**Book review**

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Demirel, Y., Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical and Biological Systems

The book is, in fact, a volume for readers primarily interested in life sciences (physiology, biology, medicine, etc.) or related fields, where insight is more important than exactness, at least initially. A broad audience has been assumed for the book by the publisher: graduate students and researchers working in the areas of physics, chemistry, biology, and engineering. Yet, especially in teaching students of physics and theoretical chemistry, the use of more rigorous treatments such as the classical textbook by De Groot and Mazur will be necessary. The book contains introductory information on several new growing applied branches of non-equilibrium thermodynamics (for example: applications of entropy and the second law in chemical engineering, exergy balancing, thermoeconomics, coupling systems theory, bioenergetics in mitochondria, active transport, etc.). The basic intention of the author seems to be to bring together many important developments in applied irreversible thermodynamics of recent years, and thereby render them accessible to a broad audience of beginners. The book extends the range of applied topics covered in earlier treatments by including some contemporary evergreen problems of application nature.

The goals and contents of the book along with basic historical aspects of the discipline are defined in the Preface. The content is organized reasonably. Chapter 1 is on equilibrium thermodynamics. It describes basic definitions, reversible and irreversible processes, equilibrium thermodynamic laws, entropy and entropy production, the Gibbs equation, equations of state, and thermodynamic potentials. In Sec. 5 of this chapter the important notion of chemical affinity $A$ is first defined, subject to the convention that the affinity is positive when the reaction proceeds from left to right. The brief review of classical issues is done well, with apt description of roles played by external part $d_eS$ and internal part $d_iS$ in the balance of total entropy $dS$. Chapter 2 is on transport and rate processes. It introduces non-equilibrium systems and outlines such issues as: kinetic approach, transport phenomena, the Maxwell-Stefan equations, transport coefficients, electric charge flow, the thermal relaxation theory, preliminaries on chemical reactions and coupled processes. The subsequent sections of Chapter 3 discuss local thermodynamic equilibrium, the second law of
thermodynamics, phenomenological equations, dissipation function, and variation of entropy production. Chemical affinity $A$ appears in Sec. 3 (again satisfying the convention that $A$ is positive when the reaction rate $J$ is positive), and the limiting linear formulae adduced here are consistent with this convention. This chapter serves to prepare the reader to understand why the proportionality between $A$ and the reaction rate $J$ can be assumed in linear descriptions. In discussing this particular chapter, it seems especially appropriate to recall that the elementary nature of the book does not release its author from the satisfaction of a certain degree of rigor and completeness. Unfortunately, this text often resembles careless lecture notes. In the text devoted to the local equilibrium assumption, no discussion on the effect of time (spatial) scales is included, and the role of Knudsen’s number is not considered. The notion of dissipation function is identified in Sec. 5 (modulo to $T$) with that of the entropy production. In general, no sharp distinction is made between bilinear structures describing entropy production and quadratic functions of dissipation.

Chapter 4 is on field description of continua where partial differential equations are suitable in description. Basic equations are obtained by the standard procedure that combines the conservation laws for mass, energy and momentum into the internal energy equation. Next, with the help of the Gibbs equation, an equation of entropy balance is found with the entropy production term. In Eq. (63) of this chapter the chemical affinity $A$ appears to be defined as in earlier sections. However, in an unnumbered equation above Eq. (63) the chemical reaction term is obtained with an incorrect sign, and this error is repeated in next equations (64) and (65). Thus, rather unexpectedly, the chemical term appears in the entropy generation equations (65) and (69) with a negative sign, in contradiction with the second law. While this error can be decoded by a careful reader, he can become truly perplexed by the change of the affinity definition within the same chapter in Eq. (73). As this change is introduced without a reasoning (compare Eqs. (63) and (73) in Chapter 4), a reader could understand this procedure as an artificial way to secure the second law. In fact, there is a reason to suspect that the author loses his control over this text. Indeed, the next two equations, (77) and (78), are in contradiction, or, speaking in different terms, the first of them can be correct only for the affinity definition (63), whereas the second – only for the affinity definition (73). Chapter 5 deals with (non-equilibrium) entropy and exergy. Principles of the exergy balance and the Gouy-Stodola law are recalled. Approximate equations are given for exergies of some systems. Preliminary information is given about the role of the exergy concept in biological systems, calculation of exergy efficiencies and ecological applications of exergy, to characterise depletion of natural resources.

Chapter 6 presents examples with convection and heat flow in ducts and packed systems, where minimizing the entropy generation leads to information about the optimum size of equipment. In particular, heat and mass exchangers are analyzed, and Tondeur’s and Kvaalen’s “principle of equipartition of the entropy production” or related “equipartition of forces” (uniformly distributed entropy generation rate or uniform forces) is discussed in some detail. The equipartition of forces is explained rather vaguely. This is not a surprise because no such thing exists, except for some strictly linear systems. In fact, as proved by Eqs. (90) and (95) of the chapter, even for
the simple Fourier’s heat conduction it is rather \( \text{grad}(\ln T) \) than \( \text{grad} T \) itself that is uniform along an optimal path. The reasoning is based on Eq. (92) of the chapter, allegedly the Euler-Lagrange equation of the variational problem. In fact, however, the incorrect Eq. (92) has very little in common with the Euler-Lagrange equation, although the final result (95) is correct. Summing up, one must be contented that at least the final result of the analysis (based on the Tondeur’s and Kvaalen’s publication [54]) is presented in a correct form. In an attempt to extend their “equipartition principle” to non-linear processes, chemical reactions, reacting flows and separation operations are next analyzed following a group of sloppy or incorrect approaches in the group of papers by Sauar and Ratkje-Kjelstrup and their coworkers, refs. [33,39,40]. As the matter is of a general nature, it is briefly discussed below.

