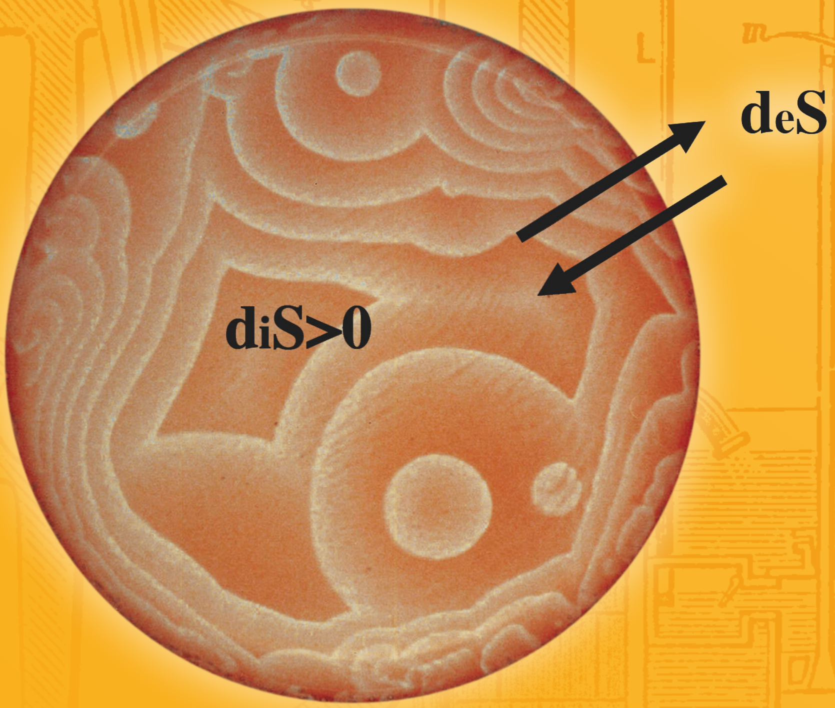
Second Edition

MODERN THERMODYNAMICS

From Heat Engines to Dissipative Structures



Dilip Kondepudi • Ilya Prigogine

with website

WILEY

Modern Thermodynamics

Modern Thermodynamics

From Heat Engines to Dissipative Structures

Second Edition

DILIP KONDEPUDI
Wake Forest University, USA

ILYA PRIGOGINE
Formerly Director, International Solvay Institutes, Belgium

WILEY

This edition first published 2015
© 2015 John Wiley & Sons, Ltd

Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. It is sold on the understanding that the publisher is not engaged in rendering professional services and neither the publisher nor the author shall be liable for damages arising herefrom. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

Library of Congress Cataloging-in-Publication Data

Kondepudi, Dilip, 1952– author.
Modern thermodynamics : from heat engines to dissipative structures / Dilip Kondepudi, Ilya Prigogine. – Second edition.
pages cm
Includes index.
ISBN 978-1-118-37181-7 (pbk.)
1. Thermodynamics. I. Prigogine, I. (Ilya), author. II. Title.
QC311.K66 2015
536′.7–dc23
2014021349

A catalogue record for this book is available from the British Library.

ISBN: 9781118371817

Set in 10/12pt Times by Aptara Inc., New Delhi, India

1 2015

To all who contributed to our knowledge of Dissipative Structures
and
to Shelley and Maryna

Contents

I HISTORICAL ROOTS: FROM HEAT ENGINES TO COSMOLOGY

II EQUILIBRIUM THERMODYNAMICS

III FLUCTUATIONS AND STABILITY

IV LINEAR NONEQUILIBRIUM THERMODYNAMICS

V ORDER THROUGH FLUCTUATIONS

Preface to the Second Edition

The first edition of this book was published in 1998 and we were pleased that it was well received. It has been used in over 25 countries as a text for courses in physics, chemistry and engineering, and it has been translated into French, Italian, Japanese, Portuguese and Russian. Thermodynamics as formulated in the twentieth century, what we chose to call 'Modern Thermodynamics' is a *theory of irreversible processes* in contrast to nineteenth century thermodynamics, which is a *theory of states*. In the latter, thermodynamics is confined to initial and final states, the processes that transform a state are not central to the theory; they are treated as another subject, 'kinetics'. In Modern Thermodynamics, however, entropy-increasing irreversible processes are central to the theory. In it, we find additional tools, such as the rate of entropy production, to characterize and analyze nonequilibrium systems, and new results, such as the Onsager reciprocal relations, that are applicable to the thermoelectric effect, thermal diffusion and other cross-effects.

