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# 1 Introduction

## 1.1 BACKGROUND

Effective thermal and fluid system design often requires a creative, iterative, and open-ended process to meet multifaceted objectives of an engineering system. It provides concepts and specifications that will optimize the function, performance, and value of a system, for the mutual benefit of users and manufacturers. Some common tools for such design include computational fluid dynamics (CFD), computer-aided design (CAD), measurement techniques such as particle image velocimetry (PIV), and others. This book focuses on how entropy and the Second Law of Thermodynamics can enhance conventional design methods by providing an iterative methodology to reduce entropy production in a thermal system, thereby improving its energy efficiency.

Industrial design methodologies were first adopted widely in the late 1930s and early 1940s, with prominent industrial designers such as Raymond Loewy, Norman Bel Geddes, and Henry Dreyfuss. The importance of their methods has risen steadily since that time for various reasons. Economics has been a key factor because a manufacturer's profitability depends on the product price in the marketplace and manufacturer's cost to produce it. As manufactured products become a commodity, cost savings are more difficult, and better industrial designs are needed to allow a product to gain higher profit margins. Also, good engineering designs can allow products to achieve certain attributes that are important for advertising and marketing purposes.

With increased worldwide awareness that the world's fossil fuel resources are limited, major efforts have focused on the design of more efficient and environmentally sustainable energy devices and processes. Energy systems are often thoroughly scrutinized for possible design improvements. Past conventional technology has generally detected energy losses on a system-wide or global scale, such as a single loss coefficient (i.e., valve loss coefficient). With the current state of this technology, the margins for improving the efficiency of existing devices can be relatively small. In this book, entropy-based design with local loss mapping is presented as a robust tool for reaching higher levels of system efficiency, thereby leading to energy savings in various industrial applications.

The fundamental principles governing the design of energy systems are Newton's law of motion and the laws of thermodynamics. Newton's Second Law of Motion and the First Law of Thermodynamics are the cornerstones on which virtually all energy systems are built today. The other laws have played a secondary support role. A limitation associated with the First Law of Thermodynamics is that it tracks only the quantity of energy. In contrast, the Second Law tracks "quality" of energy, or its work-producing potential. Thus, the Second Law has the unique advantage of offering a systematic tool

for optimal energy usage and choice of technologies. The unique capabilities of the Second Law can be used to scrutinize flow irreversibilities locally, rather than globally. In this way, the problem regions can be clearly identified by the high entropy production rates, so designers can focus on those regions for improvements. A useful analogy is a sick patient telling a doctor that he or she is sick, without knowing the part of the body that is causing the ailment. Doctors can often use diagnostic tools to pinpoint the source. Similarly for a complex engineering system, large rates of entropy production within a device can identify problematic areas of concern because a commonly desired goal of devices is improving the efficiency through reduced entropy production. This goal is generally desired regardless of application, flow conditions, system parameters, and so on.

Local exergy, or the work potential of a device, can be more readily interpreted physically than entropy production because it contains the same dimensional units as energy. It can be related directly to economic indicators. For example, multiplying the local cost of electricity (per kilowatt hour) by exergy destroyed by moving fluid through a valve over a year can indicate a yearly expense of wasted energy therein. This expense can be interpreted directly in terms of lost revenue. Thus, an economic framework can be based on local entropy production rates or exergy losses in a fluids engineering system.

Furthermore, there exists a need for a standard metric from which the energy efficiency of all devices can be characterized. For example, fuel efficiency in a car is defined differently from that of a water heater's efficiency, while still different than how a diffuser's efficiency is defined, and so on. As a result, it is difficult for regulatory and government agencies to identify a standard method for identifying the energy wasted by a given device. Entropy production gives a single, measurable quantity that is directly related to the efficiency of any device that transforms energy because it characterizes degradation of useful (mechanical) energy to less useful (internal) energy.

The utility of entropy and the Second Law have been widely documented in various disciplines, ranging from engineering fluid mechanics, to information and coding theory, economics, and biology. It will be emphasized frequently throughout this book how entropy serves as a key parameter in achieving the upper limits of performance and quality in many technologies. It can shed new light on various flow processes, ranging from optimized flow configurations in an aircraft engine to highly ordered crystal structures (low entropy) in a turbine blade, and other applications (Bejan, 1996). It is likely not possible to find any other law of nature, wherein a proposed violation would bring more skepticism than violation of the Second Law of Thermodynamics.

Consider the implications of the Second Law in the thermal design of aircraft subsystems, involving work potential (Camberos, 2000a). Past authors have observed that there is no current systematic method for tracking work potential usage in the design of aircraft subsystems (Roth and Mavris, 2000). Exergy and entropy calculations can identify the loss of work potential within each subsystem and fluid flow process during an aircraft's operation. These calculations can enable designers to identify key locations that incur the most significant losses. Moorhouse and Suchomel (2001) have discussed how flow exergy provides a unifying framework and set of metrics to more effectively analyze aircraft subsystems.

Various analytical methods have been developed over the past several decades for Second Law analysis. Notable examples include (i) estimation of the theoretical ideal operating conditions of a proposed design (called exergy analysis, or EA) and (ii) minimization of the lost available work or entropy generation by design modifications (called entropy generation minimization, or EGM; Bejan, 1996). Exergy quantifies the capacity of an energy source to perform useful work. It is a measure of the maximum capacity of an energy system to perform useful work as it proceeds to a specified final state in equilibrium with its surroundings. Exergy analysis focuses on closing the gap between maximum exergy and the actual work delivered by a device, through careful examination of the thermodynamic processes involved in a series of energy conversion steps (Dincer and Rosen, 2004). Subsequently, the exergy values at each point are used to evaluate Second Law efficiencies, which quantify the magnitude of irreversibilities (or exergy destruction) associated with the energy conversion process (Bejan, 1997; Rosen and Dincer, 2004). The method of EGM involves fluid mechanics, heat transfer, material constraints, and geometry, in order to obtain relationships between entropy generation and the optimal configuration. Typically, a functional expression for the entropy production in a process is derived (Poulikakos and Bejan, 1982; Zubair et al., 1987). Then the extremum of the derived expression that guarantees a minimum entropy generation is determined by methods of calculus. Because analytical methods are often limited to simplified geometries, this book extends analytical EGM to numerical and experimental methods.

Opportunities for design optimization based on the Second Law can be enhanced through CFD as a design tool for complex problems and geometries. Entropy production can be obtained by postprocessing of the predicted flow fields (Sciubba, 1997). Many industrial problems in metallurgy, power generation, energy storage, aerodynamics, and other applications have been successfully solved by CFD. A designer can choose an optimum design from many possible alternatives at a remarkable speed using CFD. Combined EGM with CFD provides an emerging technology with promising potential for design optimization of practical industrial problems.

For example, an application involving the design of air-cooled gas turbine blades was presented by Natalini and Sciubba (1999). The full Navier–Stokes equations of motion for turbulent viscous flow and the energy equations were solved with a finite element approach and a two-equation turbulence closure. By identifying the entropy generation rates corresponding to the fluid friction and heat transfer irreversibility, the authors determined which configurations had minimal thermodynamic loss in a turbine cascade. The computed flow field for pitched turbine blades (Kresta and Wood, 1993) can be postprocessed to identify regions of high local losses, thereby guiding engineers in local redesign of the blade profile to reduce such losses. Predictions of entropy production have been used in various other applications such as free convection in inclined enclosures (Baytas, 2000), mixed convection in a vertical channel with transverse fin arrays (Cheng et al., 1994), laminar and turbulent flow through a smooth duct (Demirel, 1999; Sahin, 2000, 2002), flow in concentric cylinder annuli with relative rotation (Mahmud and Fraser, 2002), and diffusers (Adeyinka and Naterer, 2005). These studies are examples of how entropy production computations can successfully complement CFD technology.

Industrial flow problems usually involve turbulence. Numerical predictions of entropy production in a turbulent flow were given by Moore and Moore (1983). Moore's work was the first documented effort to develop a numerical model for turbulent entropy production. The Moore model assumes that turbulent fluctuations of the heat flux and viscous dissipation in the positive definite entropy equation can be modeled by the addition of a turbulent conductivity and turbulent viscosity to the molecular conductivity and viscosity, respectively. It has been used to predict the mean local entropy production in a bent elbow (Moore and Moore, 1983), turbulent plane oscillating jet (Cervantes and Soloris, 2002), and a jet impinging on a wall (Drost and White, 1991). A finite volume method for predicting the mean viscous dissipation and entropy production in turbulent flows, based on the time-averaged turbulence equations, was described by Kramer-Bevan (1992).