What is true in the linear case (Tondeur’s and Kvaalen’s equipartition) is not in non-linear ones. Extensions of “equipartitions of forces” to non-linear systems are based on two incorrect assumptions, of which the first is at best a doubtful approximation and the second is simply wrong. The first assumption rests on the false supposition that in any state region the reaction rate \( J \) can be uniquely linked with the chemical affinity \( A \) by a formula of the type \( J = f(A) \). In fact, no such relation does exist for chemical kinetics far from equilibrium, and formulae can be found in other parts of the book, e.g. Eq. (75) of Chapter 3, which prove that this is impossible. Stemming from the kinetic mass action law, Eq. (75) of Chapter 3 links \( J \) with \( A \) in a non-linear way, \( J = r^f(1 - \exp(-A/RT)) \), where the forward reaction rate \( r^f \) is not a constant but a function of all concentrations, i.e., \( r^f = r^f(C) \). Therefore, only when the reaction is very close to equilibrium and the approximation \( r^f(C) = r^f(C_{eq}) \) is allowed, can the forward rate \( r^f \) be treated as a constant and can the reaction rate \( J \) be a unique function of the affinity \( A \). In conclusion, any affinity-based optimization of chemical reactions can consistently be organized only in state regions close to equilibrium. This conclusion renders questionable all optimizations of chemical reactions far from equilibrium if these are based on the formula \( J = L(X)X \), where \( X = A \), [Eq. (128) of Chapter 6 and its consequences]. In particular, the validity of Eq. (130) of Chapter (6), \( X + J(dx/dJ) = \text{constant} \), which describes the Lagrange multiplier \( \lambda \) and the others that follow next, is debatable. Unfortunately, there is also a second assumption involved in analyses of this sort, the (unfounded) constancy of Lagrange multiplier \( \lambda \), accepted without any proof in the original works cited above, refs. [33,39,40], which the author uncritically repeats. It may be shown that the assumption of a constant \( \lambda \) ceases to be valid in non-linear chemical regimes. This is, in fact, not a big surprise for someone who knows that Lagrange multipliers are generally functions of independent coordinates and may be constant only in special cases. In the considered problem, the change of the Lagrange multiplier \( \lambda \) with coordinate \( x \) (which should not be confused with the thermodynamic force \( X \)) is described by the extremum condition of a Lagrange functional with respect to the reaction progress variable \( \zeta \). When the Onsager description of dissipation is applied, the extremum conditions of the entropy dissipation functional with respect to the reaction progress variable \( \zeta \) and the Lagrange multiplier \( \lambda \) can be given a canonical form based on the thermodynamic Hamiltonian function \( H(J, \zeta, \lambda) \equiv \Phi(J, C(\zeta)) + \Psi(C(\zeta)) + \lambda J \) which contains the kinetic (flux dependent) term, static term (allowing
a constant $C \cong C_{eq}$ for states close to equilibrium) and the term related to the constraint. The rate $J$ is the control variable (in general it is a rate vector that includes rates of all chemical reactions and the rate of external heat exchange as the last coordinate). In accordance with the Pontryagin principle, the extremum condition of the dissipation functional with respect to $J$ as a control corresponds with the extremum of $H$ with respect to $J$. In the stationary optimum case the condition $\partial H/\partial J = 0$ holds, which proves that the Lagrange variable $\lambda$ equals the affinity $A$ modulo, a constant multiplier. Thus the constancy of the affinity $A$ cannot be verified by any procedure that assumes a constant $\lambda$ (what is assumed cannot be proven). This fact was largely ignored both in the previous works [33,39,40] and in the present book where the affinity $A$ appears constant whenever $\lambda$ is fixed at a constant level by assumption, and this is why a uniform profile of $A$ was numerically “verified” [40]. But the true nature of $\lambda$ and $A$ should follow from the optimization solution. However, from the canonical equations for variables $\zeta$ and $\lambda$ one can easily conclude that (except of the linear case with a constant chemical conductance) the reaction progress $\zeta$ induces the changes in the Lagrange multiplier $\lambda$ or the changes in the reaction affinity. In effect, the affinity profile $A(x)$ ceases to be uniform whenever the dissipation integrand is concentration dependent, which is the case in non-linear chemical dynamics. Thus, $\lambda$ or $A$ can be constant in rare linear models, and cannot when passing to non-linear descriptions. A criterion for constancy of $\lambda$ is not taken into consideration in the book and the source works cited, rather a constant $\lambda$ is assumed without any prior tests.

