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Edited by Bhavik R. Bakshi, Timothy G. Gutowski and Dusan P. Sekulić
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Introduction

Bhavik R. Bakshi, Timothy G. Gutowski, and Dušan P. Sekulić

1 Resources and Sustainability

This book is about the application of thermodynamic thinking to those new areas of study that are concerned with the human use of resources and the development of a sustainable society. Exactly what a sustainable society is, is a highly debated topic, somewhat subject to personal value preferences. However, what is not sustainable is easier to identify. For example, in Jared Diamond's popular book, *Collapse* [1], he identified a variety of ancient and modern societies that failed. No one would dispute this claim. Although the reasons for these failures were complex, an important and common contributing factor was an inability to manage Earth's resources and thereby meet the needs of the society. For example, the inhabitants of Easter Island apparently became consumed with building giant stone statues (called *moai*), which required large timbers for their construction and for their transport from the quarry to the installation site. Apparently this building process, along with the destruction of the seeds wrought by the Polynesian rats, led to the destruction of most, if not all, of their trees. One result from this was a loss of the primary building material for their canoes. Because most fish were some distance from the shore, a lack of building materials for canoes meant fewer fish to eat and the inability to move to other islands. This desperate situation ultimately resulted in the islanders resorting to cannibalism. Not all resource-accounting problems are as dramatic or as straightforward as just outlined (including the full accounting for Easter Island). But it is well known that a lack of resources to sustain life and to allow the members of society to prosper will lead to severe difficulties for society, and even collapse. Particular resources of concern would include building materials, food resources, water, and energy sources, including biomass, fossil fuels, geothermal heat, and sunlight. In addition, ecological systems can provide many useful services needed to support life. Examples are plants removing carbon dioxide from the atmosphere by photosynthesis, vegetation preventing soil erosion and thereby maintaining clean water, limestone soils buffering acidic deposits, and many, many others [2]. Each of these resources and processes can be analyzed as thermodynamic systems. In particular, the transformations required to provide ecosystem services or to produce or convert (or both) material resources to other forms can all be analyzed by

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thermodynamics [3–6]. Thermodynamics therefore should be an important contributor to any new science that focuses on resource use.

Thermodynamics is a well-established phenomenological discipline used by scientists and engineers to describe and generalize empirical evidence needed for predicting the behavior of physical systems exposed to material and thermal energy interactions with their surroundings. As such, and though still under development, thermodynamics has "aged" through a sequence of phases. These would include a number of steps through which all new sciences would have to advance, for example: (1) observation and data collection, (2) data classification and quantification, (3) simplification and abstraction, (4) symbolic representation, (5) symbolic manipulation, and finally, (6) prediction and verification. Each of these formal steps is needed to enhance knowledge and understanding. Furthermore, they are repeated as new insights are obtained. In this book we focus on the application of thermodynamics to much "younger" areas of study. These would include, for example, large natural or manmade systems, such as those that would be considered in the fields of ecology and industrial ecology and that play a central role in our sustainability. These newer areas of study, in particular their application to large complex systems, such as large, integrated ecological, economic, industrial systems (i.e., systems that combine human activities with ecosystems), cannot yet make the claim of being predictive sciences. The reasons for this have to do with both the age and the complexity of the areas of study, as well as the ambition of the models. Systems of interest to industrial ecologists involve interactions among ecological, economic, industrial, and societal processes, making them highly multidisciplinary in nature. Thermodynamics can be used to analyze these systems, however, provided that we (1) very clearly define the system under study and (2) focus primarily on material and energy transformations.

Although such an approach cannot capture all the multidisciplinary aspects of the problem, it can provide tremendous insight into those aspects that have to do with resource use and transformation. Many other aspects, such as those involving human valuation and societal and cultural preferences, may also benefit from the results of thermodynamic analysis. However, thermodynamics by itself cannot capture these aspects.