In addition to the previous physical characteristics of entropy production, it can be interpreted alternatively in computational terms. Physical processes of viscous dissipation and heat transfer lead to entropy production. Past Second Law studies have shown how numerical procedures may also produce or destroy entropy, due to discretization errors, artificial dissipation, and nonphysical numerical results (Cox and Argrow, 1992; Naterer, 1999). Solutions of differential equations that do not satisfy an "entropy condition" may be characterized by a lack of uniqueness, oscillations, and other unusual behavior (Adeyinka, 2002; Hughes et al., 1985; and others). Cox and Argrow (1992) computed local entropy production with a finite difference method for compressible flow. Jansen (1993) and Hauke (1995) applied an entropy-based stability analysis to turbulent flows. Jansen (1993) showed that the exact Navier–Stokes equations for compressible flow could lead to an entropy inequality, through a linear combination of equations. The study determined what constraints the Second Law places on modeling of the averaged equations by linking entropy production to the solution variables. A major difficulty with numerical predictions can be the inability to ascertain error bounds. Solutions can be very sensitive to various parameters associated with the numerical algorithm (Naterer, 1999). This can make it difficult to judge the extent to which the computed results agree with reality. In numerical predictions of complex industrial flows, limited or no experimental data may be available for validation purposes. In these cases, checking where predicted entropy production rates are positive (realistic) or negative (unrealistic) is a valuable tool for verification.

## 1.2 GOVERNING EQUATIONS OF FLUID FLOW AND HEAT TRANSFER

### 1.2.1 VECTOR AND TENSOR NOTATIONS

In this book, conventional notations for vectors and tensors will be used. A vector will be denoted by boldface font or a vector hat. A unit vector is a vector of unit magnitude. For example,  $\mathbf{i}$  and  $\mathbf{j}$  refer to the unit vectors in the  $x$  and  $y$  coordinate directions, i.e.,  $(1, 0)$  and  $(0, 1)$ , respectively. The symbol  $|\mathbf{v}|$  designates the magnitude

of the indicated vector. When performing operations with matrices in this book, matrices are contracted when their individual entries are multiplied by each other and summed. For example, if

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}; \quad \mathbf{B} = \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} \quad (1.1)$$

then

$$\mathbf{A} : \mathbf{B} = a_{11}b_{11} + a_{12}b_{12} + a_{21}b_{21} + a_{22}b_{22} \quad (1.2)$$

Tensors are generalized notations for scalars (rank of zero), vectors (rank of 1), matrices (rank of 2), and so on. A tensor is denoted by a variable with subscripts. For example,  $a_{ij}$  represents the previously described matrix, where the range of subscripts is  $i = 1, 2$  and  $j = 1, 2$ . When tensors use indices in this way, the notation is called *indicial notation*. The *summation convention* of tensors requires that repetition of an index in a term denotes a summation with respect to that index over its range. For example, in the previously cited case (dot product) involving two vectors,

$$u_i v_i = u_1 v_1 + u_2 v_2 \quad (1.3)$$

The range of the index is a set of specified integer values, such as  $i = 1, 2$  in the previous equation. A *dummy index* refers to an index that is summed, whereas a *free index* is not summed. The rank of a tensor is increased for each index that is not repeated. For example,  $a_{ij}$  contains two nonrepeating indices, thereby indicating a tensor of rank 2 (i.e., matrix).

## 1.2.2 MASS AND MOMENTUM EQUATIONS

The governing equations of fluid flow and heat transfer can be expressed in either vector or tensor notations. For two-dimensional flows, the mass conservation equation is given by

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0 \quad (1.4)$$

For incompressible flows, this equation may be simplified wherein that the divergence of the velocity field ( $\nabla \cdot \mathbf{v}$ ) equals zero. The divergence of velocity may be interpreted as the net outflow from a control volume (fully occupied by fluid), which must equal zero at steady state, because any inflows are balanced by mass outflows.

The momentum equations represent a form of Newton's law. Forces on a fluid element like pressure and shear forces balance the particle's mass times its acceleration (i.e., total, or substantial derivative of velocity). The x-direction and y-direction

momentum equations can be expressed as

$$\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho uu)}{\partial x} + \frac{\partial(\rho vu)}{\partial y} = \frac{\partial\sigma_{xx}}{\partial x} + \frac{\partial\tau_{yx}}{\partial y} + F_{bx} \quad (1.5)$$

$$\frac{\partial(\rho v)}{\partial t} + \frac{\partial(\rho uv)}{\partial x} + \frac{\partial(\rho vv)}{\partial y} = \frac{\partial\tau_{xy}}{\partial x} + \frac{\partial\sigma_{yy}}{\partial y} + F_{by} \quad (1.6)$$

where  $F_b$  refers to a body force.

These equations cannot be solved in this form because there are more unknowns (i.e., stresses, velocities, and pressure) than available equations. As a result, additional relations called constitutive relations between the stresses and velocities are needed. In Newtonian fluids, the stresses are proportional to the rate of deformation (or strain rate). For incompressible flows of Newtonian fluids, we have the following two-dimensional constitutive relations for stresses in terms of the pressure and velocity fields:

$$\sigma_{xx} = -p + 2\mu \frac{\partial u}{\partial x} \quad (1.7)$$

$$\sigma_{yy} = -p + 2\mu \frac{\partial v}{\partial y} \quad (1.8)$$

$$\tau_{yx} = \mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) = \tau_{xy} \quad (1.9)$$

Substituting these constitutive relations into the previous  $x$ -momentum equation and using continuity (mass conservation) to rewrite the left side,

$$\rho \frac{\partial u}{\partial t} + \rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + F_{bx} \quad (1.10)$$

together with a similar  $y$ -momentum equation represents the two-dimensional Navier–Stokes equations. Analytical solutions of these equations are usually limited to simplified geometries because of the difficulties inherent in the nonlinear and coupled (with continuity equation) nature of the equations.

Fluid flow regions are generally classified as viscous or nearly inviscid regions. In a viscous region, such as a boundary layer, frictional forces are significant. A boundary layer refers to the thin diffusion layer near the surface of a solid body, where the fluid velocity decreases from its freestream value to zero at the wall over a short distance. In contrast to viscous regions, frictional forces are often small in comparison to fluid inertia in regions far from a surface or boundary layer. The Euler equations are a special form of the Navier–Stokes equations for frictionless (or inviscid) flow. An inviscid fluid refers to an idealized fluid with no viscosity. In this situation, the terms involving viscosity are absent from the governing equations.

The fluid motion can be characterized as a potential flow, whereby the reduced governing equations can be written in terms of a scalar potential function.

### 1.2.3 ENERGY TRANSPORT EQUATIONS

In addition to the fluid flow equations, energy is another transported quantity of key importance in the analysis of thermal and fluid systems. The mechanical energy equations can be obtained by multiplying each  $u_i$  momentum equation by  $u_i$  (where  $i = 1, 2$  for two-dimensional flows) and adding them together. Using the substantial derivative notation, we obtain

$$\frac{1}{2} \frac{D}{Dt} (u^2 + v^2) = -u \frac{\partial p}{\partial x} - v \frac{\partial p}{\partial y} + u \frac{\partial \tau_{xx}}{\partial x} + u \frac{\partial \tau_{yx}}{\partial y} + v \frac{\partial \tau_{xy}}{\partial x} + v \frac{\partial \tau_{yy}}{\partial y} + u F_x + v F_y \quad (1.11)$$

Using the product rule and generalizing to a vector notation, the following mechanical energy equation is obtained:

$$\frac{1}{2} \rho \frac{D}{Dt} (V^2) = -[\nabla \cdot (p\mathbf{v}) - p\nabla \cdot \mathbf{v}] + [\nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) - \boldsymbol{\tau} : \nabla \mathbf{v}] + \mathbf{v} \cdot \mathbf{F} \quad (1.12)$$

where  $V = \sqrt{u^2 + v^2}$  refers to the total resultant magnitude of the velocity. The first term (left side) represents the rate of increase of kinetic energy of a fluid element with respect to time. On the right side, the second term gives the flow work done by pressure on the differential control volume to increase its kinetic energy. The third term represents an energy sink due to fluid compression in the mechanical energy equation, and it becomes zero for incompressible flows. The difference between the fourth and fifth terms on the right side gives the net fluid work done by viscous stresses to increase the kinetic energy of the fluid within the control volume. The latter portion represents work lost through viscous dissipation, which is a degradation of mechanical energy into internal energy through viscous effects. This viscous dissipation is represented by  $\boldsymbol{\tau} : \nabla \mathbf{v}$ , which refers to the viscous stress tensor contracted with the velocity gradient.

For two-dimensional incompressible flows of a Newtonian fluid, it can be shown that the viscous dissipation term can be written as

$$\boldsymbol{\tau} : \nabla \mathbf{v} = 2\mu \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial v}{\partial y} \right)^2 \right] + \mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)^2 \equiv \mu \Phi \quad (1.13)$$

where  $\Phi$  refers to the positive-definite viscous dissipation function. This function is greater than or equal to zero. As a result, the conversion of mechanical energy into internal energy through viscous dissipation is an energy sink in the mechanical energy equation. Thus, mechanical energy is not conserved, but instead a portion of this energy is degraded and lost to internal energy through viscous dissipation.