The context in which thermodynamics is being taught is rapidly changing. Therefore we have added new sections to chapters, which show more applications of the subject. The following is a partial list. In Chapter 2 we have included 'energy flows' in turbines and jet engines, and basics of renewable energies such as solar and wind energy. We have also included a description of the hurricane as a heat engine in Chapter 3. Chapter 11 now has sections on nonequilibrium electromagnetic radiation. In Chapter 19, we have included rates of entropy production in dissipative structures. In response to suggestions by users of this text, we have included a chapter on Statistical Thermodynamics, which makes this text self-contained by the inclusion of derivations of heat capacities of solids and Planck's law of blackbody radiation. Several other changes have been made to improve the presentation of the concepts.

Entropy and entropy-producing irreversible processes are generally thought of as agents of disorder. A central message of this book is that, under far-from-equilibrium conditions, irreversible processes are, in fact, the drivers of self-organization and order we see all around us in Nature. These emergent structures, called *dissipative structures*, are distinct from machines and are a good thermodynamic basis on which we may begin to build a theory of biological organisms. It is an important direction for future developments in thermodynamics. We have included a section on this topic in the final chapter.

Preface to the First Edition
Why Thermodynamics?

I

Since half a century ago, our view of Nature has changed drastically. Classical science emphasized equilibrium and stability. Now we see fluctuations, instability, evolutionary processes on all levels from chemistry and biology to cosmology. Everywhere we observe irreversible processes in which time symmetry is broken. The distinction between reversible and irreversible processes was first introduced in thermodynamics through the concept of 'entropy', the arrow of time, as Arthur Eddington called it. Therefore our new view of Nature leads to an increased interest in thermodynamics. Unfortunately, most introductory texts are limited to the study of equilibrium states, restricting thermodynamics to idealized, infinitely slow reversible processes. The student does not see the relationship between irreversible processes that naturally occur, such as chemical reactions and heat conduction, and the rate of increase of entropy. In this text, we present a modern formulation of thermodynamics in which the relation between the rate of increase of entropy and irreversible processes is made clear from the very outset. Equilibrium remains an interesting field of inquiry but in the present state of science, it appears essential to include irreversible processes as well.

It is the aim of this book to give a readable introduction to present-day thermodynamics, starting with its historical roots as associated with heat engines but including also the thermodynamic description of far-from-equilibrium situations. As is well known today, far-from-equilibrium situations lead to new space–time structures. For this reason the restriction to equilibrium situations hides, in our opinion, some essential features of the behavior of matter and energy. An example is the role of fluctuations. The atomic structure of matter leads to fluctuations. However, at equilibrium or near equilibrium, these fluctuations are inconsequential.

Indeed a characteristic feature of equilibrium thermodynamics is the existence of extremum principles. For isolated systems entropy increases and is therefore maximum at equilibrium. In other situations (such as constant temperature) there exist functions called thermodynamic potentials which are also extrema (that is maximum or minimum) at equilibrium. This has important consequences. A fluctuation that leads to a temporal deviation from equilibrium is followed by a response that brings back the system to the extremum of the thermodynamic potential. The equilibrium world is also a stable world. This is no longer so in far-from-equilibrium situations. Here fluctuations may be amplified by irreversible dissipative processes and lead to new space–time structures which one of us (I. Prigogine) has called 'dissipative structures' to distinguish them from 'equilibrium' structures such as crystals. Therefore distance from equilibrium becomes a parameter somewhat similar to temperature. When we lower the temperature, we go from the gaseous state to a liquid and then a solid. As we shall see, here the variety is even greater. Take the example of chemical reactions. Increasing the distance from equilibrium we may obtain in succession oscillatory reactions, new spatial periodic structures and chaotic situations in which the time behavior becomes so irregular that initially close trajectories diverge exponentially.

