# INTRODUCTION TO
# MODERN THERMODYNAMICS

*Dilip Kondepudi*

Thurman D Kitchin Professor of Chemistry

Wake Forest University

For the memory of Ilya Prigogine,
poet of thermodynamics.

# PREFACE

## What is Modern Thermodynamics?

In almost every aspect of nature, we see irreversible changes. But it is Isaac Newton's mechanical paradigm, the clockwork universe governed by time-reversible laws of mechanics and its grand success in explaining the motion of heavenly bodies, that has dominated our thinking for centuries. During the twentieth century, however, the dominance of the mechanical paradigm slowly began to wane. We now recognize that the paradigm for periodic phenomena in nature is not a 'mechanical clock', such as a pendulum, based on time-reversible laws of mechanics, but a 'thermodynamic clock' based on irreversible processes, such as chemical reactions. The flashing of a firefly, the beating of a heart, and the chirping of a cricket are governed by irreversible processes. Modern thermodynamics is a theory of irreversible processes.

*Classical thermodynamics*, as it was formulated in the nineteenth century by Carnot, Clausius, Joule, Helmholz, Kelvin, Gibbs and others, was a theory of initial and final *states* of a system, not a theory that included the irreversible *processes* that were responsible for the transformation of one state to another. It was a theory confined to systems in thermodynamic equilibrium. That is the way it is still presented in most introductory texts. Thermodynamics is treated as a subject concerned only with equilibrium states. Computations of changes in entropy and other thermodynamic quantities are done only for idealized reversible processes that take place at an infinitely slow rate. For such processes, the change in entropy $\mathrm{d}S = \mathrm{d}Q/T$. Time does not explicitly appear in this formalism: there are no expressions for the rate of change of entropy, for instance. For irreversible processes that take place at a nonzero rate, it is only stated that $\mathrm{d}S > \mathrm{d}Q/T$. The student is left with the impression that thermodynamics only deals with equilibrium states and that irreversible processes are outside its scope. That impression is an inevitable consequence of the way nineteenth-century classical thermodynamics was formulated.

*Modern thermodynamics*, formulated in the twentieth century by Lars Onsager, Theophile De Donder, Ilya Prigogine and others, is different. It is a theory of irreversible processes that very much includes time: it relates entropy, the central concept of thermodynamics, to irreversible processes. In the modern theory, $\mathrm{d}S$ is the change of entropy in a time interval $\mathrm{d}t$. The change in entropy is written as a sum of two terms:

$$dS = d_eS + d_iS$$

in which $d_eS$ is the entropy change due to exchange of energy and matter ($d_eS = dQ/T$ for exchange of heat) and $d_iS$ is the entropy change due to irreversible processes. Both these changes in entropy, $d_eS$ and $d_iS$, are computed using rates at which irreversible processes, such as heat conduction and chemical reactions, occur. Indeed, the rate at which entropy is produced due to irreversible processes, $d_iS/dt$, is clearly identified – and it is always positive, in accord with the second law. Irreversible processes, such as chemical reactions, diffusion and heat conduction that take place in nonequilibrium systems, are described as thermodynamic flows driven by thermodynamic forces; the rate of entropy production $d_iS/dt$ is, in turn, written in terms of the thermodynamic forces and flows. In contrast, in most physical chemistry texts, since classical thermodynamics does not include processes, students are presented with two separate subjects: thermodynamics and kinetics. Each irreversible process, chemical reactions, diffusion and heat conduction, is treated separately in a phenomenological manner without a unifying framework. In the modern view, all these irreversible processes and the ways in which they interact are under one thermodynamic framework. In addition to all the classical thermodynamic variables, the student is also introduced to the concept of rate of entropy production, a quantity of much current interest in the study of nonequilibrium systems.

Modern thermodynamics also gives us a paradigm for the order and self-organization we see in Nature that is different from the clockwork paradigm of mechanics. The self-organization that we see in the formation of beautiful patterns in convecting fluids and in the onset of oscillations and pattern formation in chemical systems are consequences of irreversible processes. The maintenance of order or structure in such systems comes at the expense of entropy production. While it is true that increase of entropy can be associated with increase in disorder and dissipation of usable energy, entropy-producing irreversible processes can yet generate the ordered structures we see in Nature. Such structures, which are created and maintained by irreversible processes, were termed *dissipative structures* by Ilya Prigogine. It is a topic that fascinates students and excites them with the prospect of making new discoveries in the field of thermodynamics.

The dancing Siva or Nataraja on the jacket of the book by Peter Glansdorff and Ilya Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations,* sums up the role of irreversible processes in Nature. In his cosmic dance, Siva carries in one hand a drum, a symbol of creation and order; in the other, he holds fire, a symbol of destruction. So it is with irreversible processes: they create order on the one hand and increase disorder (entropy) on the other hand. I hope this text conveys this enduring view to the student: irreversible processes are creators and destroyers of order.

This text is an offshoot of *Modern Thermodynamics: From Heat Engines to Dissipative Structures,* whichI co-authored with Ilya Prigogine in 1998. It is intended for use in a one-semester course in thermodynamics. It is divided into three parts. Part I, Chapters 1–5, contains the basic formalism of modern thermodynamics. Part II, Chapters 6–11, contains basic applications, covering both equilibrium and nonequilibrium systems. Chapter 11 is a concise introduction to linear nonequilibrium thermodynamics, Onsager reciprocal relations and dissipative structures. Part III contains additional topics that the instructor can include in the course, such as thermodynamics of radiation, small systems and biological systems. The text ends with an introductory chapter on statistical thermodynamics, a topic that is often taught along with thermodynamics.

## Acknowledgements

As student and researcher, I had the privilege of working with Ilya Prigogine, poet of thermodynamics, as his colleagues thought of him. My gratitude for this privilege is more than words can express. I have also had the wonderful opportunity to discuss thermodynamics with Peter Glansdorff, whose knowledge of thermodynamics and its history has greatly enriched me. I profited much by my visits to the Institut Carnot de Bourgogne, University of Burgundy, where I enjoyed the stimulating discussions and warm hospitality of Florence Baras and Malek Mansour. My thanks to Abdou Lachgar, Jed Macosco and Wally Baird for reading some chapters and making suggestions to improve their content and clarity. I am very grateful to Wake Forest University for awarding me Reynolds Leave to complete this book.