It is degraded in the sense that a certain quality of energy is lost in the irreversible transformation, as internal energy normally has less ability than kinetic energy to perform useful work.

The conservation of total energy (internal plus mechanical energy) is called the First Law of Thermodynamics. Performing a total energy balance on a differential control volume within the fluid stream, it can be shown that the total energy equation can be written as

$$\rho \frac{D}{Dt} \left( \hat{e} + \frac{1}{2} V^2 \right) = -\nabla \cdot q - \nabla \cdot (p v - \tau \cdot v) + F \cdot v + \dot{S} \quad (1.14)$$

where  $\hat{e}$  refers to internal energy and  $S$  is a source term. The rate of increase of total energy within the control volume equals the rate of energy addition by conduction, plus work done by pressure, viscous and external forces, plus internal energy generated per unit volume ( $\dot{S}$ ).

The internal energy equation can be derived by subtracting the mechanical energy equation from the First Law (total energy equation). Performing this subtraction and writing the results in a general vector form, we have

$$\rho \frac{D\hat{e}}{Dt} = -\nabla \cdot q - p \nabla \cdot v + \tau : \nabla v + \dot{S} \quad (1.15)$$

where the fourth term (right side) refers to the viscous stress tensor contracted with the velocity gradient. It represents an internal energy source because it arises from the conversion of mechanical energy to internal energy through viscous dissipation. In the thermal energy equation, viscous dissipation represents an energy source, which corresponds to the energy sink previously observed in the mechanical energy equation. In other words, its magnitude is identical, but its sign changes in transposing from the mechanical to internal energy equations.

### 1.3 MATHEMATICAL PROPERTIES OF ENTROPY AND EXERGY

Numerous past studies have examined the significance of exergy as a measure of work potential or maximum useful work (Boehm, 1989b, 1992). A common aspect in all of these analyses is the identification of exergy with useful work potential. For example, Szargut et al. (1988) define exergy as “the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium.” Similar definitions were documented by Bejan (1996) and Kotas (1985). Although engineers have accepted the capacity to do work as a measure of quality of energy, this does not invalidate another, less anthropomorphic approach. By conceptualizing “exergy” as a distance functional, one eliminates the need to introduce additional terms also found in the literature (e.g., “anergy,” “essergy,” etc.) or to fragment exergy into multiple forms as often done with energy. Concise and critical reviews of the origins and history of exergy have been reported by Bejan (1996), Haywood (1974), Kotas (1985), and Szargut et al. (1988).



The previous section has outlined the governing equations for conserved variables of mass, momentum, and total energy. In this section, entropy and the Second Law will be formulated, particularly fundamental properties associated with the nonconserved variables of entropy and exergy. Thermodynamics began as the science of heat, intended to provide extended mechanics that would account for a common experience, namely, that doing work on a body sometimes makes it hotter, and sometimes heating a body causes it to do work (Truesdell, 1985). Common experience shows that mechanical action does not always result in a mechanical response, so we need to add the concept of heating alongside the concept of working or power. The Second Law is often expressed in terms of “work potential” or exergy. The balance of exergy equation represents a synthesis of the First and Second Laws. Exergy places all thermodynamic processes in a given system on the same basis by providing a common reference and metric. This section examines the essence of the Second Law of Thermodynamics as a statement involving the existence of entropy, with particular mathematical properties, from which a corresponding statement for the existence of exergy follows. It will be shown that exergy represents an abstract, mathematical distance functional. The concept of exergy will be interpreted as a thermodynamic functional representing the distance of a given system from the state of equilibrium at a reference state.

### 1.3.1 CONCAVITY PROPERTY OF ENTROPY

The Second Law of Thermodynamics represents a natural foundation for thermophysical processes. The concept of entropy, however, is often viewed as abstract. A fundamental feature of the Second Law reflects a concavity property of entropy (Camberos, 2000a). Given a set of thermodynamic variables,  $\xi$  and  $\zeta$ , there exists a functional, entropy,  $S = S(\xi, \zeta)$  such that  $S$  is a concave function of its arguments. This framework can be useful to unify various formulations of the Second Law, including the principle of nonnegative entropy generation itself (Lavenda, 1991).

Consider an example of a rigid material body at some temperature  $T$  immersed in a thermal reservoir at temperature  $T_0$  (e.g., a hot rock inside a cold room). Suppose  $T > T_0$  and we let the cooling process proceed from the initial time,  $t$ , to  $t_0$  when the body reaches thermodynamic equilibrium with its surroundings. The transfer of energy as the body cools equals

$$\int_t^{t_0} Q dt = U_0 - U \quad (1.16)$$

where  $U_0 = U(T_0)$  at a final time  $t_0$  and  $U = U(T)$  at the initial time  $t$ . The variables  $Q$  and  $U$  refer to heat transfer rate and internal energy, respectively.

The Second Law of Thermodynamics requires that entropy is produced, but never destroyed, in an isolated system. Thus,  $S_{\text{gen}} \geq 0$  for an isolated system, where  $S_{\text{gen}}$  refers to the entropy generation. In the current example, the entropy flow associated with heat transfer is  $-Q/T_0$ , so the entropy balance equation is

$$S_{\text{gen}} = S_0 - S - \frac{1}{T_0} \int_t^{t_0} Q dt \quad (1.17)$$

where  $S = S(T)$  and  $S_0 = S(T_0)$ . Substituting Equation 1.16 into Equation 1.17,

$$S_{\text{gen}} = S_0 - S - \frac{1}{T_0}(U_0 - U) \quad (1.18)$$

To write the change of energy in terms of temperature, we can use the definition of the specific heat ( $C_V = \partial U/\partial T$ ). The entropy generated during the cooling process is then

$$S_{\text{gen}} = S_0 - S - \frac{C_V}{T_0}(T_0 - T) \quad (1.19)$$

Using standard thermodynamic relations between the specific heat and entropy ( $C_V/T = \partial S/\partial T$ ), the expression for entropy generation becomes

$$S_{\text{gen}} = S_0 - S - \left. \frac{\partial S}{\partial T} \right|_0 (T_0 - T) \quad (1.20)$$

This expression indicates a concavity property of entropy as a function of  $T$ .

To clarify the meaning of the concavity property, consider some arbitrary function  $F = F(X)$  such that  $F'' < 0$ , where the inequality indicates that  $F$  is a concave function of its argument. Integration by parts requires

$$-\int_{X_1}^{X_2} (X - X_1)F''(X)dX = F(X_2) - F(X_1) - F'(X_2)(X_2 - X_1) \quad (1.21)$$

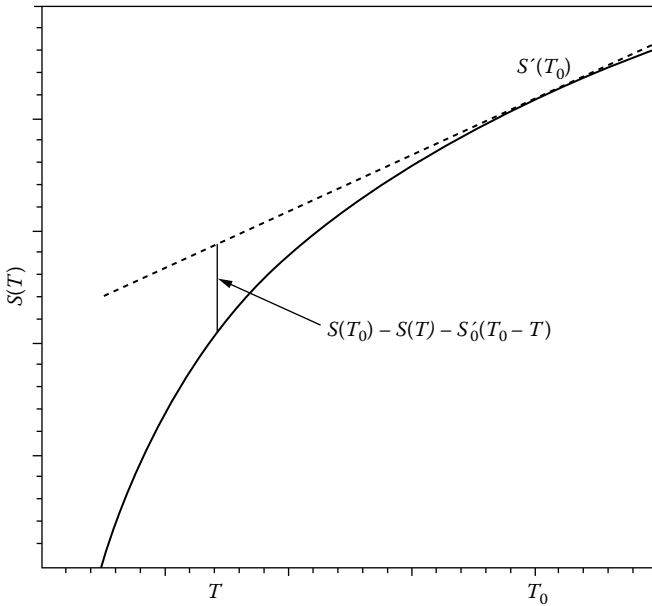
The result on the right-hand side has a geometric interpretation. [Figure 1.1](#) illustrates the right side of the equation with a vertical line. Geometrically, we have

$$F(X_2) - F(X_1) - F'(X_2)(X_2 - X_1) \geq 0 \quad (1.22)$$

where the equality holds if and only if  $X_2 = X_1$ . Comparing this result with Equation 1.20, it can be observed that positive entropy generation (the Second Law) is equivalent to asserting the concavity property of entropy when  $S = S(T)$ .