The early history of thermodynamics was concerned with the problem of how to obtain work from heat. This work developed the seminal ideas that led to workable versions of the first and second laws of thermodynamics [7]. Much of this work was carried out coincidentally with the development of the steam engine, which provided many experimental opportunities. Further development of thermodynamics refined these laws and expanded beyond primarily thermal interactions with application to new systems and areas of study. This led to many new and useful concepts such as Gibb's free energy, available energy, and many others. Although this work continues, the application of thermodynamics to mechanical systems, chemical systems, and simple ecological systems is now well established [5, 6, 8–13]. It is now clear that thermodynamics deals with a very broad class of phenomena involving the so-called well-defined *thermodynamic systems* and obeying a limited number of *natural (thermodynamic) laws*. This success has encouraged the widespread application of thermodynamic thinking to many different areas including economic theory [14–19] and social systems [20], as well as applications to systems as small as one particle or

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as large as the ecosystem services of our planet [3, 21, 22] and even the universe [23]. Please note that some of these applications however are not without controversy.

2 Thermodynamics and Resources

The point of this book in focusing on larger complex systems is to expand and extend these principles and to look carefully at their application to problems, particularly those related to ecology, industrial ecology, and issues of sustainability. Here, as suggested in our title, the greatest leverage will be concerning problems of resource use, resource transformations, and resource destruction. Clearly the resources we use to establish and maintain life, to construct our society, to improve economic well-being, and to provide for our progeny, will all play a central role in any discussion of sustainable behavior. Of particular interest will be accounting for these resources; how available they are, how efficiently they are used, and how they become depleted, and allocation of these resources between different species and generations on this planet. Thermodynamics is particularly well suited to address the first issue, the accounting for resources, and, by providing rigorous allocation and accounting metrics, it can contribute to the second issue.

The proper domain for thermodynamics is in energy interactions, and through these interactions, the accomplishment of useful effects, the depletion of energy resources, and the generation of unavoidable wastes. Because of the necessity of energy interactions to maintain life and the often close correlations between energy resources use and economic growth as well as waste generation, emissions and pollution, energy and how it is used often dominate many discussions about the future of humankind on this planet. What is of paramount importance here is that, once a system is established as a so-called well-defined thermodynamic system, it must obey the laws of thermodynamics. It is our belief, and the central tenet of this book, that many, if not all, of the systems we care about can be interpreted as thermodynamic systems. This of course is not to say that all we care about are thermodynamic interactions. The sustainability of human activities is far more complex, and thermodynamics is only one part of it.

The first chapter of this book [24] establishes what constitutes a thermodynamic system. The definition, however, is quite broad. Basically it includes any kind of material resources from manmade to natural, and this system may be acted on by any kind of energy and heat interactions, for example, including those in power plants, industrial systems, and living systems. Once established, the behavior of these systems has to obey the laws of thermodynamics, including the laws of other scientific disciplines and related constraints. The focus of this book, on the use, efficiency of transformation, and the destruction of resources naturally leads us to the second law of thermodynamics and the concepts of entropy and available energy or exergy. Unfortunately these concepts are probably among the most mysterious and misunderstood concepts in all of science, striking fear in the hearts of engineering students and, often enough, even professionals. This misunderstanding has not gone unnoticed, however, and a debate among scientists and engineers has resulted in careful expositions of the thermodynamic theory, for example, Gyftopolous and Beretta (G&B) [25].

