimate relationships between the molecular-statistical aspects of many-molecule systems with their thermodynamic behavior. We noted, however, that this name has already been used by McQuarrie in his own excellent book, and have thus decided to compromise on a somewhat different title. There are several other good books that combine the statistical and classical treatments. We think that students and the teacher should have a choice.

Chapter 1. THERMODYNAMICS AND MOLECULES

This introductory chapter previews some of the basic concepts and phenomena that will be discussed in later chapters, and outlines our approach to their presentation. Take a deep breath! This chapter is only intended as a first acquaintance with the subject. Concepts that at first may seem obscure and unsubstantiated, will become transparent in later chapters. The discussion here will be rather casual and associative, postponing rigorous definitions, mathematical proofs, and detailed analyses to Chapter 2 and onwards. We shall still assume that the reader is familiar, at least qualitatively, with some elementary concepts, such as thermal equilibrium, heat transfer, or mechanical work. The discussion also emphasizes the relationships between the thermodynamic properties of macroscopic systems, such as pressure temperature or heat capacity, and the microscopic characteristics and inter-molecular of their constituent particles. This notion underlies the general approach of this book, whereby statistical thermodynamic interpretations and molecular-level insights are interweaved with the more methodical and traditional presentation of classical thermodynamics. Although less systematic mathematically, the synergic discussion of classical and statistical thermodynamics is, in our opinion, considerably more intuitive and thus comprehensible to chemistry students.

Along with a few historical remarks, in Section 1.1 we emphasize both the power and elegance of classical thermodynamics, as well as its limitations, and the remedies provided by the statistical theory. In this very brief survey, we shall mention some (yet hardly a small fraction) of the names of the many great founding researchers of the science of thermodynamics. The history of this wide and exciting field has been documented in various books as well as in electronic documents. Some of the relevant bibliography will be mentioned in the lists of reference closing the chapters. In Section 1.2 we mention the two basic laws of thermodynamics and the two fundamental thermodynamic functions that are directly related to these laws: energy and entropy. Using the mixing behavior of two molecular liquids as an example, we qualitatively demonstrate the interplay between energy and entropy in Section 1.3. Finally, Section 1.4 provides an outlook on the rest of the book, where (unlike the casual nature of this chapter) the discussion is systematic, progressing methodically from one chapter to the next.

1.1 Classical and Statistical Thermodynamics

Thermodynamics is concerned with the properties of *macroscopic systems* and their changes of state. By definition, macroscopic systems are composed of many particles, such as atoms, molecules, paramagnetic spins, or photons. *Classical thermodynamics* provides general relationships between the various *state functions* that determine the mechanical and thermal properties of these systems, as well as the rules dictating how these functions change in the course of different kinds of processes. The state functions, such as the energy, pressure, temperature and volume, are so named because they are fully determined by the state of a system, irrespective of the way the system reached that state, or its history..

The foundations of classical thermodynamics were established in the nineteenth century, based on the seminal works of Carnot, Clausius, Joule, Kelvin, and many others, who studied the interplay between heat and work and the efficiency of heat engines. Their studies led to the formulation of the *first law* and *second law of thermodynamics*, and to Clausius' colossal revelation of a new fundamental thermodynamic function – *entropy*. The beauty and power of classical thermodynamics are largely due to its general physical applicability and its mathematical elegance. Based mainly on the first and second laws and the knowledge of a small set of independent state functions (e.g., the number of molecules in the system, its volume, and the temperature) classical thermodynamics provides general mathematical relationships that allow to derive all other thermodynamic function of the system of interest. One example among numerous relationships of this kind is the equation, sometimes referred to as the *thermodynamic equation of state*,

$$\left(\frac{\partial E}{\partial V}\right)_{N,T} = -P + T\left(\frac{\partial P}{\partial T}\right)_{N,V} \tag{1.1}$$

This equation relates the change in the energy, E, of a macroscopic system containing N particles, upon varying its volume, V, at constant temperature, T, to the change in its pressure P as a function of temperature at constant volume. The changes accounted for by the partial derivatives correspond to infinitesimal transitions between neighboring equilibrium states of the system. Remarkably, this equation is valid for any thermodynamic system in equilibrium. Thus, for instance, for a dilute gas obeying the ideal gas law

$$PV = NkT \tag{1.2}$$

Eq. (1.1) yields $\left(\partial E / \partial V\right)_{N,T} = 0$, indicating that the energy of the ideal gas is independent of its volume. Indeed, from experiment we know that the energy of, say, a monatomic ideal gas (in reality this is found for very dilute gasses) is given by $E = (3/2)NkT = (3/2)nRT$, with T denoting the absolute, or Kelvin scale temperature, $n = N / N_A$ is the number of moles, where $N_A = 6.022\times10^{23}$ is Avogadro's number, $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$ is the gas constant, and $k = R / N_A = 1.38\times10^{-16}\ \mathrm{erg\ K^{-1}}$ is Boltzmann's constant.

