Book Review

Non-equilibrium Thermodynamics for Engineers.

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272 pages.

All real industrial and living systems involve the transport of matter (mass, volume, species…) and of energy (heat, electric charge, kinetic energy, momentum…) with or without the presence of chemical or biochemical reactions. All these systems are out of equilibrium.

Classical equilibrium thermodynamics provides information on the limiting behavior of such systems, but not on their dynamics or kinetics. The usual engineering description of transport phenomena is often limited to a single entity, mass or heat or momentum or electric charge, and provides no general and consistent framework when such phenomena occur simultaneously and are coupled, *a fortiori* in the presence of chemical reactions.

Non-Equilibrium Thermodynamics (NET), also designated as Thermodynamics of Irreversible Processes (TIP), fills this gap. It, thus, addresses the domains usually covered by engineers but in a generalized fashion and with somewhat different tools which complete and enrich the engineering approach.

This book makes the link between the two domains. It can be used as an introduction to non-equilibrium thermodynamics, as a book of applications and exercises in chemical and mechanical engineering, but also for certain parts, as an advanced treatise with original features and with some more difficult aspects. Although the presentation is based on thermodynamic science, its focus is actually on energy efficiency in transport and reaction processes. Thus, this book rightly targets chemical and mechanical engineers.

The central concept of NET or TIP is **entropy production**, and a large part of the book is devoted to establishing usable expressions for it in different processes. Entropy production is a thermodynamic measure of waste, of inefficiency, of irreversibility, of lost work, of exergy destruction, of energy dissipation and is ,therefore, of interest *per se* in evaluating a process and identifying the potentials for improving it. It can also be used as an objective function in a thermodynamic process optimization.

The overall entropy production in a process can be obtained by conventional means, i.e. making an entropy balance at the boundaries of the process. However, this approach gives no or little information about the nature, reasons and location of entropy production **inside** the process. NET on the other hand does provide such information, because the detailed expressions for entropy production lead to consistent and general relations between the coupled fluxes and forces at play in complex processes, providing keys to understanding and analyzing them.

The approach of this book follows the classical line of linear NET, consisting of the following basic steps:

- Establish general expressions for the entropy production
- Use such expressions to identify the so-called conjuguate driving forces and fluxes
- Write linear phenomenological relations between the vector of fluxes and the vector of driving forces through a set of phenomenological coefficients
- Establish properties of these coefficients and evaluate them
- Evaluate quantitatively the entropy production
- Seek process configurations and/or operating conditions which minimize entropy production.

Chapter 1 sets the background with a recollection of Onsager's basic equations: the second law and the positivity of entropy production, linear flux-force relations, the reciprocity relations of the phenomenological coefficients.

Chapter 2 makes the link between this formalism and engineering approaches. It shows how the generalized Onsager flux-force relations include and extend the usual "engineering" flux-gradient transport equations and how the industrial notion of lost work relates to the formalism of the first and second law.

Chapter 3 derives detailed expressions of the entropy production using mass and energy conservation and the local Gibbs equations in systems without flow where diffusion, electric conduction, and chemical reactions are taking place along a single space coordinate. Conjuguate fluxes and forces are identified. Numerous examples and exercises illustrate the approach and some specific aspects, sometimes delicate like the reference frames of the fluxes, are discussed in detail.

Chapter 4 introduces the classical "linear" flux-force relations and the corresponding matrix of phenomenological coefficients (either as conductivities or as resistivities). The relations between these coefficients are discussed, in particular, Onsager's reciprocity relations.

The coupling effects expressed by these formulations are illustrated, for example, for simultaneous transfer of heat and mass (Dufour and Soret effects), transport of heat and electric charge (Peltier and Seebeck effects), transport of mass and charge (electrochemical couplings), transport of volume and charge (charged membrane transport).

Chapter 5 is devoted to multicomponent diffusion. The Maxwell-Stefan equations are re-derived in the framework of NET. Their extension to different reference frames is discussed and their extension to non-isothermal situations presented.

Chapter 6 deals with reactive systems under viscous flow. It is shown how the Navier-Stokes equations relate to the entropy production and how the conjuguate fluxes and forces are derived in the case of simultaneous chemical reactions, heat transfer, and viscous dissipation. This approach is then illustrated with a plug-flow tubular reactor at steady-state.

Chapter 7 shows how rational rate laws for chemical reactions can be derived from NET by considering it as a transport process along a reaction coordinate and that this approach is coherent with a mass-action equilibrium relation.

Chapter 8 deals with the analysis of the industrial example of alumina electrolysis, a case where the energy consumption is crucial. This example illustrates a "mapping" of the location and nature of lost work (exergy destruction) in the process (thermal, electric, reactive) which allows one to determine where improvements in energy usage can be made.

Chapters 9 and 10 deal with thermodynamic optimization through NET. Thermodynamic optimization can be viewed as minimizing entropy production under specifications and constraints, which in turn can be viewed as an optimal control problem, leading to an optimal distribution of entropy production along the process path. This problem is illustrated with ideal gas expansion, with a simple heat exchanger (Chap 9), with a plug-flow reactor, and with a distillation column (Chap 10).

Who should be interested in this book

Engineers concerned with process analysis and optimization, who look for more insight into the fundamentals.

Researchers concerned with the link between thermodynamics and engineering.

What the book is about

1. Providing an introduction to the purpose of non-equilibrium thermodynamics and a general scientific and historic background of the underlying linear theory. The reader does not need to have a background in the specific field.
2. Establishing in a comprehensive and pedagogic way the entropy production, flux-force relations, and energy efficiency analysis of a large number of situations dealing with the simultaneous transport of heat, mass, and charge in the presence or absence of chemical reactions.
3. Showing how this approach may be used in certain optimization problems.
4. Providing a concrete and practical approach through a large variety of examples.

What the book touches on

1. The reader is assumed to be familiar with the basic variables and concepts of thermodynamics and with the basics of engineering (balance equations). However, a number of these are introduced the text as well or treated in the Appendices. In particular, the balance equations are developed thoroughly in Appendix A1, and the chemical potential, partial molar quantities, Gibbs-Duhem equation are introduced in Appendices A2 and A3.
2. Exergy analysis: exergy destruction is akin to entropy production. With a slight change in language and notation, this whole approach might have been called an exergy analysis. The authors chose not to adopt the exergy language, perhaps because the latter is often associated with macroscopic, engineering type analysis. However, the link between the two notions is properly established.

What the book is not about

1. It is not about the fundamental theory of NET, which is to be found in the original publications of Onsager or for example in De Groot and Mazur's book.
2. It is not about "extended" non-equilibrium thermodynamics: one of the essential premises of the approach is local (microscopic) equilibrium. It does not cover very fast transfers under extremely high gradients, for example, where the basic thermodynamic quantities, such as temperature, need to be redefined.
3. It is not about "far-from-equilibrium" thermodynamics: the description contains equilibrium as a limiting case, as the end-point of a spontaneous evolution. Prigogine qualified this as being "on the equilibrium branch", as opposed to regimes that may arise beyond the first instability.

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