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Let us start by admitting that there has been a proliferation of intimidating sounding e-words in thermodynamics, which in themselves can be off-putting and probably undermine their use. Among these, *energy* is probably the least off-putting and most widely used term and has been incorporated into the analysis of economic, industrial, and ecological systems' [26]. Energy includes contributions from internal energy (say, molecular motion), kinetic energy (involving velocity of a mass), and potential energy (related to displacement in a force field such as a gravitation field and others), to mention a few, and the quantity of its flow is governed by the first law of thermodynamics – sometimes called the law of energy conservation. However, energy does not capture the actual ability to do work, or even the interpretation of most laypeople or the dictionary meaning of "the ability to do work" [27]. Thermodynamicists have responded by developing other concepts such as entropy and exergy to address these issues. These off-putting e-words often represent concepts of paramount importance to our theme and must eventually be mastered. In truth, these concepts are quite accessible. Let us start, as G&B did, by establishing the idea that there is something called the "available energy" of a system. This is exactly what the name implies, the amount of energy that is available to do some useful work or have some other useful effect. This is what most laypeople and dictionaries usually mean by the word energy. The name "available work" has been supplanted by the much more esoteric-sounding term "exergy," but the two mean the same thing. And because "exergy" is short, easy to write, and now well accepted, we use it too. Exergy then measures the energy potential of a system to do some useful task. When the system interacts with the surroundings to do some useful task, it will use or transfer some of this exergy. If the process is an ideal "reversible" process, the exergy change for the system will be exactly equal to the amount of exergy used to do the task. However, no real process is ideal, and so for real systems the exergy change for the system will be greater than the exergy effectively used to do the task. This difference represents the exergy destruction. This loss is real and irretrievable. It represents a destruction of available energy potential.

The *exergy lost* is always positive for real systems and is proportional to another e-concept, the *entropy generated*. So both concepts, *exergy lost* and *entropy generated*, can be used to measure the destruction of a thermodynamic resource. These concepts derive from both the first and the second laws of thermodynamics and are used in what is called second law analysis. Second-law analysis can tell us how efficient a process is by distinguishing between what is lost and what is gained. First law analysis, on the other hand, is based on the conservation laws for energy and mass. First law analysis can tell us energy-transfer requirements needed to effect certain changes, but it cannot tell us a complete story about the efficiency of these changes. These concepts are illustrated in the Fig. I.1.

In the figure we see that the difference between the exergy supplied to the system (marked by the system boundary) and the total exergy out of the system is equal to the "exergy losses." For example, if the inputs are two separate streams of hot and cold water and the output is the mixture at an intermediate temperature established by the energy balance, the internal exergy losses represent the lost potential of the water inputs caused by mixing, i.e., by the equalization of the temperatures of the individual streams. Note that an energy balance for the mixing problem without or with "losses" to the environment would show the same total energy out as in.

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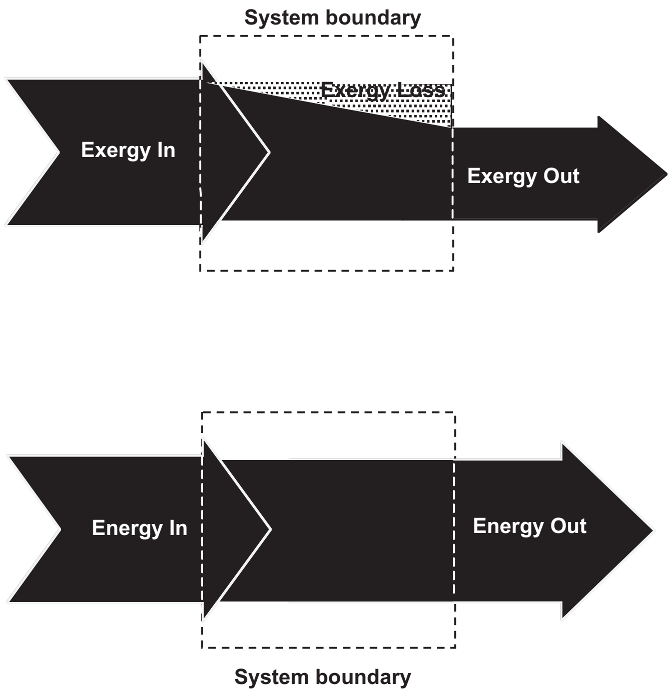

Figure I.1. Grassmann (exergy flow) and Sankey (energy flow) diagrams. In general, it is assumed that a total energy flow “supplied” to the system carries the corresponding exergy (available energy) flow. The system changes the state, and the available energy, passing through the system, is reduced because of irreversibilities inherent to the change of state. The exergy flow available for a useful effect is reduced (exergy is not conserved). However, the energy flow features the conservation principle and the total energy in must be equal to the total energy out.