In addition to providing essential theoretical relationships between different thermodynamic function, mathematical identities such as Eq. (1.1), are often of great practical interest because they supply the means for evaluating hardly measured properties based on observables that are more accessible. In this particular case, E can be derived using information about the more easily measured quantities P, V, N, and T. More generally, we note that the minimal number of independent observables needed to evaluate all other thermodynamic properties is very small. Specifically, only a triad of observables, for instance N,V,T or N,V,E, or P,V,T, suffice to determine all the other thermodynamic state functions of a system containing a single chemical component. Two component systems involve a minimal set of four observables, e.g., N_1,N_2,V,T or N_1,P,V,T, three-component systems require one additional independent observables, etc. The minimal set of independent observables is reduced by one when *intensive properties* – those whose values are the same everywhere in the system, such as P, T, or the number density, $\rho = N / V$ – are concerned. Thus, only two intensive properties suffice to determine the values of all the other intensive properties of a single-component system. Using again the ideal gas example, we note that ρ and T for instance, determine the pressure of the gas, $P = \rho kT$, the average kinetic energy per particle, $\varepsilon = E / N = (3/2)kT$, and all other intensive properties of the gas. The thermodynamic functions whose values are proportional to the size of the system, such as

N, V and E, are known as *extensive* functions. Rigorous definitions of extensive and intensive functions will be given in Chapter 3.

While useful and elegant, the general thermodynamic identities provided by the classical theory yield limited insight into the microscopic underpinnings of thermodynamic systems and their changes of state. Following the realization that matter is composed of atoms and molecules rather than consisting of continuous media, during the second half of the nineteenth century the gap between the molecular and the macroscopic aspects of thermodynamic systems began to be bridged, leading to the development of the theory of *statistical thermodynamics* (or *statistical mechanics*). In addition to providing the means for expressing and evaluating thermodynamic functions in terms of the molecular properties and interactions, statistical thermodynamics also provides information on fluctuations in the values of these functions around their mean values. The notion of fluctuations is altogether absent in classical thermodynamics. It should be emphasized, however, that statistical thermodynamics does not replace, but rather complements, the classical theory. That is, the thermodynamic relationships in the classical theory remain valid in the statistical treatment, with the statistical averages of the thermodynamic observables fulfilling the roles of their (non-fluctuating) classical analogs, as briefly elaborated below, and in more detail in Chapter 7.

Historically, the first significant step toward relating the thermal properties of many-particle systems with their particulate nature was the formulation of the *kinetic theory of gases* and the Maxwell-Boltzmann distribution of molecular velocities, in the second half of the nineteenth century – well before the structures of atoms and molecules were known. The major developments of the statistical theory, establishing the relationships between the thermodynamic functions of macroscopic systems and the collective behavior of their constituent particles, followed soon afterwards. The most remarkable milestones in this development took place in the 1870s. These were the statistical definition and probabilistic interpretation of the entropy by Boltzmann, and the independent, essentially equivalent definition and interpretation of the entropy by Gibbs, who also introduced the concept of *statistical ensembles*.

Statistical thermodynamics provides the means for calculating the probabilities of finding a macroscopic system in any of its microscopic states – often referred to as "microstates". These probabilities, and hence all the thermodynamic properties of macroscopic systems can be derived based on one crucial hypothesis – the fundamental postulate of statistical thermodynamics – which states that: *all the microscopic states of an isolated system in equilibrium are equally probable*. Although originally stated before the days of quantum mechanics this postulate is applicable in both the classical and quantum mechanical versions of statistical thermodynamics. (Recall, that quantum mechanics was formulated roughly fifty years after the probabilistic interpretation of entropy.) The classical and quantum mechanical definitions of the microstates of a macroscopic system, and the correspondence between them, will be discussed in considerable detail in Chapter 5. At this point we suffice with the statement that the quantum mechanical microstates are specified by the complete set of quantum numbers of the particles comprising the system, while in classical mechanics they are specified by the momentary coordinates and momenta of these particles.

