Preface

The study of thermodynamics is often limited to classical thermodynamics where minimal laws and concepts lead to a wealth of equations and applications. The resultant equations best describe systems at equilibrium with no temporal or spatial parameters. The equations do, however, often provide accurate descriptions for systems close to equilibrium. . Statistical thermodynamics produces the same equilibrium information starting with the microscopic properties of the atoms or molecules in the system that correlates with the results from macroscopic classical thermodynamics. Because both these disciplines develop a wealth of information from a few starting postulates, e.g., the laws of thermodyamics, they are often introduced as independent disciplines. However, the concepts and techniques developed for these disciplines are extremely useful in many other disciplines. This book is intended to provide an introduction to these disciplines while revealing the connections between them.

Chemical kinetics uses the statistics and probabilities developed for statistical thermodynamics to explain the evolution of a system to equilibrium. Irreversible thermodynamics, which is developed from the equations of classical thermodynamics, centers on distance-dependent forces, and time-dependent fluxes. The force flux equations of irreversible thermodynamics lead are generated from the intensive and extensive variables of classical thermodynamics. These force flux equations lead, in turn, to transport equations such as Fick's first law of diffusion and the Nernst Planck equation for electrochemical transport.

The book illustrates the concepts using some simple examples. These examples provide a physical basis that facilitates understanding of the more complicated systems. Probabilities and averages in statistical thermodynamics are developed for systems with only two or three energy levels. The effects of interactions can be demonstrated effectively with such systems. The same techniques are then applied to continuous systems such as Maxwell Boltzmann velocity and energy distributions. The probability that a molecule has sufficient energy to react is developed using the same techniques.

Some models are developed within different disciplines (chapters) to contrast the different approaches. The Ehrenfest urn (or dog-flea) model, originally used to contrast states and distributions in statistical thermodynamics, is also used to describe the kinetic approach to equilibrium and the stationary state produced by a directional

flow of particles through the system. Bose Einstein statistics are introduced in statistical thermodynamics and then applied in kinetics to calculate the probability that sufficient energy will collect in a bond to rupture it.

The first law of thermodynamics in Chapters 1–3 is expressed as a generic equation that leads easily to specific applications such as adiabatic and isothermal expansions of both ideal and real gases. Entropy is considered from both thermodynamic (Chapter 4) and statistical (Chapter 5) points of view. The statistical chapter includes some information theory. It also presents some paradoxes, which, when explained, help clarify the statistical nature of entropy.

The free energies and their physical significance are presented in Chapter 6 and applied in Chapter 7 for Maxwell's equations and thermodynamic equations of state. These equations are not limited to a study of gases. They are used to develop equations such as those for electrocapillarity and adiabatic demagnetization. The thermodynamics of solutions is developed through partial molar quantities and chemical potential in Chapter 8. Balance of the chemical potential at equilibrium is used to develop solution equations for freezing point depression and osmotic pressure and other equations such as the barometric and Clausius Clapeyron equations. The chemical potential balance equations for ionic systems also lead to equations for the electrochemical potential and the Donnan equilibrium.

Statistical thermodynamics begins with some mathematical background. The most probable distribution is illustrated for systems with two or three particles. The most probable distributions are then developed for some simple systems before the introduction of the method or undetermined multipliers that leads to the Boltzmann factor for molecules with different energies. Bose Einstein and Fermi-Dirac statistics are introduced and contrasted with Boltzmann statistics using some minimal state models.

The use of the Boltzmann factor for energy is illustrated with systems having two or three energy levels to illustrate probabilities and averaging techniques in Chapter 11. The Boltzmann factor in chemical potential is illustrated with enzymes having one or two binding sites. The probabilities and average values for these enzyme systems are compared with the same parameters developed from equilibrium macroscopic binding equilibria.

Probabilities and averaging techniques developed for discrete systems are expanded and used for continuous energy systems. The connection between a sum over Boltzmann factors for two or three energy states and the integrals over Boltzmann factors for a continuum of energy states is emphasized. The equation developed to determine average energy from the partition function for two or three states is shown to give the average energy for the continuum of states once the partition function is known. Phase space is introduced as well as the connection between quantum and classical two-dimensional systems. .The average energy for a dipole in an electric field is determined from the relevant partition function to generate the Langevin equation for the average dipole moment.

Basic interactions are illustrated in Chapter 15 using enzyme/substrate systems. Transfer matrices are introduced to describe larger one-dimensional systems with nearest neighbor operations, and the continuum Debye Huckel theory is

introduced for interactions between a charged surface and ions in solution. The one-dimensional analyses serve as a precursor to more complicated two and three-dimensional systems.

Chemical kinetics merges thermodynamics with time. The Ehrenfest urn model for systems at equilibrium is expanded to show the temporal evolution to equilibrium. The statistics of this temporal evolution are developed using stochastic methods. Bose Einstein statistics are used to establish the number of states in unimolecular reaction theory and the probability that sufficient energy will accumulate in a single bond for reaction. Bose–Einstein statistics are also used to develop probabilities for energy transfer between molecules.

The irreversible thermodynamics in Chapter 16 develops a generalized force flux equation and uses it to develop some illustrative pairings. The velocity of an irreversibly expanding piston, for example, is equivalent to a flux as defined by the generalized equations. Force–flux equations are used to develop transport equations such as Fick's diffusion equation and the Nernst–Planck electrodiffusion equation. The Goldman equation, the constant field solution of the Nernst–Planck equation is developed for both ion and charge fluxes, and these two equations are used as a specific example of the Onsager reciprocal relations. The coupling of vector (diffusion) and scalar (chemical reaction) fluxes is illustrated using the transport of ions through membranes as aion/ionophore complex.

The final chapter includes some simple flow models that open avenues to some of the more active areas of modern thermodynamics, transport, and chemical research. Such models illustrate the overall reduction in entropy in a system held at steady state by a flow. Simple oscillatory systems such as nerve action potentials and oscillating reactions are described.

The book is intended to provide a solid grounding in both the mathematical techniques and the physical concepts they describe. Chapter problems are directed toward developing and using new equations to show that the reader has mastered the techniques developed in the chapters. The text lays the framework to help the student proceed to more advanced treatises on the material.

This book was developed and refined from my courses on thermodynamics, statistical thermodynamics, and kinetics. I am indebted to the students whose perceptive questions and insights helped me find the most effective ways to present the material.