Consider another example of a simple compressible substance, subject to both heat transfer,  $Q$ , and work,  $W$ , when relaxing to equilibrium with an environment at  $T_0, P_0$ , where  $P_0 = P(T_0, V_0)$ . Solving for the heat flow from an energy balance and writing the net compression/expansion work of the gas in terms of pressure and a volume difference,

$$\int Q dt = (U_0 - U) + P_0(V_0 - V) \quad (1.23)$$



**FIGURE 1.1** Downward concave function (entropy).

The entropy balance then becomes

$$S_{\text{gen}} = S_0 - S - \frac{1}{T_0}(U_0 - U) - \frac{P_0}{T_0}(V_0 - V). \quad (1.24)$$

Alternatively, by substituting the appropriate thermodynamic relations and using  $S_{\text{gen}} \geq 0$ ,

$$S_0 - S - \frac{\partial S}{\partial T}\bigg|_0(T_0 - T) - \frac{\partial S}{\partial V}\bigg|_0(V_0 - V) \geq 0. \quad (1.25)$$

The inequality asserts the concavity of entropy as a function of  $T$  and  $V$ . Equality holds if and only if  $(T, V) = (T_0, V_0)$ .

Exergy represents the maximum work potential when bringing the system to equilibrium with its surroundings. In this example, it is given by

$$X = T_0(S_0 - S) - C_V(T_0 - T) - P_0(V_0 - V). \quad (1.26)$$

Standard thermodynamic relations provide

$$\frac{C_V}{T} = \frac{\partial S}{\partial T} \quad \frac{P}{T} = \frac{\partial S}{\partial V} \quad (1.27)$$

Multiplying the entropy inequality in Equation 1.24 leads to

$$T_0(S_0 - S) - (U_0 - U) - P_0(V_0 - V) \geq 0, \quad (1.28)$$

where  $C_v(T_0 - T)$  can be interchanged with  $(U_0 - U)$ . Identifying the left side as exergy and taking the time rate of change,

$$\dot{X} = -T_0\dot{S} + C_v\dot{T} + P_0\dot{V}. \quad (1.29)$$

Also, from the entropy balance equation for this problem,

$$\dot{S} = \dot{S}_{\text{gen}} + \frac{\partial S}{\partial T}\dot{T} + \frac{\partial S}{\partial V}\dot{V}. \quad (1.30)$$

Substituting Equation 1.30 into Equation 1.29 and replacing terms defined by  $\partial S/\partial U = 1/T$  and  $\partial S/\partial V = P/T$  yields

$$\dot{X} - \left(1 - \frac{T_0}{T}\right)C_v\dot{T} - \left(P_0 - T_0\frac{P}{T}\right)\dot{V} = -T_0\dot{S}_{\text{gen}}. \quad (1.31)$$

From the definition of exergy, it can be shown that the following thermodynamic relations hold:

$$\frac{\partial X}{\partial V} = \left(P_0 - T_0\frac{P}{T}\right); \quad \frac{\partial X}{\partial T} = \left(1 - \frac{T_0}{T}\right)C_v. \quad (1.32)$$

Because the entropy generation is nonnegative, the previous relations yield

$$\dot{X} - \frac{\partial X}{\partial T}\dot{T} - \frac{\partial X}{\partial V}\dot{V} \leq 0. \quad (1.33)$$

This result asserts the mathematical property of convexity for  $X = X(T, V)$ . Thus, the concavity of entropy is equivalent to the convexity of exergy.

Figure 1.2 shows an example of exergy as a convex function of temperature. A geometric complementary relation exists between entropy and exergy, as shown by the concavity inequality for entropy and the line segment that defines exergy (see Figure 1.3). Exergy has an absolute minimum at the point of equilibrium. The tangent slope at this point coincides with the horizontal axis of zero exergy. The straight vertical line from an arbitrary initial state in Figure 1.2 represents the corresponding distance to equilibrium. The distance to equilibrium is represented equally well by the vertical line shown in Figure 1.1 (concavity of entropy) or the horizontal line in Figure 1.3 (geometric representation of exergy).

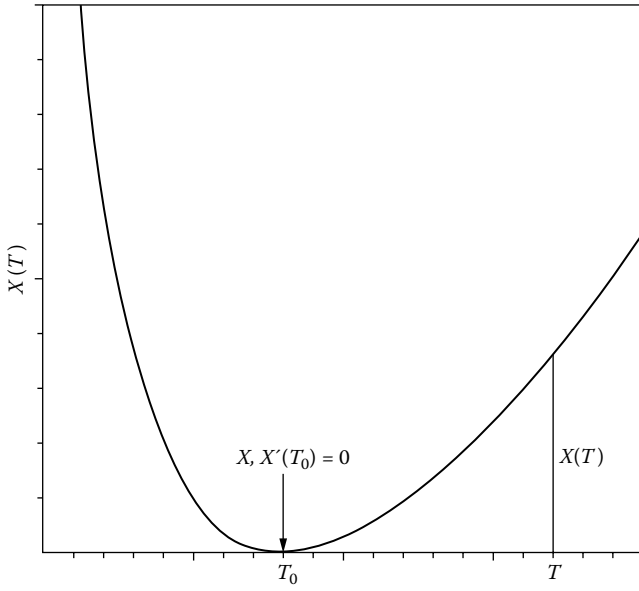


FIGURE 1.2 Exergy function as a convex function of  $T$ .

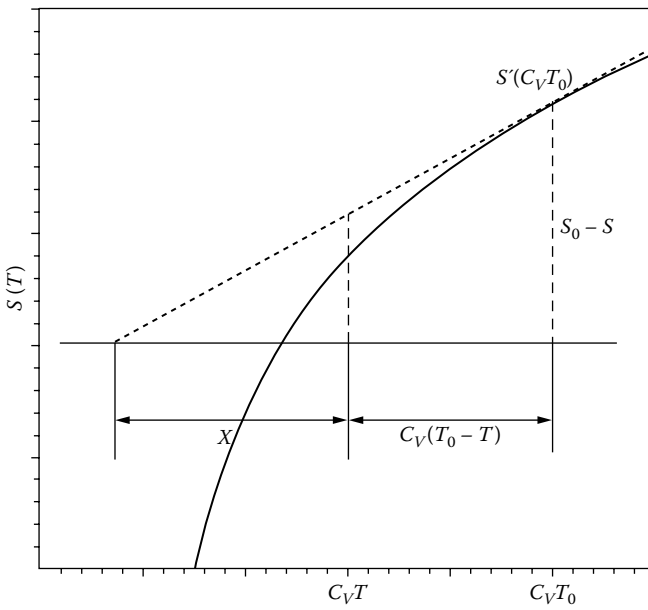


FIGURE 1.3 Geometric representation of entropy.

### 1.3.2 DISTANCE FUNCTIONAL WITH RESPECT TO EQUILIBRIUM CONDITIONS

In addition to its convexity property, exergy may be interpreted as a thermodynamic metric or distance functional. Define a metric,  $x$ , based on the Hessian of entropy (second-order tensor of derivatives with respect to temperature and volume) and the following inner product,

$$(x, x) \equiv x^T \cdot (-S_{xx})_0 \cdot x \quad (1.34)$$

where

$$(S_{xx})_0 = \begin{bmatrix} \frac{\partial^2 S}{\partial T^2} & \frac{\partial^2 S}{\partial T \partial V} \\ \frac{\partial^2 S}{\partial T \partial V} & \frac{\partial^2 S}{\partial V^2} \end{bmatrix}_0 \quad (1.35)$$

represents the Hessian. The superscript  $T$  refers to matrix transpose and

$$x^T \equiv (T, V) \quad (1.36)$$

represents an algebraic vector of the corresponding thermodynamic variables. The inner product of  $(x, x)$  results in nonnegative values, as guaranteed by the concavity property of entropy. A general mathematical metric can be defined by the following distance functional:

$$\|x - x_0\| \equiv (\Delta x, \Delta x)^{1/2} \quad (1.37)$$

where  $\Delta x = x - x_0$ .

To clarify the importance of these equations with respect to exergy, consider the construction of the norm  $\|x\|$ , which requires evaluation of the second-derivative terms of the Hessian. Thermodynamic relations for a simple compressible substance (Bejan, 1996) give

$$\frac{\partial^2 S}{\partial T^2} = -\frac{C_v}{T^2} \quad (1.38)$$

$$\frac{\partial^2 S}{\partial T \partial V} = -\frac{1}{\kappa T^2} (\kappa P - \beta T) \quad (1.39)$$

$$\frac{\partial^2 S}{\partial V^2} = -\frac{1}{\kappa T^2} \left( \frac{\kappa P^2 - 2\beta TP}{C_v} + \frac{C_p T}{C_v V} \right) \quad (1.40)$$

where

$$\beta \equiv \frac{1}{V} \frac{\partial V}{\partial T} \quad (1.41)$$

and

$$\kappa \equiv -\frac{1}{V} \frac{\partial V}{\partial P} \quad (1.42)$$

represent the volumetric coefficients of thermal expansion and isothermal compressibility of the gas, respectively. Using these definitions to calculate the Hessian yields the following inner product:

$$(x, x) = \frac{1}{\kappa C_V T_0} \left\{ \frac{\kappa H^2}{T_0} - 2\beta H V + \frac{C_P V^2}{V_0} \right\} \quad (1.43)$$

where  $H = C_V T + P_0 V$ .