By definition, an *isolated system* contains a fixed number of particles, say N molecules of the same species, within a vessel of fixed volume V, whose thermally insulating– also known as *athermal* – walls prevent the exchange of energy with the surroundings, so that its energy, E, is also fixed. The probability of finding this "N,V,E" system in any of its equi-energetic states, s, is thus a constant

$$p_s = \frac{1}{\Omega} \qquad (1.3)$$

where $\Omega = \Omega(N,V,E)$ is the total *number of microstates* of the system in question, so that the probability distribution is normalized to unity, $\sum_s p_s = 1$. Besides its role as a normalization factor, Ω, or more precisely its logarithm, is of fundamental thermodynamic significance. Explicitly,

$$S = k \ln \Omega \qquad (1.4)$$

is the *statistical definition of entropy* introduced by Boltzmann[1]. This equality is a corner stone of statistical thermodynamics, which together with the fundamental hypothesis

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[1] Rather than Ω Boltzmann used the symbol W, standing for *Wahrscheinlichkeit*, meaning probability in German. We reserve here the letter W for "work".

embodied by Eq. (1.3), provides the basis for the statistical interpretation of the second law of thermodynamics, as will be discussed in detail in Chapters 5-7.

Most systems of experimental relevance are not surrounded by thermally insulating walls, but rather by so-called *diathermal* walls, that allow the system to exchange energy in the form of *heat*, through particle collisions or radiation, with its surroundings. In many cases we are also interested in systems that can change their volume, or are open with respect to particle exchange with their surrounding environment. The probability distributions of these more complicated systems also follow from Equations (1.3) and (1.4). Consider for instance a *closed system* which, by definition, contains a given number of particles (say, all of the same kind) N, within a vessel of fixed volume V, surrounded by a heat reservoir of temperature T. When thermal equilibrium prevails, the temperature of the system is also T. The thermodynamic state of this system is fully specified by the triad N,V,T of boundary conditions. In Chapter 5 we shall see that the probability distribution of finding such systems in their various microstates follows directly from the fundamental postulate of statistical thermodynamics stated above, as embodied by Eq. (1.3). The result is the *Boltzmann distribution*

$$p_s = \frac{1}{Q} e^{-\frac{E_s}{kT}} \tag{1.5}$$

where $E_s = E_s(N,V)$ is the energy of the system in microstate s, whose value depends on the number of particles in the system, and generally also on its volume. For the special case of an ideal gas Eq. (1.5) is equivalent to the Maxwell-Boltzmann distribution of molecular velocities, that was originally derived based on kinetic consideration, Exercise 1.x. Like $\Omega(N,V,E)$ in Eq. (1.3), $Q = Q(N,V,T) = \sum_s \exp\left(-E_s / kT\right)$ ensures the normalization of distribution, $\sum_s p_s = 1$. More significantly, in analogy to the thermodynamic significance of $\ln\Omega$ as (being proportional to) the entropy, $\ln Q$ is proportional to another central thermodynamic function, known as *the work function* or the *Helmholtz free energy*, A. A glimpse into the fundamental importance of this function will be given in the next section.

Thermal equilibrium in a system of given N, V and T is a dynamical condition, in the sense that heat is constantly exchanged between the system and its surrounding heat bath, resulting in instantaneous fluctuations in the energy of the system around its average value,

$$\langle E \rangle = \sum_s p_s E_s \tag{1.6}$$

Like the equilibrium probabilities, p_s, the average energy is a well defined and time-independent function of N, V and T. A common quantitative measure of the energy fluctuations is the standard deviation,

$$\sigma_E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = \sqrt{\left\langle \left(E - \langle E \rangle \right)^2 \right\rangle} \tag{1.7}$$

and calculated using the same state probabilities used to calculate $\langle E \rangle$ or any other property, (Exercise 1.1). Similar definitions apply to the fluctuations in pressure, the fluctuations in the number of particles in open systems, etc. [Figure]

The concept of fluctuations does not exist in classical thermodynamics but, as noted above, the thermodynamic identities of the classical theory still hold in the statistical treatment, except that fluctuating functions in the statistical theory replace their non-fluctuating averages in the classical treatment. For instance, Eq. (1.1) is still applicable to a statistical ensemble of systems each with the same N, V, T, yet with $\langle E \rangle$ replacing E and $\langle P \rangle$ replacing P. Similarly, in systems characterized by fixed N, P, T the energy and the volume undergo fluctuations, and Eq. (1.1) remains valid with $\langle E \rangle$ and $\langle V \rangle$ replacing E and V, respectively. Under most circumstances, the dynamical fluctuations in macroscopic systems are negligibly small, explaining the great success of the classical theory in explaining most the many relationships among thermodynamic functions. This is because the fluctuations are generally proportional to the number of particles in the system, N, implying extremely small values of the relative fluctuations, e.g., $\sigma_E / \langle E \rangle \approx \sqrt{N}$, (Exercise 1.2). Similar scaling behaviors correspond to fluctuations in other quantities. In certain cases, however, in the vicinity of critical points for instance, the fluctuations can become very significant, as briefly mentioned in Section 1.3 and further elaborated in subsequent chapters.

