ENTROPY AND ENTROPY GENERATION

Understanding Chemical Reactivity

Volume 18

The titles published in this series are listed at the end of this volume.

Entropy and Entropy Generation

Fundamentals and Applications

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PREFACE

Entropy and entropy generation are fundamental quantities. They play essential roles in our understanding of many diverse phenomena ranging from cosmology to biology. Their importance is manifest in areas of immediate practical interest such as engineering as well as in others of a more fundamental flavor such as the origins of macroscopic irreversibility from microscopic reversibility and the source of order and complexity in nature. They also form the basis of most modern formulations of thermodynamics, both equilibrium and nonequilibrium. Today much progress is being made in our understanding of entropy and entropy generation in both fundamental aspects and application to concrete problems. The purpose of this book is to present some of these recent and important results in a manner that not only appeals to the entropy specialist but also makes them accessible to the nonspecialist looking for an overview of the field.

Although entropy has played an essential role in both equilibrium and nonequilibrium thermodynamics since the beginning, there are still many fundamental questions open. One of the most important is how to achieve an irreversible description of macroscopic phenomena when the underlying theory, quantum mechanics, is itself reversible. Kaufmann *et al.* address this question in their article *On Positivity of Rate of Entropy in Quantum-Thermodynamics* and find the answer in terms of quantum thermodynamics by using only restricted macroscopic information. Rateitschak *et al.* also use several concepts developed in information theory and nonlinear dynamics to study the *Entropy of Sequences Generated by Nonlinear Processes: the Logistic Map.* They find that higher-order entropies and the entropy per step are keys to the analysis of nonlinear processes and that quantities related to higher-order entropies can serve as measures of complexity. In his article *Developments in Normal and Gravitational Thermodynamics* Sewell reviews different facets of entropy governing the structure of equilibrium states in normal systems, where it is an extensive quantity, and in gravitational systems, where it is not. In the former case, he provides a precise specification of the conditions under which a set of macroscopic observables yield a complete thermodynamical description of a system. In the latter case, he discusses both non-relativistic systems, which support phases with negative *microcanonical* specific heat, and relativistic ones, involving black holes. In particular, he derives the generalised second law by an argument based exclusively on observable quantities and thus not involving the spurious notion of a black hole entropy.

Entropy generation is intimately related to problems of transport and energy conversion, particularly in the context of nonequilibrium thermodynamics. Indeed, transport phenomena were historically the first treated by nonequilibrium thermodynamics, and the derivation of the transport equations from the expression for the entropy generation illustrates the relation between entropy and transport. Since entropy generation implies dissipation, this relation immediately leads to the subject of the conversion of energy from one form to another. Of course energy can be converted between many other forms than those of heat and transport. Thus, it should come as no surprise that most of the articles of a more applied nature deal with transport and/or energy conversion. It is also understandable that many of the contributors to this volume could be described as thermodynamicists.

The relation between entropy generation and transport is particularly explicit in the form of nonequilibrium thermodynamics known as extended irreversible thermodynamics, although it is not restricted to transport problems. In *Extended Irreversible Thermodynamics: Statements and Prospects* Lebon *et al.* review the main statements of the theory, treat several examples, and discuss many of the questions which still remain to be resolved. J. Camacho *(Extended Thermodynamics and Taylor Dispersion)* uses extended irreversible thermodynamics to treat Taylor dispersion, a problem which is applicable to contaminant dispersion in rivers, for example. Woods treats *Higher Order Transport* and concludes that the constitutive equations can not be deduced from the condition that the entropy production be positive semidefinite. Muschik *et al.* develop the *Mesoscopic Theory of Liquid Crystals.*

Problems in energy conversion are especially amenable to treatment by finite-time thermodynamics. This form of nonequilibrium thermodynamics differs from most other formulations in that the irreversibilities are described macroscopically. Its concepts have been used to improve the performance of simulated annealing algorithms; the optimal path is the one producing least entropy. All this is discussed by Andresen in *Finite-time Thermodynamics and Simulated Annealing.* Biological systems may well be the ultimate energy conversion machines. In *Entropy, Information and Biological Materials* Cole argues that energy and order rejected by living entities at one level may be accepted by others at another lower level. He offers the hypothesis that information is conserved in the universe and that information lost during expansion after the "big bang" can be countered by a local increase in information by formation of more complex atomic/molecular arrangements which will show characteristics of elementary biological materials. Symmetry properties are of principal importance for energy conversion. Shiner and Sieniutycz demonstrate the validity of

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a *Phenomenological Macroscopic Symmetry in Dissipative Nonlinear Systems* for a broad class of systems with arbitrary nonlinearities far from equilibrium.

Transport and energy conversion are often important aspects of problems of practical as well as fundamental importance. Cole discusses *The Provision of Global Energy* with emphasis on maximum possible work transfers within the restrictions of thermodynamics. The basic energy sources available – solar (including direct radiation, biomass, wind and waves), gravitational, geothermal and nuclear – and their suitability for global or for local applications are treated. This work provides a rational basis for the development of global energy policies. The conversion of solar energy to electricity in particular plays a prominent role in planning for the future provision of energy. In the direct conversion of radiant energy to electricity by semiconductor solar cells, it is found that the open-circuit voltage is less than the semiconductor energy gap by precisely the Carnot factor. In *Multiple Source Photovoltaics* Landsberg *et al.* show that this apparently fundamental feature is lost as soon as the usual single pump is replaced by several pumping sources. They also obtain other new results, including a novel form of the solar cell equation. The interrelations between transport, energy conversion and entropy generation become even more explicit in the article by Ratkje and Hafskjold, *Coupled Transport* of *Heat and Mass. Theory and Applications,* and Shiner *et al.* treat electrochemical systems in *Lagrangian and Network Formulations of Nonlinear Electrochemical Systems*.

The contributors to this volume were asked to either prepare a review of their recent work or present their most important new results in a manner which would make their contributions accessible not only to thermodynamicists and other specialists in their respective fields but also to other workers in the natural sciences. Each contribution was reviewed by at least two experts and the contributions revised accordingly. With this procedure it is hoped that a common failing of many multi-author books, namely that the level and quality of the individual contributions are very variable, has been avoided.

The contributions show that the volume promises to be of value to researchers both in academia and in industry, and to persons involved in the whole range of thermodynamics, from fundamentals to application. We hope that it will appeal to scientists from all disciplines – physicists, chemists, biologists – and engineers interested in fundamentals and applications of thermodynamics.

This book arose out of a workshop held in Spåtind, Norway in April 1994 and organized under the auspices of a research network of thermodynamicists supported by Human Capital and Mobility Contract No. CHRX-

Ct.92-0007 from the European Union. Some of the contributions were presented in preliminary form there, but others were solicited from outside the network. The concept of the book was further refined at the Gordon Research Conference on *Modern Developments in Thermodynamics,* held in Irsee, Germany in October of the same year. The contributors express their gratitude to the European Union as well as to the Gordon Research Conferences. Appreciation is also due to the Office of Naval Research and the International Science Foundation for their support of the Gordon Research Conference. Finally, as editor of this volume I am indebted to S.R. Berry, M. Davison, S. Sieniutycz, and L.C. Woods for their efforts in the realization of this work.

Bern, February 1996 J.S. Shiner