Consider two cases: an ideal gas and an incompressible substance. For an ideal gas,

$$\kappa P = 1 \quad \beta T = 1 \quad (1.44)$$

and the inner product simplifies to

$$(x, x) = C_V \left( \frac{T}{T_0} \right)^2 - \frac{P_0^2 V^2}{C_V T_0^2} + \frac{C_P P_0 V^2}{C_V T_0 V_0} \quad (1.45)$$

Simplifying further with the ideal gas equation of state,

$$PV = \hat{R}T \quad (1.46)$$

together with the following relations:

$$C_V = \frac{\hat{R}}{\gamma - 1} \quad C_P = \frac{\gamma \hat{R}}{\gamma - 1} \quad \gamma \equiv \frac{C_P}{C_V} \quad (1.47)$$

yields

$$(x, x) = \frac{\hat{R}}{\gamma - 1} \left( \frac{T}{T_0} \right)^2 + \hat{R} \left( \frac{V}{V_0} \right)^2 \quad (1.48)$$

where  $\hat{R} = mR/M$  and  $m$ ,  $M$ , and  $R$  are the mass, molecular weight, and universal gas constant, respectively. The subscript  $O$  denotes reference conditions for pressure and temperature. Replacing  $(U, V)$  with the corresponding differences  $(U - U_0, V - V_0)$  yields the following square of a true mathematical distance functional,

$$\|x_0 - x\|^2 = \frac{\hat{R}}{\gamma - 1} \left( 1 - \frac{T}{T_0} \right)^2 + \hat{R} \left( 1 - \frac{V}{V_0} \right)^2 \quad (1.49)$$

Following the same procedure for an incompressible substance, where  $\kappa, \beta \rightarrow 0$ , and  $C_p, C_v \rightarrow C$ , yields

$$\|x_0 - x\|^2 = C \left( 1 - \frac{T}{T_0} \right) \quad (1.50)$$

This result of a mathematical distance functional can be directly related with exergy. Consider a system near equilibrium conditions and expand the entropy function in a Taylor's series. Using the previous definition of  $x^T = (T, V)$  and neglecting higher-order terms,

$$S \approx S_0 + \frac{\partial S}{\partial T} \Big|_0 (T - T_0) + \frac{\partial S}{\partial V} \Big|_0 (V - V_0) + \frac{1}{2} (x - x_0)^T \cdot S_{xx} \Big|_0 \cdot (x - x_0) \quad (1.51)$$

Using the definition of exergy from the previous section, entropy derivatives in terms of exergy and the previous result for the distance functional, it can be shown that

$$X \approx \frac{1}{2} T_0 \|x - x_0\|^2 \quad (1.52)$$

This formulation of exergy as a distance functional with respect to equilibrium conditions provides a more systematic and mathematically rigorous interpretation than various definitions of “work potential” in undergraduate textbooks. The previous results show that exergy represents a physical measure of the distance from equilibrium conditions for a system at some arbitrary state.

The convexity and distance functional properties of exergy have been presented here to aid understanding of exergy. The concept of exergy has been interpreted through a connection between a system and its environment. Standard textbooks often introduce and discuss “availability” or exergy in the context of “a system’s potential to do work in a reversible manner.” Many modern texts (such as Cengel and Boles, 1989; Müller, 1985) also introduce a number of work terms (reversible work, available work, etc.) in an effort to clarify and expand on the subject. However, this can lead to more confusion and cluttering of terminology. This situation was observed more than 30 years ago (Haywood, 1974a,b). Second Law analyses have found well-deserved attention (Szargut et al., 1988), but the cluttering of terminology and obscurity in the definitions often remain. By providing fundamental mathematical properties of exergy as a state variable, this section has provided a valuable alternative interpretation.

The Second Law has deep and significant implications for engineering systems. As future machines become increasingly complex and sophisticated in their ability to transform energy into various forms, exergy and the Second Law will have an increasingly important role in prescribing their upper limits of performance. Since the industrial revolution, the Second Law served only a secondary role by prescribing what the real physical world allowed. Complex machines of the future will require a more interconnected relationship, as they press toward the maximum limits



of engineering design, precisely where the true power of the Second Law becomes evident. Therefore, it is essential that fundamental properties of entropy and exergy as state variables are well understood. Systematically developing the foundations of the Second Law from the essence of entropy as a concave function of state variables, we can advance that concept, together with a simplicity that will make it possible for future engineers and scientists to achieve what we can now only imagine.

## 1.4 GOVERNING EQUATIONS OF ENTROPY AND THE SECOND LAW

The First and Second Laws are physical principles governing all thermophysical processes, and the addition of constitutive relations describes the response of various classes of materials (Truesdell, 1984, 1985). As discussed in the previous section, a general axiom of thermodynamics postulates the existence of a concave thermodynamic variable called entropy. The Second Law then stipulates that the rate of entropy generation must be nonnegative in all thermophysical processes, that is,  $\dot{S}_{\text{gen}} \geq 0$ . The mathematical property of concavity implies certain restrictions on the constitutive relations for any material body. This section will use this property to develop the governing equations for entropy and the Second Law.

### 1.4.1 CLOSED SYSTEM

For a closed system, let  $\xi_k$  represent independent variables in the constitutive functional relation, such that  $U = U(\xi_k)$ ,  $W = W(\xi_k)$ , etc. Then the mathematical expression for the Second Law can be written as

$$\dot{S} - \sum_k \frac{\partial S}{\partial \xi_k} \dot{\xi}_k - \dot{S}_{\text{gen}} = 0 \quad (1.53)$$

For  $S = S(U, V)$ , the Second Law becomes

$$\dot{S} - \frac{\partial S}{\partial U} \dot{U} - \frac{\partial S}{\partial V} \dot{V} - \dot{S}_{\text{gen}} = 0 \quad (1.54)$$

Simplifying this result by using thermodynamic relations for the derivatives ( $C_V/T = \partial S/\partial T$ ,  $P/T = \partial S/\partial T$ , and  $C_V = \partial U/\partial T$ ) and the First Law,

$$\dot{S} - \frac{Q+W}{T} - \frac{P}{T} \dot{V} - \dot{S}_{\text{gen}} = 0 \quad (1.55)$$

Relating the work term and third term yields

$$\dot{S} - \frac{Q}{T} - \dot{S}_{\text{gen}} = 0 \quad (1.56)$$

which represents the entropy balance for a closed system from classical thermodynamics. This result is well known, although the previous derivation has shown that it follows from the concavity property of entropy.

High-quality energy refers to energy from which a great amount of useful work can be extracted, so exergy is used to refer to the work potential of that energy. Lower quality energy like internal energy can produce less work and therefore reflects also lower exergy. Thus, exergy quantifies a qualitative aspect of energy. In standard practice, to derive an equation representing the balance of exergy, one typically considers a closed system at some uniform arbitrary state,  $(P, T)$ , relative to ambient conditions at  $(P_0, T_0)$ . To measure the distance of a system from the reference or so-called “dead state,” imagine a reversible process whereby the system relaxes to thermodynamic equilibrium with the surroundings. The energy balance equation simplifies to

$$U_{\text{in}} - U_{\text{out}} = \Delta U \quad (1.57)$$

where the total change in energy is

$$\Delta U = U(t_2) - U(t_1) = \int_t^{t_0} \dot{U} dt \quad (1.58)$$

A closed system relaxes to equilibrium with its surroundings through work and heat transfer. Integrating the balance of energy equation over time,

$$\int_t^{t_0} Q dt + \int_t^{t_0} W dt = \Delta U \quad (1.59)$$

with the integral limits defined at an initial time when the system is at  $(P, T)$  and the final time when the system has reached equilibrium with the surroundings at  $(P_0, T_0)$ . To replace the heat interaction term with a state variable, one can use the following definition of entropy:

$$\int \dot{S} dt = \frac{1}{T_0} \int Q dt \quad \Rightarrow \quad T_0(S_0 - S) = \int Q dt \quad (1.60)$$

For the work term, the energy quality directly relates to the useful work extracted. It is the maximum amount of work done during a thermodynamically reversible process. For a simple compressible substance,

$$\int W dt = - \int P \dot{V} dt = - \underbrace{\int (P - P_0) \dot{V} dt}_{W_{\text{useful}}} - P_0 \int \dot{V} dt \quad (1.61)$$

The first term on the right-hand side defines the maximum “useful work” available, and the second term represents the work done by the ambient pressure acting on a

moving boundary. Substituting the previous two equations into the energy balance,

$$T_0(S_0 - S) - W_{\text{useful}} - P_0(V_0 - V) = U_0 - U \quad (1.62)$$

where the subscripts indicate the value at reference conditions. Solving for the useful work term gives

$$W_{\text{useful}} = T_0(S_0 - S) - (U_0 - U) - P_0(V_0 - V) \quad (1.63)$$

which is equivalent to the exergy defined earlier as

$$X \equiv T_0(S_0 - S) - (U_0 - U) - P_0(V_0 - V) \quad (1.64)$$

Dividing by the total mass gives the specific exergy (in other words, exergy per unit mass):

$$\phi \equiv T_0(s_0 - s) - (u_0 - u) - P_0(v_0 - v) \quad (1.65)$$

Generalizing to include kinetic and gravitational potential energy requires only that we replace  $u$  with  $e$ , which is the total specific energy given by  $e = u + \frac{1}{2}V^2 + gz$ . Typically,  $V_0 = 0$  and  $z_0 = 0$  at the reference state.