One aspect is common to all these nonequilibrium situations, the appearance of long-range coherence. Macroscopically distinct parts become correlated. This is in contrast to equilibrium situations where the range of correlations is determined by short-range intermolecular forces. As a result, situations that are impossible to realize at equilibrium become possible in far-from-equilibrium situations. This leads to important applications in a variety of fields. We can produce new materials in nonequilibrium situations where we escape from the restrictions imposed by the phase rule. Also, nonequilibrium structures appear at all levels in biology. We give some simple examples in Chapters 19 and the postface. It is now generally admitted that biological evolution is the combined result of Darwin's natural selection as well as of self-organization, which results from irreversible processes.

Since Ludwig Boltzmann (1844–1906) introduced a statistical definition of entropy in 1872, entropy is associated with disorder. The increase of entropy is then described as an increase of disorder, as the destruction of any coherence that may be present in the initial state. This has unfortunately led to the view that the consequences of the Second Law are self-evident, are trivial. This is, however, not true even for equilibrium thermodynamics, which leads to highly nontrivial predictions. Anyway, equilibrium thermodynamics covers only a small fraction of our everyday experience. We now understand that we cannot describe Nature around us without an appeal to nonequilibrium situations. The biosphere is maintained in nonequilibrium through the flow of energy coming from the Sun and this flow is itself the result of the nonequilibrium situation of our present state of the universe.

It is true that the information obtained from thermodynamics both for equilibrium and nonequilibrium situations is limited to a few general statements. We have to supplement them by the equation of state at equilibrium or the rate laws, such as chemical reaction rates. Still the information we obtain from thermodynamics is quite valuable precisely because of its generality.

II

Our book is subdivided into five parts. The first, Chapters 1 to 4, deals with the basic principles. The systems considered in thermodynamics are large systems (the number of particles N is a typical Avogadro number). Such systems are described by two types of variables, variables such as pressure or temperature, which are independent of the size of the system and are called 'intensive' variables, and variables such as the total energy, which are proportional to the number of particles ('extensive variables'). Historically thermodynamics started with empirical observations concerning the relation between these variables (e.g. the relation between pressure and volume). This is the main subject of Chapter 1. However, the two conceptual innovations of thermodynamics are the formulation of the 'First Law' expressing conservation of energy (Chapter 2) and of the 'Second Law' introducing entropy (Chapter 3).

Ignis mutat res. Fire transforms matter; fire leads to chemical reactions, to processes such as melting and evaporation. Fire makes fuel burn and release heat. Out of all this common knowledge, nineteenth century science concentrated on the single fact that combustion produces heat and that heat may lead to an increase in volume; as a result, combustion produces work. Fire leads, therefore, to a new kind of machine, the heat engine, the technological innovation on which industrial society has been founded.

What is then the link between 'heat' and 'work'? This question was at the origin of the formulation of the principle of energy conservation. Heat is of the same nature as energy. In the heat engine, heat is transferred into work but energy is conserved.

However, there was more. In 1811 Baron Jean-Joseph Fourier, the Prefect of Isère, won the prize of the French Academy of Sciences for his mathematical description of the propagation of heat in solids. The result stated by Fourier was surprisingly simple and elegant: heat flow is proportional to the gradient of temperature. It is remarkable that this simple law applies to matter, whether its state is solid, liquid or gaseous. Moreover, it remains valid whatever the chemical composition of the body, whether it is iron or gold. It is only the coefficient of proportionality between the heat flow and the gradient of temperature that is specific to each substance.

Fourier's law was the first example describing an irreversible process. There is a privileged direction of time as heat flows according to Fourier's law, from higher to lower temperature. This is in contrast with the laws of Newtonian dynamics in which the past and future play the same role (time enters only in Newton's law through a second derivative, so Newton's law is invariant in respect to time inversion). As already mentioned, it is the Second Law of thermodynamics that expresses the difference between 'reversible' and irreversible processes through the introduction of entropy. Irreversible processes produce entropy.

The history of the two principles of thermodynamics is a most curious one. Born in the middle of technological questions, they acquired rapidly a cosmological status. Let us indeed state the two principles as formulated by Rudolph Clausius (1822–1888) in the year 1865:

> The energy of the universe is constant.
> The entropy of the universe approaches a maximum.

It was the first evolutionary formulation of cosmology. This was a revolutionary statement as the existence of irreversible processes (and therefore of entropy) conflicts with the time-reversible view of dynamics. Of course, classical dynamics has been superseded by quantum theory and relativity. However, this conflict remains because, in both quantum theory and relativity, the basic dynamical laws are time-reversible.