1.2 Energy, Entropy and the Basic Laws

There are three basic laws of thermodynamics. The first law is concerned with the balance of energy between the system and its surroundings. The second law distinguishes between allowed and processes and those that cannot be realized in nature. The subject matter of the third law is the behavior of thermodynamic systems at temperatures close to the absolute zero[2]. In this section we briefly introduce and comment on the first two laws of thermodynamics.

The first law of thermodynamics, reading

$$\Delta E = W + Q \tag{1.8}$$

is the manifestation of the law of conservation of energy in macroscopic systems. It was first stated in this form by Clausius in 1850, relying on earlier studies of heat engines by Carnot and Clapeyron, and the equivalence of heat and mechanical work by Joule, Thompson (Lord Kelvin) and Rankin. This law states that in any process that a thermodynamic system goes through, the change in its *internal energy*, ΔE, is the sum of the *heat*, Q, and *work*, W, that the system exchanges with its surroundings. In Eq. (1.8) W is positive when work is done on the system, e.g., a gas is compressed to a smaller volume. Similarly, Q is positive when heat flows into the system, through contact with a hotter body. The internal energy, or simply – the energy of a thermodynamic system – is the sum of all the energies of its constituent particles. For instance, the internal energy of a molecular liquid includes the kinetic energy of the molecules, their internal (vibrational, rotational and electronic) energies, as well as the inter-molecular interaction energies. The translational and rotational energies of the system as a whole are not included in E.

Heat engines are thermodynamic systems undergoing a cyclic process during which they exchange heat with several reservoirs of different temperatures, perform work on their surroundings, and return to their initial state at the end of each cycle. In 1824 Carnot showed that among all the heat engines operating between two heat reservoirs, a hot one of temperature T_2 and a cold one of temperature T_1, *reversible* engines achieve the highest possible efficiency, $\eta = -W/Q_2$, as defined by the ratio between the work

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[2] A fourth law, often referred to as the zeroth law of thermodynamics, states that if systems A and B are each in thermal equilibrium with a third system C, they must also be in thermal equilibrium with each.

performed and the heat extracted from the hot reservoir, per cycle of the engine. The notion of reversibility will be clarified in more detail in Chapter 4. For now suffice it to mention that a reversible process is one that can be traced back, such that everywhere along the reversed transition the heat and work that the system exchanges with its surroundings are of the same magnitudes but of opposite signs to those exchanged in the original process. Carnot also showed that all reversible engines operating between T_1 and T_2 have exactly the same efficiency. and that this efficiency is only a function of the two temperatures of the reservoirs. This Carnot's efficiency is given by

$$\eta = -\frac{W}{Q_2} = 1 - \frac{T_1}{T_2} \tag{1.9}$$

Note that in a cyclic process $\Delta E = 0$, so that by the first law, Eq. (1.8), $-W = Q_1 + Q_2$, remembering that W and Q_1, are both negative.

In the early 1850s, based largely on Carnot's principle, Clausius and Kelvin postulated two different, yet equivalent, forms of the second law of classical thermodynamics. Clausius' version states that *a heat engine whose sole result is the transfer of heat from a cold to a hot reservoir cannot exist*. In other words, such a process must involve the investment of work, rather than its production. The inverse cyclic process whose sole result is the transfer of heat from a hot to a cold reservoir is possible, and does not require work input. The second version of the second law, by Kelvin, states that *there are no heat engines whose sole result is the extraction of heat from a single heat reservoir and its complete conversion into work*. Here again, the inverse process, whereby mechanical work is fully converted into heat, is indeed possible. These two classical statements of the second law are equivalent, as we prove in Chapter 6.

Following these developments, in 1862 Clausius realized the existence of a new thermodynamic function of state: the *entropy* S. He also concluded that the total entropy, namely the sum of the entropies of a system and its surrounding – which together form one large isolated "super system" – never decreases. More explicitly, it always increases in irreversible processes, but remains unchanged in reversible ones. While in general we are interested in system that interact with their surroundings, irreversible process can also take place in isolated systems of finite size, always as a result of the removal of an *internal constraint*. Irreversible process of this kind is, for instance, the spontaneous mixing process taking place upon the removal of a partition separating between two compartments of an overall isolated system, each containing a different gaseous species. Other spontaneous processes involving an increase in entropy are, for example, the water formation reaction occurring when hydrogen and oxygen are allowed to mix and react, the flow of heat from a hot to a cold body upon bringing them into contact, or the diffusion of ink molecules when a drop of ink is added to a glass of water. Any removal of constraint results in a spontaneous process that increases the entropy, once all the internal constraints within an isolated system have been removed, the system reaches a state of complete equilibrium, at which point its entropy is maximal.