Only a second law analysis shows the loss of available energy. This is one of the big advantages of exergy analysis. In the context of the title of this book, the internal and external exergy losses represent resource destruction. These are either irretrievable (such as caused by mixing) or partially retrievable (say, if some heat losses can be reduced by better system insulation). The exergy is useful because the person who frames the problem deems this application useful or the available energy at the exit from the system can be utilized for some other useful effect. For example, the useful exergy could represent the warm water (as a mixture of a hot and a cold stream) you use in the morning to shower. This would correspond to our preceding water-mixing example. However, this water will eventually go down the drain and lose all of its potential too. Hence the total “exergy input” represents a resource that is consumed. On the other hand, the warm water may be used to heat another fluid stream; hence any remaining exergy potential would be available for use in such a new application. To be more specific, the input exergy resource could be the available energy extracted from coal needed to make the hot water. After the shower, you have a clean body, but the coal and all or most of its potential is gone. The point is this: Exergy analysis will show you what will be lost (internal and external loses) to obtain some useful effect. It will also show you what useful potential remains (the exergy still available). Theoretically this remaining exergy could be used to obtain some other useful effect, but often in our society we do not use it; we throw

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it away. Exergy analysis will help direct our attention to losses. How humans may value the useful effect and the resources used, however, is a problem that calls for an analysis that would go beyond thermodynamics. These thermodynamics concepts are presented much more rigorously in Chaps. 1 and 2.

Recently exergy analysis has become much more prevalent in the industrial ecology literature, which has led to new results as well as new scrutiny of the concept. On the one hand, this second law concept has provided us with new insights; for example, it shows beyond a shadow of a doubt that such claims as "zero wastes" or "zero emissions" are unobtainable and should be discarded from the lexicon of industrial ecology or replaced by "zero avoidable waste." On the other hand, it is the case that first law analyses (energy balances and mass balances) can often provide some of the very same results as exergy analysis. This is the case when an analyst is not interested in the quality of the resource utilization but only in the quantity. We do not dispute these claims, but rather will attempt to show how second law analysis can be made quite accessible and that it provides new insights not obtainable from the first law. Perhaps the single most important dimension that second law analysis brings to any discussion of energy interactions is the notion of quality. For example, exergy analysis can define what the high-quality resources are by establishing a reference state, often referred to as the "dead state." That is, when the system of interest is in mutual stable equilibrium with this reference, it too is "dead" in the sense that it can do no work. The quality of a resource then is related, in energy units, to its distance from this reference state [28]. As it turns out, establishing just exactly what constitutes the reference state on Earth is not at all trivial. For one thing, the three major components of our biosphere, the crust, oceans, and atmosphere, are not themselves in stable equilibrium. For example, the high oxygen content of the atmosphere tends to oxidize exposed elements from the crust, etc. Nevertheless, and not without controversy, some reasonable reference states for these three components of our environment have been worked out. Notably the reference compositions and resulting exergy values of all the elements and many important chemical compounds have been established and several proposals for reference states exist. For example, the reference states proposed by Szargut are referred to frequently and are included here (see Appendix A). An important point then is that, armed with these data and other relevant information, such as mass balances, the work of performing a second law analysis for systems is reduced to an algebraic accounting exercise. Furthermore, the results from these exercises can provide important insights, such as whether or not a process is thermodynamically feasible, what is lost, what is gained, and what is the efficiency of the transformation.