The traditional answer to this question is to emphasize that the systems considered in thermodynamics are so complex (they contain a large number of interacting particles) that we are obliged to introduce approximations. The Second Law of thermodynamics would have its roots in these approximations! Some authors go so far as to state that entropy is only the expression of our ignorance!

Here again the recent extension of thermodynamics to situations far-from-equilibrium is essential. As we mentioned already, irreversible processes lead then to new space–time structures. They therefore play a basic constructive role. No life would be possible without irreversible processes (see Chapter 19). It seems absurd to suggest that life would be the result of our approximations! We can therefore not deny the reality of entropy, the very essence of an arrow of time in nature. We are the children of evolution and not its progenitors.

Questions regarding the relation between entropy and dynamics have received great attention recently but they are far from simple. Not all dynamical processes require the concept of entropy. The motion of the Earth around the Sun is an example in which irreversibility (such as friction due to tides) can be ignored and the motion described by time symmetric equations. However, recent developments in nonlinear dynamics have shown that such systems are exceptions. Most systems exhibit chaos and irreversible behavior. We begin to be able to characterize the dynamical systems for which irreversibility is an essential feature leading to an increase in entropy.

Let us go back to our book. In our presentation a central role is played by entropy production. As we show in Chapter 15, entropy production can be expressed in terms of thermodynamic flows J_i and thermodynamic forces X_i. An example is heat conduction where J_i is the flow of heat and X_i the gradient of temperature. We can now distinguish three stages. At equilibrium both the flows and the forces vanish. This is the domain of traditional thermodynamics. It is covered in Chapters 5 to 11. The reader will find many results familiar from all textbooks on thermodynamics. However, some subjects neglected in most textbooks are treated here. An example is thermodynamic stability theory, which plays an important role both at equilibrium and out from equilibrium. This forms the second part of the book.

Thermodynamic theory of stability and fluctuation, which originated in the work of Gibbs, is the subject of Chapters 12 to 14. Here, first we go through the classical theory of stability, as Gibbs formulated it, which depends on thermodynamic potentials. We then discuss the theory of stability in terms of the modern theory of entropy production, which is more general than the classical theory. This gives us the foundation for the study of stability of nonequilibrium systems discussed in the later part of the book. We then turn to the thermodynamic theory of fluctuations, which has its origin in Einstein's famous formula that relates the probability of a fluctuation to a decrease in entropy. This theory also gives us the basic results that will later lead us to Onsager's reciprocal relations, discussed in Chapter 16.

The fourth part, Chapters 15 to 17, is devoted to the neighborhood of equilibrium, which is defined by linear relations between flows and forces (such as realized in Fourier's law). This is a well-explored field dominated by Onsager's reciprocity relations. Indeed in 1931, Lars Onsager discovered the first general relations in nonequilibrium thermodynamics for the linear, near-equilibrium region. These are the famous 'reciprocal relations'. In qualitative terms, they state that if a force, say 'one' (corresponding, for example, to a temperature gradient), may influence a flux 'two' (for example a diffusion process), then force 'two' (a concentration gradient) will also influence the flux 'one' (the heat flow).

The general nature of Onsager's relations has to be emphasized. It is immaterial, for instance, whether the irreversible processes take place in a gaseous, liquid or solid medium. The reciprocity expressions are valid independently of any microscopic assumptions.

Reciprocal relations have been the first results in the thermodynamics of irreversible processes to indicate that this was not some ill-defined no-man's-land but a worthwhile subject of study whose fertility could be compared with that of equilibrium thermodynamics. Equilibrium thermodynamics was an achievement of the nineteenth century, nonequilibrium thermodynamics was developed in the twentieth century and Onsager's relations mark a crucial point in the shift of interest away from equilibrium toward nonequilbrium.

It is interesting to notice that now the flow of entropy, even close to equilibrium, irreversibility can no longer be identified with the tendency to disorder. We shall give numerous examples in the text, but let us already illustrate this conclusion in a simple situation corresponding to thermal diffusion. We take two boxes connected by a cylinder, we heat one box and cool the other. Inside the box there is a mixture of two gases, say hydrogen and nitrogen. We then observe that, at the steady state, the concentration of hydrogen is higher in one box, of nitrogen in the other. Irreversible processes here cause the flow of heat to produce both disorder ('thermal motion') and order (separation of the two components). We see that a nonequilibrium system may evolve spontaneously to a state of increased complexity. This constructive role of irreversibility becomes ever more striking in far-from-equilibrium situations to which we now turn.