The removal of an internal constraint is invariably accompanied by a substantial increase of the number of microstates available to the isolated system, as illustrated by a simple example in Figure 1.1. This notion is at the base of the probabilistic interpretation of the entropy, as mathematically cast in Eqs. (1.3) and (1.4). The irreversible nature of the spontaneous processes ensuing the removal of the constraint is the vanishingly small probability that the system will ever revisit in its initial state. Exercise (1.3), demonstrate this statement for one simple example. Other examples and a detailed discussion of the statistical origin of the entropy will be given in Chapter 5 and 6.

As mentioned above, the spontaneous direction of processes that take place in non-isolated systems can be derived by regarding the system of interest plus its surrounding as one large isolated super-system. Application of the principle of increasing entropy to this super-system yields extremum principles that depend on the boundary conditions appropriate to the system of interest. Of particular interest are processes taking place in systems coupled to a heat reservoir, so that the system temperature at the beginning and the end of any such process is the heat reservoir temperature, T. The extremum principle appropriate for systems of this kind involves a new extensive energy function

$$A = E - TS \tag{1.10}$$

known as the *Helmholtz free energy*, or the *work function*.

In any spontaneous process taking the system from an initial state 1 to a final state 2, the corresponding change in the work function is always negative,

$\Delta A = A_2 - A_1 < 0$, so that A is minimal when all constraints have been removed and the system has reached complete equilibrium. Among the numerous examples of such process are, for instance, the *isothermal* mixing of two or more different gases or liquids, chemical reactions, etc. Regardless whether heat is absorbed or released by the system in the course of a spontaneous process like this, its final and initial temperatures are equal, so that $\Delta A = \Delta E - T\Delta S < 0$. On the other hand, as will be shown in Chapters 9, when the system undergoes a controlled, reversible, isothermal process then $-\Delta A = -W_{\max}$ represents the maximal amount of work that the system can do on its surroundings, explaining the origin of the names "free energy" and "work function".

Other extremum principles correspond to systems subjected to different boundary conditions. Of special interest are systems that in addition to being coupled to heat bath, are also kept under constant pressure, P. Spontaneous processes in such systems involve a decrease in another thermodynamic function, the *Gibbs free energy*

$$G = H - TS = A + PV \tag{1.11}$$

where $H = E + PV$ is the function known as the *heat function* or *enthalpy*. Here too, in any spontaneous process $\Delta G = \Delta H - T\Delta S = \Delta E + P\Delta V - T\Delta S < 0$, with G reaching its minimum at equilibrium. Furthermore, $-\Delta G$ is the maximal work that can be extracted from a system at constant pressure and temperature, e.g., the electrical work derived from the ionic reaction taking place in an electrochemical cell. Because A and G dictate the maximal work that can be derived from macroscopic systems, they are both referred to as *thermodynamic potentials*.

1.3 Intermolecular Forces Influence Thermodynamic Behavior

A subtle interplay between energetic and entropic preferences underlies the outcomes of most thermodynamic phenomena. The balance between these – generally opposing – tendencies plays a central role in thermodynamic phase transitions, chemical reactions, surface adsorption, molecular self-assembly, and numerous other physico-chemical processes. In this section, as a preview to this central thermodynamic issue, we briefly and qualitatively consider one familiar phenomenon: the mixing of two *partially miscible* molecular liquids. The qualitative analysis of this issue is also intended to highlight the intimate linkage between the molecular and macroscopic aspects of thermodynamic phenomena.

A schematic temperature-composition diagram describing the phase behavior of two partially miscible liquids, say *A* and *B*, is illustrated in Figure 1.1, with $X = X_B$ and $X_A = 1 - X$ denoting their respective molar fractions. Specific (though less symmetrical) phase diagrams describe, for instance, the binary mixture of water and phenol (C_6H_5OH), or that of nitrobenzene ($C_6H_5NO_2$) and n-hexane (C_6H_{14}). Delineated by the convex solid curve – known as the *coexistence* (or *binodal*) *curve* – the $X-T$ plane in Figure 1.1 is separated into two distinctive regions. Everywhere outside this curve, the two components mix homogenously with each other, forming one spatially uniform liquid *phase*. On the other hand, the area enclosed by the coexistence curve marks the *two-phase* (or *biphasic*) *region*, within which the mixture breaks up into two phases of different compositions, coexisting in equilibrium with each other. Within each phase, the chemical composition, and all other intensive physical properties (e.g., density, color, refractive index) are spatially uniform. The solid blue circle at the top of the coexistence curve marks the *critical point*, specified by the critical temperature T_c and the critical composition X_c. In the nitrobenzene/n-hexane mixture, $X_c(C_6H_5NO_2) = 0.62$ and $T_c = 293K$ ($20\,^0C$), and in the phenol/water mixture $X_c(C_6H_5OH) = 0.1$ and $T_c = 340K$ ($67\,^0C$).