Of a particular relevance here then is the available energy or exergy value of a resource. Intuitively, we would suspect that fuels such as coal, oil, kerosene, and natural gas should all have high values of exergy, and they do. In fact, exergy values for these fuels give numbers that are very close, if not equal, to their heating values. But, in addition, the exergy analysis gives values for all materials, valuing them for their exergy potential. Thus nonfuel resources that are typically not in focus of an energy analysis do have an exergy content and are commonly included in exergy analysis. This feature shows up particularly prominently in certain kinds of material and energy transformation and highlights the differences between first and second

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Table I.1. *Overview of chapters*

Part number	Chapter number	Title	Author(s)	Description
Part I: Foundations	1	Thermodynamics: Generalized available energy and availability or exergy	Gyftopoulos	This is a classic treatment of the exergy concept by one of the foremost thermodynamicists. The chapter offers a rigorous formulation of the set of basic concepts and laws of Thermodynamics. The concept of available energy (exergy) is devised as a primitive concept, while entropy is formulated as a derivative concept. This representation is unique since it introduces thermodynamic concepts via a different sequence than what is present in most traditional expositions.
	2	Energy and exergy: Does one need both concepts for a study of resources use?	Sekulić	In this chapter, concepts of energy and exergy are reexamined in the context of balance equations and their applications to the modeling of resources use. The presentation argues a clear distinction between the concepts of energy/exergy resources and their meaning as thermodynamic properties.
	3	Accounting for resource use by thermodynamics	Bakshi, Baral, Hau	This chapter introduces and evaluates various thermodynamic methods for resource accounting. This includes methods based on energy, exergy and emergy analysis. It links these methods and demonstrates their pros and cons via an application to the life cycle of some transportation fuels.
Part II: Products and Processes	4	Materials separation and recycling	Gutowski	This chapter reviews both thermodynamic and information theory approaches to characterize separation and recycling processes. Applications areas include mining and minerals extraction as well as product recycling.
	5	Entropy-based metric for transformational technologies development	Sekulić	This chapter offers a hypothesis that metric for the evaluation of existing technologies and/or new technologies in the context of energy resources utilization can be the entropy generation, and illustrates its use for non-energy systems.

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Table I.1 *(continued)*

Part number	Chapter number	Title	Authors	Description
	6	Thermodynamic analysis of resources used in manufacturing processes	Gutowski, Sekulić	This chapter reviews both the theoretical and the actual thermodynamic performance of many different manufacturing processes from conventional processes such as machining, casting and injection molding through advanced machining processes as well as micro electronics and nanotechnology processes.
	7	Ultrapurity and energy use: Case study of in semiconductor manufacturing	Williams, Krishnan, Boyd	This chapter provides a broad overview of the energy requirements of purification processes using a number of techniques, but primarily relying on cost of ownership models and environmental input/output modeling.
	8	Energy resources and use: The present situation, possible sustainable paths to the future, and the thermodynamic perspective	Lior	This chapter is a brief summary of the state of current energy resources and use, and of their limitations and consequences (2008), and of possible paths to the future, including energy research funding trends, especially in the U.S.
Part III: Life-Cycle Assessments and Metrics	9	Using thermodynamics and statistics to improve the quality of life-cycle inventory data	Bakshi, Kim, Goel	Errors in life cycle inventory data are common and affect the quality of the results from LCA. This chapter describes an approach based on imposing the laws of thermodynamics to the available data along with statistical information to improve their quality. The resulting data are reconciled with the laws of thermodynamics and expected to be more accurate.
	10	Developing sustainable technology: Metrics from thermodynamics	Van der Vorst DeWulf, Langenhove	This chapter shows how thermodynamics can be used for defining metrics that provide insight into the sustainability of technological activities and products. With the help of various examples, it illustrates the use of concepts such as cumulative exergy consumption and abatement exergy.
	11	Entropy production and resource consumption in life-cycle assessments	Gößling-Reisemann	This is a well argued promotion of the entropy generation concept for modeling resource consumption.