With the exergy defined in this manner, one can study the change in exergy when the state of a system changes. As a system undergoes a process from one thermodynamic state to another, a corresponding change in exergy occurs. Combining the First and Second Laws as expressed by the energy and entropy balance equations for a compressible substance of fixed mass leads to an exergy balance equation. In integral form, the First and Second Laws become

$$L_1 : \int Q dt + \int W dt = U_2 - U_1 \quad (1.66)$$

and

$$L_2 : \int \frac{Q}{T} dt + S_{\text{gen}} = S_2 - S_1 \quad (1.67)$$

Combining by taking  $L_1 - T_0 L_2$  gives

$$\int Q dt + \int W dt - T_0 \int \frac{Q}{T} dt - T_0 S_{\text{gen}} = U_2 - U_1 - T_0(S_2 - S_1) \quad (1.68)$$

Collecting terms and replacing the right-hand side with equivalent terms using the definition of exergy gives

$$\int \left(1 - \frac{T_0}{T}\right) Q dt + \left\{ \int W dt + P_0(V_2 - V_1) \right\} - T_0 S_{\text{gen}} = X_2 - X_1 \quad (1.69)$$

Other than a difference in sign on the work term, Equation 1.69 is a typical result found in textbooks on elementary thermodynamics (Cengel and Boles, 1989). If we identify the first term on the left side as “exergy transfer due to heat interaction” in the same sense that we identify entropy transfer due to heat interactions, and the second term (in brackets) as the “exergy transfer due to work interaction,” then Equation 1.69 reduces to the following result:

$$I_x - X_{\text{des}} = \Delta X \quad (1.70)$$

where  $I_x$  is the exergy current due to work and heat transfer and  $X_{\text{des}} = T_0 S_{\text{gen}}$  is the exergy destruction (called the Gouy–Stodola identity).

Alternatively, it is useful to interpret the quantity expressed by  $X_{\text{des}}$  as the distance from which the system approaches thermodynamic equilibrium with its environment. Recognizing the Second Law through the increase of entropy principle, it is required that

$$T_0 S_{\text{gen}} \begin{cases} > 0 & \text{Real World} \\ = 0 & \text{Ideal World} \\ < 0 & \text{Impossible} \end{cases} \quad (1.71)$$

Because we have associated exergy as equivalent to a measure of work potential, this term can be described as “exergy degeneration” or a loss of potential work due to real-world, irreversible effects. Entropy generation has a corresponding destruction of exergy:

$$X_{\text{des}} = T_0 S_{\text{gen}} \quad (1.72)$$

A system in the real world undergoes spontaneously a process that brings it closer to thermodynamic equilibrium with its surroundings.

### 1.4.2 OPEN SYSTEM

During an unsteady process where a substance goes from an initial (inlet; subscript “in”) to a final (exit; subscript “out”) state, the quality of energy changes, and a corresponding change occurs in its thermodynamic distance from equilibrium. Combining the First and Second Laws as expressed in the energy and entropy balance equations for an unsteady process, one may obtain the balance equation for exergy. This derivation is commonly provided in undergraduate thermodynamics textbooks. The First Law for a control volume can be expressed as

$$\sum Q_k + W + \sum \dot{m} \left( h + \frac{1}{2} V^2 + gz \right)_{\text{in}} - \sum \dot{m} \left( h + \frac{1}{2} V^2 + gz \right)_{\text{out}} = \dot{E}_{\text{CV}} \quad (1.73)$$

where  $\dot{m}$ ,  $h$ , and  $E_{CV}$  refer to the mass flow rate, enthalpy and time rate of change of energy in the control volume, respectively.

The corresponding form of the Second Law is

$$\sum \frac{Q_k}{T_k} + \sum \dot{m}s \Big|_{\text{in}} - \sum \dot{m}s \Big|_{\text{out}} + \dot{S}_{\text{gen}} = \dot{S}_{\text{CV}} \quad (1.74)$$

Combining these equations yields

$$\begin{aligned} \sum \left(1 - \frac{T_0}{T}\right) Q_k + W + \sum \dot{m} \left( h + \frac{1}{2} V^2 + gz \right)_{\text{in}} \\ - \sum \dot{m} \left( h + \frac{1}{2} V^2 + gz \right)_{\text{out}} - T_0 \dot{S}_{\text{gen}} = \frac{d}{dt} (E - T_0 S)_{\text{CV}} \end{aligned} \quad (1.75)$$

If we define a specific “flow exergy,”  $\psi$ , in the same sense that enthalpy represents a “flow energy,” then the exergy balance equation simplifies to

$$\sum \left(1 - \frac{T_0}{T}\right) Q_k + (W + P_0 \dot{V}) + \sum \dot{m}\psi_{\text{in}} - \sum \dot{m}\psi_{\text{out}} - T_0 \dot{S}_{\text{gen}} = \dot{X}_{\text{CV}} \quad (1.76)$$

where

$$\psi = \phi + (P - P_0)v \quad (1.77)$$

and  $\phi$  is the specific exergy,  $(e - e_0) + P_0(v - v_0) - T_0(S - S_0)$ . Identifying the first two terms on the left side of Equation 1.76 as the transfer of exergy due to work and heat transfer, respectively, and the third and fourth terms as exergy transfer due to mass flow, the exergy balance equation for a control volume reduces to

$$\dot{X}_{\text{in}} - \dot{X}_{\text{out}} - T_0 \dot{S}_{\text{gen}} = \dot{X}_{\text{CV}} \quad (1.78)$$

where “in” and “out” terms represent the flow of exergy into and out of the control volume.

In addition to its role in determining the direction of natural processes and a criterion for thermodynamic equilibrium, the Second Law can also characterize the efficiency of engineering devices (Bejan, 1996). Carnot (1960, English translation from French by R.H. Thurston) conceived and developed the Second Law to account for the performance and limits of heat engines. Isentropic efficiency characterizes the performance of various engineering devices, such as turbines and compressors. In the context of exergy, the Second Law defines a more general measure of performance that applies not only to turbines and compressors, but heat exchangers, mixing processes, and other devices. A measure of performance for any engineering device should compare its efficiency, relative to the efficiency of an ideal device (no irreversible losses) operating under the same conditions. This measure of performance is called the “Second Law efficiency” or effectiveness, which can be

defined as follows,

$$\eta_{II} \equiv 1 - \frac{\dot{X}_{\text{des}}}{\dot{X}_{\text{supp}}} \quad (1.79)$$

where the subscripts “des” and “supp” refer to destroyed and supplied, respectively.

Past literature has interpreted this measure of performance as a “rational efficiency” of a process or device (Müller and Ruggeri, 1998). Essentially, the effectiveness of any process equals the fractional change in the exergy relative to the exergy supplied. The concept of effectiveness applies to any thermophysical process, including heat engines, refrigerators, heat exchangers, mixing, throttling, and so forth. It is always bounded between zero and one.

The Second Law of Thermodynamics will: (i) determine the direction of change for spontaneous, natural processes; (ii) establish criteria for equilibrium in thermodynamic systems; and (iii) provide the theoretical limits for the performance of engineering systems and processes. Items (i) and (ii) identify the role of the Second Law as a limiter in abstracting the differences in response of different materials via the constitutive relations. Item (iii) identifies the role of the Second Law enumerated by the concept of effectiveness, as a limiter to indicate how a system relaxes to equilibrium conditions with its surroundings while producing or consuming work.

## 1.5 FORMULATION OF ENTROPY PRODUCTION AND EXERGY DESTRUCTION

In the previous section, formulations of entropy transport and the Second Law were developed. In those equations, entropy production and exergy destruction were key parameters that characterized the efficiency of the thermal system or device. In this section, detailed expressions for these parameters will be developed, from which design methodologies can be established to reduce and minimize entropy production, thereby optimizing system performance.