The phase diagram in Figure 1.1 typifies mixtures where, on *energetic* grounds, the two molecular components prefer to stay segregated. Their reluctance to mix is due to the energetic barrier associated with the formation of $A-B$ contacts in the mixture, replacing the $A-A$ and $B-B$ prevailing in pure A and B liquids. In analogy to the energy change in a chemical reaction of the form $AA+BB \rightarrow 2AB$, a quantitative criterion to the energetic cost of mixing A and B molecules is given by

$$w = 2w_{AB} - (w_{AA} + w_{BB}) \tag{1.12}$$

where w_{AA}, w_{BB}, and w_{AB} denote the depths of the intermolecular interaction potentials between the pairs of molecules $A-A$, $B-B$, and $A-B$, respectively. As illustrated in Figure 1.2, interaction potentials are measured generally with respect to a reference state of zero energy associated with infinite distance between the interacting species. This means that w_{AA}, w_{BB}, as well as w_{AB} are all negative, because the interaction potential between any pair of electrically neutral molecules (including seemingly "repelling" pairs such as oil and water, for instance!) is always attractive, becoming repulsive only at very short distances.

Mixing is energetically unfavorable when $w > 0$. Note, however, that this does not mean that w_{AB} must be larger than both w_{AA} and w_{BB}, only larger than their arithmetic average $(w_{AA} + w_{BB})/2$ which holds true for many pairs of molecules. On the other hand, mixing is generally (though not invariably – delete?) favorable on entropic grounds, because the number of spatial arrangements available to A and B molecules in the mixture is far larger than prior to their mixing, (Exercise 1.4). The resultant of the conflict between the energetic and entropic preferences of the mixture depends on temperature and composition. The role of temperature is largely accounted for through the ratio w/kT, expressing the potential energy cost of mixing, which is of order w per molecule, relative to the average kinetic energy per molecule which is of order kT. In later chapters we shall show that kT is also on the order of the entropic contribution to the free energy, per molecule.

If $w/kT \gg 1$, as is the case for instance with oil and water at ordinary temperatures, mixing is highly unfavorable, and the two liquids remain segregated. The opposite limit, where $w/kT \ll 1$, corresponds to two liquids, e.g., Benzene and Toluene, that tend to mix with each other in all proportions. The case of partially miscible liquids described in Figure 1.1, corresponds to mixtures that are fully miscible with each other at temperatures above the critical temperature, T_c, but not below this temperature. Below

T_c the two liquids mix uniformly on both sides of the coexistence curve, but not within the two phase region. In the vicinity of the critical point the opposing entropic and energetic preferences balance each other, with kT_c and w being of comparable magnitudes.