The main novelty is that in far-from-equilibrium situations, which correspond to the third stages of thermodynamics, there is in general no longer any extremum principle (Chapters 18 and 19). As a result, fluctuations are no longer necessarily damped. Stability is no longer the consequence of the general laws of physics. Fluctuations may grow and invade the whole system. As mentioned, we have called 'dissipative structures' these new spatiotemporal organizations, which may emerge in far-from-equilibrium situations. These dissipative structures correspond to a form of supramolecular coherence involving an immense number of molecules. In far-from-equilibrium situations we begin to observe new properties of matter that are hidden at equilibrium.

We already mentioned the constructive role of irreversibility and the appearance of long-range correlations in far-from-equilibrium systems. Let us add also 'unpredictability' because the new nonequilibrium states of matter appear at so-called bifurcation points where the system may in general 'choose' between various states. We are far from the classical description of nature as an automaton.

One often speaks of 'self-organization'. Indeed, as there are generally a multitude of dissipative structures available, molecular fluctuations determine which one will be chosen. We begin to understand the enormous variety of structures we observe in the natural world. Today the notion of dissipative structures and of self-organization appear in a wide range of fields from astrophysics up to human sciences and the economy. We want to quote a recent report to the European Communities due to C.K. Biebracher, G. Nicolis and P. Schuster:

> The maintenance of the organization in nature is not – and cannot be – achieved by central management; order can only be maintained by self-organization. Self-organizing systems allow adaptation to the prevailing environment, i.e., they react to changes in the environment with a thermodynamic response which

> makes the systems extraordinarily flexible and robust against perturbations of the outer conditions. We want to point out the superiority of self-organizing systems over conventional human technology which carefully avoids complexity and hierarchically manages nearly all technical processes. For instance, in synthetic chemistry, different reaction steps are usually carefully separated from each other and contributions from the diffusion of the reactants are avoided by stirring reactors. An entirely new technology will have to be developed to tap the high guidance and regulation potential of self-organizing systems for technical processes. The superiority of self-organizing systems is illustrated by biological systems where complex products can be formed with unsurpassed accuracy, efficiency and speed.
>
> (From C.F. Biebricher, G. Nicolis and P. Schuster, *Self-Organization in the Physico-Chemical and Life Sciences*, 1994, Report on Review Studies, PSS 0396, Commission of the European Communities, Director General for Science, Research and Development)

III

This book is aimed to be an introductory text. No previous familiarity with thermodynamics is assumed. Interested readers are invited to consult more specialized texts. For this reason we have excluded a number of interesting problems often associated with 'extended thermodynamics'. These are the questions that deal with strong gradients or with very long time scales when memory effects have to be included. Every theory is based on idealizations, which have a limited domain of validity. In our presentation the assumption is that at least local quantities such as temperature and pressure take well-defined values. More precisely this is called the 'local equilibrium assumption', which is a reasonable approximation for the phenomena studied in this book.

Science has no final form and is moving away from a static geometrical picture towards a description in which evolution and history plays an essential role. For this new description of nature, thermodynamics is basic. This is the message our book wants to transmit to the reader.

Acknowledgments

This book is the outcome of decades of work. The senior author was a student of Theophile de Donder (1870–1957), the founder of the Brussels School of Thermodynamics. Contrary to the opinion prevalent at that time, de Donder considered that thermodynamics should not be limited to equilibrium situations. He created an active school in Belgium. However, his approach remained isolated. Today the situation has drastically changed. There is a major effort going on in the study of nonequilibrium processes, be it in hydrodynamics, chemistry, optics or biology. The need for an extension of thermodynamics is now universally accepted.

This book is intended to present an introductory text that covers both the traditional aspects of thermodynamics as well as its more recent developments. In the literature there are many texts devoted to classical thermodynamics and others, generally more advanced, specialized in nonequilibrium processes. We believe, however, that from the start the student has to be familiar with both aspects in order to grasp the contrasting behavior of matter at equilibrium and far from equilibrium.