### 1.5.1 CLOSED SYSTEM

From Section 1.3.1, for a closed system exchanging energy with its surroundings through work and heat transfer, the exergy balance equation can be expressed as

$$\left(1 - \frac{T_0}{T}\right)Q + (W + P_0 \dot{V}) - T_0 \dot{S}_{\text{gen}} = \dot{X} \quad (1.80)$$

Substitution for the heat flow and work term (relating compression/expansion work to pressure and change of volume) leads to

$$\left(1 - \frac{T_0}{T}\right)(\dot{U} + P\dot{V}) - P\dot{V} + P_0 \dot{V} - T_0 \dot{S}_{\text{gen}} = \dot{X} \quad (1.81)$$

Using thermodynamic relations for the exergy gradients leads to the following similar result as Equation 1.33,

$$-T_0 \dot{S}_{\text{gen}} = \dot{X} - \frac{\partial X}{\partial U} \dot{U} - \frac{\partial X}{\partial V} \dot{V} \quad (1.82)$$

which is similar to results derived previously for the convexity property of exergy in Section 1.3.1. The convexity property of exergy is intrinsically linked with the Second Law.

### 1.5.2 LINEAR ADVECTION EQUATION (WITHOUT DIFFUSION)

Entropy is transported throughout a problem domain through advection of scalar quantities like fluid momentum and internal energy. For example, scalar transport of fluid momentum leads to frictional irreversibilities, while transport of internal energy involves convective heat transfer and thermal irreversibilities. In this section, the exergy balance equation is developed with respect to scalar transport of a general scalar quantity,  $\eta(x,t)$ . The governing equation for the one-dimensional scalar advection equation without diffusion is given by

$$\frac{\partial \eta}{\partial t} + \frac{\partial f}{\partial x} = 0 \quad (1.83)$$

which represents pure advection and  $f(\eta)$  equals the “flux of  $\eta$ .”

According to the entropy concavity principle, the corresponding balance of entropy is given by

$$\frac{\partial S}{\partial t} - S' \frac{\partial \eta}{\partial t} \geq 0 \quad (1.84)$$

Substituting for the second term using Equation 1.83 and applying the chain rule,

$$\frac{\partial S}{\partial t} + S' f' \frac{\partial \eta}{\partial x} \geq 0 \quad (1.85)$$

The one-dimensional form of the entropy transport equation can also be expressed as

$$\dot{S}_{\text{gen}} = \frac{\partial S}{\partial t} + \frac{\partial F}{\partial x} \quad (1.86)$$

where  $F$  represents the “transfer of entropy with  $\eta$ .” It is a term arising from pure convective transport of  $\eta$ . Subtracting Equation 1.86 from Equation 1.85 and using the chain rule for  $\partial F/\partial x$  gives

$$(F' - S' f') \frac{\partial \eta}{\partial x} \geq 0 \quad (1.87)$$

The strict equality must be enforced to avoid violation of the Second Law, so a compatibility condition,  $F' = S' f'$ , is obtained as a constitutive restriction required by the Second Law. This result implies

$$\frac{\partial S}{\partial t} + \frac{\partial F}{\partial x} = 0 \quad (1.88)$$

and it follows that  $\dot{S}_{\text{gen}} = 0$ . This result is well known that reversible processes have zero entropy generation, although the previous derivation shows an additional requirement of compatibility between derivatives of entropy and its flux,  $F$ .

The corresponding balance of exergy equation is given by

$$\frac{\partial X}{\partial t} - X' \frac{\partial \eta}{\partial t} \leq 0. \quad (1.89)$$

Substituting for the second term using Equation 1.83 and applying the chain rule,

$$\frac{\partial X}{\partial t} + X' f' \frac{\partial \eta}{\partial x} \geq 0 \quad (1.90)$$

When the balance of exergy is written in an analogous form as entropy transport,

$$\dot{X}_{\text{gen}} = \frac{\partial X}{\partial t} + \frac{\partial G}{\partial x} \quad (1.91)$$

where  $G$  represents the “transfer of exergy with  $\eta$ .” It is a term resulting from the purely convective transfer of  $\eta$  across boundaries. Subtracting Equation 1.91 from Equation 1.90 and using the chain rule for  $\partial G/\partial x$  gives

$$(G' - X' f') \frac{\partial \eta}{\partial x} \leq 0 \quad (1.92)$$

In this case, the strict equality to satisfy the Second Law leads to an exergy compatibility condition,  $G' = X' f'$ , which is a constitutive restriction required by the Second Law. Also, it leads to

$$\frac{\partial X}{\partial t} + \frac{\partial G}{\partial x} = 0 \quad (1.93)$$

and it follows that  $\dot{X}_{\text{des}} = 0$ . In the next section, the previous procedure will be extended to scalar advection, including diffusion.

### 1.5.3 LINEAR ADVECTION EQUATION (WITH DIFFUSION)

In this section, a similar procedure will be used to derive the exergy destruction rate corresponding to scalar advection with diffusion. The governing equation for one-dimensional advection with diffusion is

$$\frac{\partial \eta}{\partial t} + \frac{\partial f}{\partial x} = D \frac{\partial^2 \eta}{\partial x^2} \quad (1.94)$$

where  $F = c\eta$  and  $c$  equals a constant advection velocity. The variable  $D$  refers to a diffusion coefficient. The corresponding balance of exergy is given by

$$\frac{\partial X}{\partial t} - X' \frac{\partial \eta}{\partial t} \leq 0 \quad (1.95)$$



Substituting for the second term using Equation 1.94 gives

$$\frac{\partial X}{\partial t} + X' \frac{\partial f}{\partial x} - DX' \frac{\partial^2 \eta}{\partial x^2} \leq 0 \quad (1.96)$$

Applying the compatibility condition and the chain rule,

$$\frac{\partial X}{\partial t} + \frac{\partial G}{\partial x} - D \frac{\partial}{\partial x} \left( X' \frac{\partial \eta}{\partial x} \right) + \underbrace{D \left( \frac{\partial \eta}{\partial x} \right)^2}_{\dot{X}_{\text{des}}} X'' \leq 0 \quad (1.97)$$

where  $G = cX$ . The exergy destruction term is labeled because it is the only term that must be nonnegative. To preclude any violation of the Second Law, the strict equality must be enforced because the magnitude of all terms on the left side is not known beforehand. Because  $X$  is convex in  $\eta$ , then  $X'' < 0$ . Hence, we arrive at two expressions for the Second Law corresponding to scalar advection with diffusion:

$$\dot{X}_{\text{des}} = D \left( \frac{\partial \eta}{\partial x} \right)^2 X'' \quad (1.98)$$

and

$$\dot{X}_{\text{des}} = D \frac{\partial}{\partial x} \left( X' \frac{\partial \eta}{\partial x} \right) - \left( \frac{\partial X}{\partial t} + \frac{\partial F}{\partial x} \right) \quad (1.99)$$

When imposing the principle of nonnegative exergy destruction, the first expression represents a constitutive restriction on the diffusion parameter:  $D \geq 0$ . The second expression represents the true exergy balance equation for this process. The third term contains the effects of the diffusive flux (diffusive transport of  $\eta$  such as fluid friction or heat conduction).

### 1.5.4 NAVIER–STOKES EQUATIONS

Since the Euler equations represent inviscid fluid motion, they are limiting cases of the Navier–Stokes equations, which describe the dynamic motion of a viscous, heat-conducting fluid. The Navier–Stokes equations can be expressed in the following tensor form,

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho V_j}{\partial x_j} = 0 \quad (1.100)$$

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_j} [E V_j + P V_j - \tau_{ji} V_i - q_j] = 0 \quad (1.101)$$

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_j} [EV_j + PV_j - \tau_{ji}V_i - q_j] = 0 \quad (1.102)$$

where  $V_j$  refers to the velocity component in the  $j$ -coordinate direction and where  $E = \rho u + \frac{1}{2} \rho V^2$  represents the total energy (internal plus kinetic energy).

These equations are underdetermined, because they contain more unknowns than equations. Consequently, additional information is required. The constitutive relations provide the additional closure information. Typically, these include the ideal gas law,  $P = \rho RT$ , the assumption of a thermally perfect gas ( $c_v$  depends only on temperature,  $T$ ), and Fourier's relation for heat conduction,

$$q_j = -k \frac{\partial T}{\partial x_j} \quad (1.103)$$

Also, the following constitutive relations will be used for the viscous stress tensor of a Newtonian fluid,

$$\tau_{ji} = \mu \left( \frac{\partial V_j}{\partial x_i} + \frac{\partial V_i}{\partial x_j} \right) + \lambda \frac{\partial V_j}{\partial x_j} \delta_{ji} \quad (1.104)$$

where  $\delta_{ij}$  is the Kronecker delta function. The entropy transport equation associated with processes modeled by the Navier–Stokes equations is

$$\dot{S}_{\text{gen}} = \frac{\partial S}{\partial t} + \frac{\partial F_j}{\partial x_j} + \frac{\partial}{\partial x_j} \left( \frac{q_j}{T} \right) \quad (1.105)$$

where  $S = \rho s$  and  $F_j = \rho s V_j$ . Because one more unknown has been added (specific entropy,  $s$ ), another constitutive relation is needed, namely, the functional relation between entropy and the other field variables. This relation must satisfy the concavity property of entropy. For an ideal gas, the entropy functional (from thermodynamics; written in nondimensional form) is

$$s(\rho, T) = \frac{1}{\gamma - 1} \ln T - \ln \rho \quad (1.106)$$

where  $\gamma$  is the ratio of specific heats.