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Part number	Chapter number	Title	Authors	Description
	12	Exergy and material flow in industrial and ecological systems	Ukidwe, Bakshi	This chapter uses exergy as a common currency for industrial and ecological systems. It develops an integrated economic-ecological model of the U.S. economy by combining an economic input-output model with physical data about ecological inputs to various economic sectors.
	13	Synthesis of material flow analysis and input–output analysis	Nakamura	Material flow analysis has been popular to account for the use of resources in a life cycle. However, it does not consider waste streams. This chapter describes the approach of waste input-output material flow analysis to address this shortcoming. Applications of this approach to the Japanese economy are also described.
Part IV: Economic Systems, Social Systems, Industrial Systems, and Ecosystems	14	Early development of input–output analysis of energy and ecologic systems	Hannon	This is an interesting and historical look at the early development of energy resource input-output modeling by one of the pioneers.
	15	Exergoeconomics and exergoenvironmental Analysis	Tsatsaronis	This chapter elaborates two methodologies relevant for resources use and sustainability studies: (i) exergoeconomics as an exergy-aided cost reduction approach that uses the exergy costing principle, and (ii) a new approach based on the so-called exergoenvironmental costing.
	16	Entropy, economics, and policy	Ruth	This chapter gives a high level tour of physical modeling applied to economics.
	17	Integration and segregation in a Population – A thermodynamicist's view	Müller	This groundbreaking research attempts to uncover the hidden kinship between thermodynamic processes such as the phase separation in a solution and social phenomena such as segregation in a society. Both may be viewed as thermodynamic – or socio-thermodynamic – equilibria with homogeneous Gibbs free energies – or socio-chemical potentials.

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Table I.1. *(continued)*

Part number	Chapter number	Title	Authors	Description
	18	Exergy use in ecosystem analysis: Background and challenges	Pastres, Fath	Ecologists have used thermodynamics for understanding ecosystems for many decades. This chapter describes the challenges in using the exergy concept for understanding ecosystems and introduces eco-exergy as a way of quantifying the work capacity of living systems. Relationship of these concepts with similar concepts in engineering is also discussed.
	19	Thoughts on the application of thermodynamics to the development of sustainability science	Gutowski, Sekulić, Bakshi	This chapter explores the role that thermodynamics can play in sustainability by accounting for resource use and availability. It considers closed and open systems and how thermodynamics can help in using insight from ecosystems for designing technological systems.

law analysis. For example, when metal oxides are reduced to produce pure metals for manufacturing, both energy and exergy accounting will take into account the fuels used in this process. But only exergy accounting will take into account the material transformation and highlight the fact that the process has greatly improved the value of the metal oxide by converting it to pure metal. That is, most pure metals have very high exergy values. This means that they are a thermodynamically valuable energy "investment," and their destruction in subsequent manufacturing, use, and end-of-life phases should be avoided. But more than that, exergy provides the tool whereby the results from these activities can be calculated. That is, our knowledge of thermodynamics in general and exergy analysis in particular is sufficient to allow the evaluation of new or previously unexplored systems and estimate on a theoretical basis their resource needs, conversion efficiencies, and losses. For example, the exergy analysis of any chemical reaction allows for a rapid evaluation of alternative energy-production schemes, or various chemical-conversion schemes. In fact, these tools are so powerful we believe that they should be included in the standard toolkit for any engineer, industrial ecologist, and many other professionals dealing with sustainability issues.

In this book we use the tools available from thermodynamics, including first law and second law analyses, as well as the applicable science from other domains to gain insight into the functioning of resource use and transformations. There is a particular emphasis on those resources that are needed to support life and human society on this planet. Furthermore, we are also interested in the application of thermodynamic thinking to new, somewhat "remote" areas that may not necessarily be considered as being thermodynamic systems per se. Nevertheless, by demonstrating strict analogies among the thermodynamic variables, constraints, and internal

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