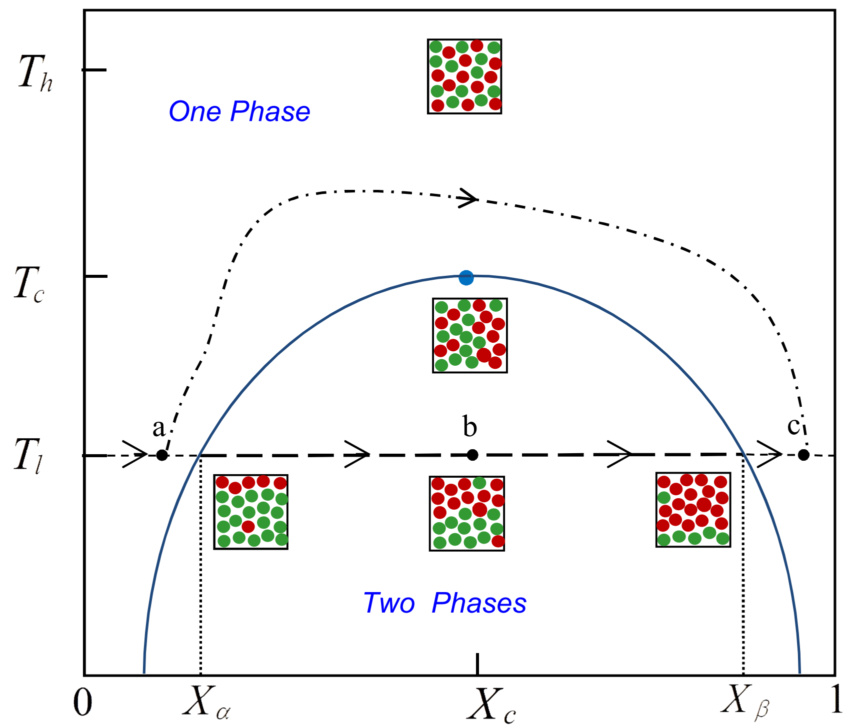

Figure 1.1 Schematic phase diagram of a mixture of two partially miscible liquids. The dashed line denotes a transition from point *a* to *b* through the two phase region, whereas the dash-dotted curve delineates a continuous transition via one phase throughout.

To illustrate the experimental content of the phase diagram in Figure 1.1 let us follow the succession of state changes along the two different trajectories leading from point a to point b. The first trajectory, represented by the horizontal dashed curve, describes an isothermal process taking place at the constant temperature T_l. At point a the mixture consists of a single uniform phase with a small fraction of B molecules randomly dispersed among the majority component A molecules. Upon gradually adding B molecules to the mixture a point is reached, corresponding to mixture composition X_α, where a droplet of a new phase, β, of different composition, X_β, appears in the system. Further addition of B molecules to the mixture enriches their mole fraction in the system, X, yet, as long as the mixture composition is still within the coexistence region, that is $X_\alpha \le X \le X_\beta$, the composition of the two coexisting phases remains unchanged, X_α and X_β. The only quantity that varies with X along the *tie line* – the line that connects points X_α, T_l and X_β, T_l – are the relative amounts of molecules in the two phases, which are related by the *lever rule* $N_\beta / N_\alpha = (X - X_\alpha)/(X_\beta - X)$, (Exercise 1.5). Once X reaches X_β, phase α disappears, and when $X \ge X_\beta$ the solution is again monophasic, but now rich in *B*.

Assuming for simplicity that at any given temperature the volume of the mixture is independent of its composition, then as briefly mentioned above, the equilibrium state of the system corresponds to the minimum value of the Helmholtz free energy $A = E - TS$ for the given temperature and mixture composition. The discontinuous emergence of a new phase upon crossing the coexistence curve, and the subsequent coexistence of the two phases – a process known as *a first order phase transition* –is also characterized by a minimum of A, except that now this function has two minima, corresponding to two different compositions, both exactly equal depth. One minimum corresponds to mixture of composition X_α and the other to X_β. In Figure 1.1 we also note that the difference $\Delta X = X_\beta - X_\alpha$, known as the *miscibility gap*, decreases as T gets lower, reflecting increasingly disparate phase compositions. This behavior indicates the increasing relative importance of the energetic over the entropic tendency as the temperature decreases, consistent with the abovementioned qualitative remark regarding the significance of the ratio w / kT. The familiar case of oil and water, which do not mix at any ordinary temperature, represents the extreme dominance of the energetic factor; their “mixture” may be regarded as a biphasic system with composed one phase of composition $X_{oil} = 1 - X_{water} \approx 0$, and the other with $X_{oil} = 1 - X_{water} \approx 1$.

Within the two-phase region, as the temperature increases the miscibility gap shrinks gradually, vanishing identically at T_c. A familiar characteristic phenomenon that takes place near the critical point is the gradual disappearance of the sharp interface (the "meniscus") separating the two phases at low temperatures, which turns into a blurry mesh of large, branched, interlacing and fluctuating clusters of the two phases. Near the critical point the typical dimension of these clusters is comparable to the wavelength region of visible light, resulting in intense light scattering reflected in a "milky" appearance of the solution, a phenomenon known as the *critical opalescence*. Above the critical point the solution is monophasic again. The second, dash-dotted trajectory in Figure 1.1 which circumvents the critical point reveals that the transition from the A-rich phase (point a) to the B-rich phase (point b) can also be achieved continuously, keeping the system monophasic at all times.

Already in the next chapter we will see that a very similar phase behavior, exhibiting analogous first order transition and critical behavior characterizes another, seemingly rather different, physical phenomenon; the gas-to-liquid phase transition. In later chapters we will see that similar phase behaviors prevails in apparently even more remote systems, such as lattices of paramagnetic solids for instance.

In closing this section it is also appropriate to mention that the not all liquid mixtures obey the phase behavior described in Figure 1.1. There are, for instance, mixtures where mixing is favored by both entropy and energy, water and ethanol is one example, and others that display lower rather than upper critical points, or even both lower and upper critical points. Some of these will be discussed in subsequent chapters.