De Donder (seated at the center) with his colleagues on the occasion of his 70th birthday.
First row (seated) L to R: Henri Vanderlinden, Frans van den Dungen, Georgette Schouls, Théophile De Donder, Yvonne De Keghel-Dupont, Georges Lemaître, Théophile Lepage; Second row (standing) L to R: Pierrs Boudoux, Frans van Bergen, Jacques Vorobeitchik, Raymond Defay, Marcel Pourbaix, Robert Debever, Raymond Couurtez, Jean Bosquet, Ilya Prigogine, Jacques Van Mieghem, R. Deladriére, Maurice Nuyens, Jean Pelseneer, Georges Homés, Jules Géhéniau

Our gratitude goes to Professor Paul Glansdorff who co-authored with the senior author, *Thermodynamic Theory of Stability and Fluctuations*.* His outstanding knowledge of the early history of thermodynamics was most helpful to us in writing Chapters 1 to 4. We are also indebted to our colleagues in Brussels: P. Borchmans, G. Dewel, A. Goldbeter, R. Lefever, M.Malek-Mansour, G. Nicolis and D. Walgraef, for numerous suggestions especially in the field of nonequilibrium thermodynamics. We thank Maarten Donkersloot for many helpful comments for improving the presentation of some topics. Thanks to John Pojman and Harry Sweeny for figures and photographs used in Chapter 19. We also thank Isabelle Stengers, the co-author of our book, *Order Out of Chaos*,† to which we refer the reader for a deeper discussion of the historical and philosophical aspects of thermodynamics. Special thanks to Mike Turvey and Claudia Carello for making the junior author aware that the origin of the behavior we see in biological organisms lies in dissipative structures, and for their warm, inexhaustible hospitality.

This book could not have been realized without the continuous support of many institutions. We especially want to thank the Belgian Communanté Française, the International Solvay Institutes in Brussels, the Department of Energy (DOE) of the United States, The Welch Foundation of Texas and the University of Texas at Austin. We would also like to thank Wake Forest University for granting Reynolds Leave for one of us (D.K.) to facilitate the writing of this second edition of the book.

We believe that we are today at a decisive moment in the history of science. At all levels of observation, we see an evolutionary universe, we see fluctuations and instabilities. Thermodynamics is the first science that brought an evolutionary view of Nature. This is in contrast with classical or even quantum mechanics, which presents us with the picture of time reversible and deterministic laws. While there is also no arrow of time and no place for instabilities in equilibrium thermodynamics, this is no more so in nonequilibrium thermodynamics where fluctuations and instabilities play an essential role. Therefore it is important that students already at an early stage become familiar with the role of nonequilibrium processes and learn how thermodynamics describes the transition between the idealized static world of classical physics and the evolving, fluctuating world in which we live.

---

*P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Stability and Fluctuations*, John Wiley & Sons, Inc., New York, London, 1971.

†I. Prigogine and I. Stengers, *Order Out of Chaos*, Bantam Books, New York, 1980; see also *The End of Certitudes*, Free Press, New York, 1997.

Notes for Instructors

The first 11 chapters and Chapter 20 (statistical thermodynamics) are intended for a one-semester introductory undergraduate course on modern thermodynamics for students in physics, chemistry and engineering. Not all chapters are meant to be for all the three branches; the instructor may drop a few chapters to emphasize others. Exercises in each chapter are chosen to illustrate applications of the subject in many areas. In the current research environment, interdisciplinary research is becoming increasingly important. It is therefore important to make the students aware of a wide variety of applications of thermodynamics at an early stage.

Chapters 12 to 19 are meant for an advanced undergraduate or a graduate course in thermodynamics. For these chapters a good knowledge of vector calculus is assumed. These chapters do not include worked examples. The exercises are designed to give the student a deeper understanding of the topics and practical applications.

Throughout the text, the reader is encouraged to use *Mathematica*[*] or *Maple*[†] to do tedious calculations or look at complex physicochemical situations. Appendix 1.2 in the first chapter introduces the reader to the use of *Mathematica*.

[Supplementary Online Material]

Full solutions to exercises, PowerPoint slides of all figures, Data Tables and Answers to Exercises, are available for instructors as PDF files at:

http://sites.google.com/site/modernthermodynamics/

These supplementary website files are password protected. Instructors can obtain the password by sending a request to Professor Kondepudi at dilip@wfu.edu. The above website also contains other useful thermodynamic information related to the book.