Because the state variables include mass, momentum, and total energy, it is convenient to define an algebraic state vector,  $q^T \equiv \{\rho, \rho V_1, \rho V_2, \rho V_3, \rho E\}$ , so that the entire set of conservation equations reduces to

$$\frac{\partial q}{\partial t} + \frac{\partial f_k}{\partial x_k} = 0 \quad (1.107)$$

where  $f$  is an algebraic flux vector. The functional relation for the entropy is  $S = S(q)$ , and the concavity property is expressed as

$$S_0 - S - \left. \frac{\partial S}{\partial q} \right|_0 \cdot (q_0 - q) \geq 0 \quad (1.108)$$

where equality holds if and only if  $q = q_0$ . The transient generalization of Equation 1.108 is the following extension of Equation 1.53 for the state variables:

$$\frac{\partial S}{\partial t} - \frac{\partial S}{\partial q} \cdot \frac{\partial q}{\partial t} \geq 0 \quad (1.109)$$

Replacing  $\partial q/\partial t$  and rearranging terms yields the following entropy generation rate:

$$\dot{S}_{\text{gen}} = \frac{\tau_{ji}}{T} \frac{\partial V_i}{\partial x_j} - \frac{q_j}{T^2} \frac{\partial T}{\partial x_j} \quad (1.110)$$

This result may be obtained by other means (Müller, 1985), but the approach here aims to emphasize the intrinsic connection between entropy concavity and the entropy generation equation in the Second Law of Thermodynamics.

Given the Fourier relation and the formula for the viscous stress tensor, the Second Law requires that

$$k \geq 0 \quad \mu \geq 0 \quad \lambda + \frac{2}{3}\mu \geq 0 \quad (1.111)$$

These results are well known, and they have been documented in past literature dealing with thermodynamics and kinetic theory (Bird, 1976, 1994; Chapman and Cowling, 1990; Müller and Ruggeri, 1998). The origin of the inequalities arrives from the mathematical property of entropy concavity, as a function of the field variables. Two expressions were obtained for the entropy generation: one that places restrictions on the constitutive relations; the other represents the entropy transport equation, Equation 1.105. The corresponding exergy destruction can be obtained by the Gouy–Stodola theorem. It may also be obtained directly by defining exergy from the concavity of entropy and then constructing the appropriate balance equation.

Consider the one-dimensional Navier–Stokes equations with the flux vectors separated into convective and dissipative parts as follows:

$$\frac{\partial q}{\partial t} + \frac{\partial f}{\partial x} + \frac{\partial f^v}{\partial x} = 0 \quad (1.112)$$

where

$$f^v = \begin{bmatrix} 0 \\ -\tau \\ -V\tau + q \end{bmatrix} \quad \begin{aligned} \tau &= \frac{4}{3}\mu \frac{\partial V}{\partial x} \\ q &= -k \frac{\partial T}{\partial x} \end{aligned} \quad (1.113)$$

From Equation 1.106 and  $S = \rho s$ , the row vector of entropy derivatives is

$$S_{,q} = \left( s + \frac{V^2}{2T} - \frac{\gamma}{\gamma-1}, -\frac{V}{T}, \frac{1}{T} \right) \quad (1.114)$$

Then the exergy can be written as

$$X(q) \equiv T_0[S_0 - S - S_{,q_0} \cdot (q_0 - q)] \quad (1.115)$$

where the subscript comma notation refers to differentiation.

The exergy balance equation and exergy destruction rate can be obtained by starting with the convexity relation for exergy in Section 1.3.1, and substituting for the time derivatives to give

$$\frac{\partial X}{\partial t} - X_{,q} \cdot \frac{\partial q}{\partial t} = \frac{\partial X}{\partial t} + X_{,q} \cdot \left( \frac{\partial f}{\partial x} + \frac{\partial f^v}{\partial x} \right) \quad (1.116)$$

where  $X_{,q} = T_0(S_{,q_0} - S_{,q})$ . Invoking the chain rule and the corresponding compatibility condition leads to

$$X_{,q} \cdot \frac{fS}{\partial q} \cdot \frac{\partial q}{\partial x} = G_{,q} \cdot \frac{\partial q}{\partial x} = \frac{\partial G}{\partial x} \quad (1.117)$$

Also, note that

$$X_{,q} \cdot \frac{\partial f^v}{\partial x} = T_0 S_{,q_0} \cdot \frac{\partial f^v}{\partial x} - T_0 S_{,q} \cdot \frac{\partial f^v}{\partial x} \quad (1.118)$$

and

$$T_0 S_{,q_0} \cdot f^v x = \left( T_0 s_0 - \frac{T_0 \gamma}{\gamma-1}, 0, 1 \right) \cdot \frac{\partial}{\partial x} \begin{bmatrix} 0 \\ -\tau \\ -V\tau + q \end{bmatrix} = \frac{\partial}{\partial x} (q - V\tau) \quad (1.119)$$

In addition, the following equation can be derived:

$$S_{,q} \cdot \frac{\partial f^v}{\partial x} = \frac{\partial}{\partial x} \left( \frac{q}{T} \right) - \frac{\tau}{T} \frac{\partial V}{\partial x} + \frac{q}{T^2} \frac{\partial T}{\partial x} \quad (1.120)$$

Substituting these results into Equation 1.116 leads to

$$\frac{\partial X}{\partial t} + \frac{\partial S}{\partial U} - \frac{\partial V\tau}{\partial x} + \frac{\partial}{\partial x} \left[ \left( 1 - \frac{T_0}{T} \right) q \right] + \underbrace{\frac{T_0}{T} \tau \frac{\partial V}{\partial x} - \frac{T_0}{T^2} q \frac{\partial T}{\partial x}}_{\text{exergy destruction}} = 0 \quad (1.121)$$

This identifies the exergy destruction term, and by comparison with Equation 1.110, note that  $\dot{X}_{\text{des}} = T_0 \dot{S}_{\text{gen}}$ . The formula for the exergy destruction becomes

$$\dot{X}_{\text{des}} = - \left( \frac{\partial X}{\partial t} + \frac{\partial G}{\partial x} \right) + \frac{\partial V \tau}{\partial x} - \frac{\partial}{\partial x} \left[ \left( 1 - \frac{T_0}{T} \right) q \right] \quad (1.122)$$

Because the equations of fluid flow presume local thermodynamic equilibrium, there is no inconsistency when applying classical thermodynamic principles as represented by entropy concavity and exergy convexity. These principles are mathematical properties, not limited to thermodynamics.

To apply the Second Law of Thermodynamics for availability analyses in practice requires the balance of exergy equation and a functional formula for exergy. The construction of the entropy and exergy balance equations has been derived without specifying an entropy formula, except for the case of an ideal gas. To obtain the proper formula for  $S = S(\xi)$ , general optimization principles can be applied. For example, Jaynes' Maximum Entropy Principle (Jaynes, 1991; Levine and Tribus, 1979) is based on a generalization of the Second Law, when applied to constrained equilibria. Kapur and Kesavan (1992) provide a comprehensive and detailed procedure for generalized entropy optimization principles. If the domain of the dependent variable  $\xi$  is known, then the Maximum Entropy Principle obtains the proper form of entropy for a probability distribution function that quantifies fluctuations in that variable about its mean value. For example, if  $\xi \in [0, \infty)$ , then the MaxEnt principle prescribes  $S = \ln \xi$ . If the dependent variable  $u \in (-\infty, \infty)$ , then MaxEnt prescribes  $S = -u^2/2\sigma^2$ , where  $2\sigma^2 = 1$  is set without loss of generality. The Second Law, in essence, provides a way to (i) obtain a formula for entropy, and (ii) construct the balance equation for entropy (Liu, 1972; Müller, 1967).

The mathematical property of entropy concavity has served multiple purposes, including restricting the types of constitutive relations allowed for modeling of real-world processes. The Second Law is a powerful concept that determines how physical processes can be modeled, so that mathematical models reflect physical reality. This chapter has developed formulae for the balance of entropy and exergy, as required to enforce the restrictions prescribed by the Second Law. The advantage of using exergy balances (instead of entropy) is that they provide a concept that unifies the First and Second Laws into a single principle. This unified approach provides the basis for constructing a single metric across the spectrum of possible thermophysical systems and processes.

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