1.4 Approach and Outlook

Both classical and statistical thermodynamics are complete theories that can be cast in rigorous and elegant mathematical-physical terms. Indeed, many outstanding textbooks are devoted to either one of these theories. Being mainly intended to chemistry majors, this book includes most of the topics that generally appear in classical textbooks of chemical thermodynamic. Our approach is, however, rather “flexible”, in the sense that statistical and molecular-level interpretations are often interwoven in the discussion, sometimes preceding the classical treatment. In Chapter 2, we describe the phase behavior of real gases, and interpret this behavior in terms of the long- and short-ranged interactions between the molecules. Chapter 3 provides the basic thermodynamic terminology, namely, the definition of various types of systems, and the elementary mathematics of state functions and their differentials. The first law of thermodynamics is introduced in Chapter 4, along with examples demonstrating its application to reversible and irreversible processes. Deviations from traditional chemical thermodynamics textbooks appear mainly in Chapters 5, 6 and 7. These chapters are devoted to the introduction and discussion of entropy, the second law of thermodynamics, and the derivation of several elementary statistical thermodynamic concepts, such as the probability distribution in the canonical ensemble. Chapter 5 begins with the fundamental hypothesis of statistical thermodynamics, stating that in the state of equilibrium all the microstates of an isolated system are equally probable. After discussing and demonstrating how the number of microstates of a macroscopic system depend on it volume, energy and the number of particles, we introduce Boltzmann's statistical definition of entropy and its basic properties. The law of increasing entropy is then derived based on the notion that entropy increase is a consequence of removal of constraints, and thus an increase in the number of microstates available to the system. This leads to Clausius inequality in Chapter 6, based on which we arrive (in reversed chronological order) at the original statements of the second law by Clausius and Kelvin in terms of heat engines operation, and then to the classical definition of entropy. In Chapter 7 we derive the Boltzmann probability distribution, introduce the canonical partition function and apply these concepts to several simple systems. The combination of the first and second law of thermodynamics, the definition of free energies and the mathematical consequences of Maxwell relations appear in Chapter 8. The significance of free energies as thermodynamic potentials that determine maximal work, spontaneity, and thermodynamic stability are discussed in Chapter 9. Open systems and the important role of the chemical potential are the subject matter of Chapter 10.

The principles and tools developed in the first ten chapters are applied to various systems and phenomena, starting in Chapter 11 onwards. The topics considered include both classical thermodynamic phenomena such as chemical equilibrium and phase transitions, as well as some less frequently discussed systems such as liquid crystals and solutions of self-assembling molecules. In the spirit of previous chapters, wherever appropriate, a statistical-thermodynamic interpretation supplements the classical treatment. Chapter 11 deals in considerable detail with chemical reactions and their approach to equilibrium, adding the statistical expression of the law of mass action as a quotient of partition functions. Transition state theory and Langmuir adsorption will also be discussed in this chapter. The subject matter of Chapter 12 is phase transitions and equilibria in one component systems. Here, in addition to Clausius-Clapeyron equation, phase diagrams, and Gibbs phase rule, we shall also discuss, albeit briefly, the classical theory of nucleation and the role of dimensionality in phase transitions. Chapter 13 extends the discussion to multi-component systems, in which context we introduce the concept of partial molar properties, analyze liquid-vapor equilibria of ideal and non-ideal mixtures, and discuss the colligative properties of liquid solutions. The phase behavior of non-ideal binary mixture is analyzed using lattice models and mean field theory in Chapter 14, emphasizing the analogy to the phase behavior of real gases and paramagnetic spin systems. Chapter 15 provides an introduction to the properties of ionic solutions, ionic reactions, and the principles of operation of electrochemical cells. Chapters 16 and 17 are concerned with the properties of complex fluids. Polymer solutions and liquid crystals are briefly discussed in Chapter 16, and self-assembling systems, such as micellar solutions, phospholipid membranes, and viruses, in Chapter17.

Incorporated in the main text of each chapter are several solved illustrative problems. In addition, each chapter ends with a list of relevant exercises.

This book is intended for students who participated already in general chemistry and elementary physics courses and are thus familiar with basic chemical and physical concepts, including familiarity with calculus, linear algebra, as well as classical and quantum mechanics. We shall also assume that the reader is familiar with the common physical and thermal units, and the values of the universal constants (e.g., Avogadro's number or Boltzmann's constant). Nevertheless, as we go along, we shall occasionally repeat the definition of a given concept, or the value of a certain constant, wherever such a reminder seems helpful.