---

[*] *Mathematica* is the registered trademark of Wolfram Research Inc.

[†] *Maple* is the registered trademark of Waterloo Maple Inc.

List of Variables

Variables

a	van der Waals constant
a_k	activity of k
A	affinity
A_k	affinity of reaction k
b	van der Waals constant
c_x, $[x]$	concentration of x (mol L^{-1})
c^0	standard state concentration
C	heat capacity
C_{m}	molar heat capacity
$C_{\mathrm{m}p}$	molar heat capacity at constant pressure
$C_{\mathrm{m}V}$	molar heat capacity at constant volume
e	electron charge
E_{a}	activation energy
f	fugacity
F	Faraday constant
F	Helmholtz energy
F_{m}	molar Helmholtz energy
g	acceleration due to gravity
G	Gibbs free energy
G_{m}	molar Gibbs (free) energy
ΔG_{f}	Gibbs (free) energy of formation
ΔG_{f}^0	standard Gibbs energy of formation
ΔG_{r}	Gibbs (free) energy of a reaction
ΔG_{fus}	enthalpy of fusion
ΔG_{vap}	enthalpy of vaporization
$G^{\ddagger}$	transition-state Gibbs energy
$h_{T,p}$	heat of reaction per unit ξ
h	enthalpy density
H	enthalpy
H_{m}	molar enthalpy
$H_{\mathrm{m}k}$	partial molar enthalpy of k
ΔH_{f}	enthalpy of formation
ΔH_{f}^0	standard enthalpy of formation
ΔH_{r}	enthalpy of a reaction
ΔH_{fus}	enthalpy of fusion
ΔH_{vap}	enthalpy of vaporization
$H^{\ddagger}$	transition-state enthalpy
I	electric current
J_k	thermodynamic flow
k	rate constant
k_{B}	Boltzmann constant
$K(T)$	equilibrium constant at temperature T
K_i	Henry's constant of i
m_k	molality, concentration (in moles of solute/kilogram of solvent)
m^0	standard state molality
M_k	molar mass of component k
n_k	concentration (mol m^{-3})
N	molar amount of substance
$\tilde{N}$	number of molecules
N_k	total molar amount of k
N_{A}	Avogadro constant
p^0	standard state pressure
p	total pressure
p_{c}	critical pressure
p_k	partial pressure of k
q	molecular partition function
Q	total partition function
$R_{k\mathrm{f}}$	forward rate of reaction k
$R_{k\mathrm{r}}$	reverse rate of reaction k
$s(x)$	entropy density at x
S	total entropy
S_{m}	molar entropy
$S^{\ddagger}$	transition-state entropy
T	temperature
T_{b}	boiling point
T_{c}	critical temperature
T_{m}	melting point
u	energy density
U	total internal energy
U_{m}	total molar energy
v $(\mathrm{d}\xi/\mathrm{d}t)$	velocity of reaction or rate of conversion
V	total volume

V	voltage or potential difference
V_m	molar volume
V_mc	critical molar volume
$V_{\mathrm{m}k}$	partial molar volume of k
$[x]$, c_x	concentration of x (mol L^{-1})
x_k	mole fraction of k
z_k	ion-number of k
Z	compressibility factor

Greek letters

α	isothermal compressibility
β	Stefan–Boltzmann constant
ϕ	electrical potential
ϕ_k	osmotic coefficient of k
γ	ratio of molar heat capacities
γ	surface tension
γ_k	activity coefficient of
Γ_k	general mobility k in a field
μ_k	chemical potential of k
μ_k^0	standard chemical potential of k
$\mu_\pm$	mean activity coefficient
ν_{jk}	stoichiometric coefficients of reaction k
Π	osmotic pressure
ρ	density
Σ	interfacial area
ξ	extent of reaction
$\mathrm{d}\xi/\mathrm{d}t$ (v)	velocity of reaction or rate of conversion
ξ_k	extent of reaction of reaction k
$\mathrm{d}\xi_k/\mathrm{d}t$ (v_k)	velocity of reaction k or rate of conversion k
$\tau_k\psi$	interaction energy per mole of k due to potential ψ

Part I

Historical Roots: From Heat Engines to Cosmology