In Chapter 7 thermoeconomics is introduced. A distinction between purely thermodynamic optimization and approaches leading to thermoeconomic optima is analysed. Availability and exergy destruction number are discussed in the context of exhaustion of non-renewable resources and ecological costs. Equipartition and optimization are treated following the techniques similar to those applied in Chapter 6. In Chapter 8 molecular diffusion phenomena are treated with the help of the Maxwell-Stefan frictional model. Next, diffusion in non-electrolyte systems is compared with diffusion in electrolyte systems. For those latter, the role of chemical potentials of electroneutral combinations and the Gibbs equation written in terms of electrically neutral species is pointed out. Irreversible processes in electrolytes are described in terms of electrochemical affinities along with diffusion and conductivity coefficients, transference numbers and corresponding mobilities. In Chapter 9 coupled heat and mass transfer is treated along with thermal diffusion (Soret effect) and the Dufour effect of the heat flow caused by a concentration gradient. Heat of transport, entropy of transport and degree of coupling are defined.

Chapter 10 deals with thermodynamic aspects of chemical and biochemical reactions. Again, within the same chapter, some formulae are correct for chemical affinities defined positively [e.g., Eqs. (1), (12), (13)], and the others – for affinities defined as negative quantities [e.g., Eqs. (2) and (3)]. Still they are formulae in which both conventions of $A$ must be used to make them correct, see, e.g., Eqs. (10) and (42) supplemented by the affinity definition below that is inconsistent with it. Chemical dissipation, Michaelis-Menten kinetics and coupled chemical reactions can still run! In Chapter 11 the classical information on membrane transport is based primarily on
the research of Katchalsky and his coworkers. Passive transport, electrokinetic effects, facilitated transport and active transport are reviewed. Chapter 12 brings valuable newer information on thermodynamics and biological systems. It describes mitochondria and related bioenergetics, oxidative phosphorylation and identification of proper pathways in a vicinity of reference steady states far from equilibrium. Further information is provided on multiple inflection points, coupling in mitochondria, linear approximations, coupling variation and thermodynamic regulation in bioenergetics. Considerable text is devoted to facilitated transport, active transport, molecular evolution and molecular machines. A classical evolution criterium is linked with Tellegen’s theorem for network systems. Chapter 13 discusses some other thermodynamic approaches amongst which are network approach with bond graph, mosaic thermodynamics and rational thermodynamics. Chapter 14 is devoted to extended non-equilibrium thermodynamics, yet the thermodynamic stability conditions it adduces are classical. It also outlines ordering in physical and biological structures and bifurcations in Bernard cells. Extended non-equilibrium thermodynamics in the commonly understood sense, i.e., as the theory based on the Gibbs equation extended by the presence of dissipative fluxes, is considered in the last section of the chapter.

In recent decades thermodynamics has attained a remarkable level of competence in advanced design of practical devices, complex energy and industrial systems, bioprocesses, chemical reactors, reacting flows, separations and even (recently) flying objects. One of the key concepts of TIP is that it can take account of the dynamic behavior of systems and pathwise constraints of processes. Some recent developments in TIP aim at extending the range of its application to far-from equilibrium regimes (extended thermodynamics, only briefly discussed in the book) by abandoning assumption of local equilibrium. Consequently problems in TIP are formulated as typical or extended macroscopic problems of thermodynamic networks or fields. New developments consider also various aspects of material structure, in particular polymeric fluids and rheological bodies described by general rheological equations of state and bodies with continuous spectra. Still other developments stress similarities of the field with the theory of bifurcating and chaotic systems. In the last decade, an intense activity has been modifying and improving our understanding of statistical mechanics and thermodynamics, and extending its applicability to small and non-extensive systems, systems exhibiting violations of the standard ergodic and mixing properties, or other anomalies. In fact, none of these newer topics is discussed in the book in question. The book represents a traditional approach; it describes phenomena at the macroscopic level leaving out some recent evergreen problems such as catastrophes, statistical disequilibria and chaos, although many applications can be found there as well. In spite of all its shortcomings, the book reviewed is one of a few books on non-equilibrium phenomena that penetrates the subject in a simple way, yet gives a broad overview of contemporary applications.

Nonequilibrium Thermodynamics is the one of the rare books to provide a vast treatment, bringing together many advances in applications. The treatment is largely self-contained and provides a unified perspective on those applied problems which are beyond the realm of conventional analytical and computational techniques of
engineering sciences. The book summarizes these new applications as tools that can be used in thermodynamically optimal designs and in understanding diverse phenomena in natural processes. As scientific rigor is not a basic virtue of this book and the number of errors, inconsistencies and typos is remarkable, *Nonequilibrium Thermodynamics* is not free of flaws, but is nevertheless an ambitious, inspiring and timely book, a treatise giving a broad overview of nontrivial applications available to date only in research papers, a book which may be read by researchers and students interested in concise presentation of the theory and exhaustive treatment of applications, including those in biological systems. The book is attractively printed. As this is book of considerable didactic quality, in spite of its shortcomings it is worth reading.

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