1 Thermodynamics: Generalized Available Energy and Availability or Exergy

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1.1 Introduction

Ever since Clausius postulated that "the energy of the universe is constant" and "the entropy of the universe strives to attain a maximum value," practically every scientist and engineer shares the beliefs that: (i) Thermodynamics is a statistical theory, restricted to phenomena in macroscopic systems in thermodynamic equilibrium states; and (ii) entropy – the concept that distinguishes thermodynamics from mechanics – is a statistical measure of ignorance, ultimate disorder, dispersion of energy, erasure of information, or other causes, and not an inherent property of matter like rest mass, energy, etc.

These beliefs stem from the conviction that the "known laws" of mechanics (classical or conventional quantum) are the ultimate laws of physics and from the fact that statistical theories of thermodynamics yield accurate and practical numerical results about thermodynamic equilibrium states.

Notwithstanding the conviction and excellent numerical successes, the almost-universal efforts to compel thermodynamics to conform to statistical and other nonphysical explanations, and to restrict it only to thermodynamic equilibrium states [1–3] are puzzling in the light of many accurate, reproducible, and nonstatistical experiences and many phenomena that cannot possibly be described in terms of thermodynamic equilibrium states.

Since the advent of thermodynamics, many academics and practitioners have questioned the clarity, unambiguity, and logical consistency of traditional expositions of the subject. Some of the questions raised are: (i) Why is thermodynamics restricted to thermodynamic equilibrium states only, given that the universally accepted and practical statements of energy conservation and entropy nondecrease are demonstrably time dependent? (ii) Why do we restrict thermodynamics to macroscopic systems, given that Gibbsian statistics [4, 5] and systems in states with negative temperatures [6] prove beyond a shadow of a doubt that thermodynamics is valid for any system? (iii) How can any of the proposed statistical expressions of entropy be accepted if none conforms to the requirements that must be satisfied by the entropy of thermodynamics [7]? and (iv) Why do so many professionals continue to believe that thermodynamic equilibrium is a state of ultimate disorder despite the fact that both experimental and theoretical evidence indicates that such a state represents ultimate order [8, 9]?

The purposes of this chapter are as follows: (i) to present a brief summary of a novel exposition of thermodynamics, (ii) to provide the rigorous definition of generalized available energy, and (iii) to define and illustrate by specific applications the concept of availability or exergy. The novel exposition was conceived by Gyftopoulos and Beretta [10].

1.2 Summary of Basic Concepts

1.2.1 Systems, Properties, and States

A well-defined *system* is a collection of constituents determined by the following specifications:

1. the type and the range of values of the *amount* of each *constituent*,
2. the type and the range of values of the *parameters* that fully characterize the *external forces* exerted on the constituents by bodies other than the constituents, such as the parameters that describe the size and geometrical shape of an airtight container, and an applied electrostatic field,
3. the *internal forces* between constituents,
4. the *internal constraints* that characterize the interconnections between separated parts, such as the condition that the overall volume of the two variable-volume parts be fixed, and that define the modeling assumptions such as the condition that some or all chemical reactions be inactive.

Everything that is not included in the system is called the *environment* or the *surroundings* of the system.

For a system consisting of r different types of constituents, we denote their amounts by the vector $\boldsymbol{n} = \{n_1, n_2, \ldots, n_r\}$. For a system with external forces described by s parameters, we denote the parameters by the vector $\boldsymbol{\beta} = \{\beta_1, \beta_2, \ldots, \beta_s\}$. One parameter may be volume V.

Two systems are *identical* if they consist of the same types of constituents, experience the same internal and external forces, and have the same ranges of values of amounts of constituents and parameters and the same constraints. If any of these identities is not valid, the two systems are *different*.

At any instant in time, the amount of each type of constituent and the parameters of each external force have specific values within the corresponding ranges of the system. By themselves, these values do not suffice to characterize completely the condition of the system at that time. We also need the values of all the properties at the same instant in time. Each *property* is an attribute that can be evaluated at any given instant of time by means of a set of measurements and operations that are performed on the system and result in a numerical value – the *value* of the property. This value is independent of the measuring devices, other systems in the environment, and other instants in time.

Two properties are *independent* if the value of one can be varied without affecting the value of the other. Otherwise, the two properties are *interdependent*. For example, position and velocity of a molecule are independent properties, whereas speed and kinetic energy of a molecule in classical mechanics are interdependent.

For a given system, the values of the amounts of all the constituents, the values of all the parameters, and the values of a complete set of independent properties encompass all that can be said about the system at an instant in time and about the results of any measurements or observations that may be performed on the system at that same instant in time. As such, the collection of all these values constitutes a complete characterization of the system at that instant in time. We call this characterization at an instant in time the *state* of the system.

1.2.2 Changes of State in Time

The state of a system may change in time spontaneously because of the internal dynamics of the system, or as a result of interactions with other systems, or both.

A system that experiences only spontaneous changes of state, that is, a system that does not affect the state of its environment, is called *isolated*. In general, a system that is not isolated interacts with other systems in a number of different ways, some of which may result in net flows of properties from one system to another.

The relation that describes the evolution of the state of a system as a function of time is the *equation of motion*. Such an equation was discovered by Beretta et al. [11, 12] but is not discussed in this chapter.

Rather than through the explicit time dependence, which requires the complete equation of motion, here a change of state is described in terms of the *end states*, that is, the initial and the final states of the system, the *modes of interaction* that are active during the change of state, and conditions on the values of properties of the end states that are consequences of the laws of thermodynamics, that is, conditions that express, not all, but most of the general and well-established features of the complete equation of motion. Each mode of interaction is characterized by means of well-specified net flows of properties across the boundaries of the interacting systems. For example, after the properties energy and entropy are defined, we will see that some modes of interaction involve the flow of energy across the boundaries of the interacting systems without any flow of entropy, whereas other modes of interaction involve the flow of both energy and entropy. Among the conditions on the values of properties of the end states that are consequences of the laws of thermodynamics – conditions that express well-established features of time-dependent behavior of systems – we will see that the energy change of a system must equal the energy transferred into the system, and that its entropy change must be greater than or at least equal to the entropy transferred into the system.

The end states and the modes of interactions associated with a change of state of a system specify a *process*. The modes of interactions may be used to classify processes into different types. For example, a process that involves no interactions and, therefore, no flows across the boundary of the system is called a *spontaneous process*. Again, a process that involves interactions that result in no external effects other than a change in elevation of a weight (or an equivalent mechanical effect) is called a *weight process*.

Another important classification of processes is in terms of the possibility of annulling all their effects. A process may be either reversible or irreversible. A process is *reversible* if it can be performed in at least one way such that both the system and its environment can be restored to their respective initial states. A process is *irreversible* if it is impossible to perform it in such a way that both the system and its environment can be restored to their respective initial states.

We will see that any irreversible process involves the irrecoverable degradation of a valuable resource, whereas no reversible process involves such a degradation. For this reason, putting aside all economic, social, and environmental considerations, we sometimes say that a reversible process is the "best possible." For example, for a given change of state of a system, an irreversible weight process results in either a smaller raise or a larger drop in the weight than do the corresponding results of a reversible process.

In general, a system A that undergoes a process from state A_1 at time t_1 to state A_2 at time t_2 is well defined at these two times but is not necessarily well defined during the lapse of time between t_1 and t_2. The reason is that the interactions that induce the change of state may involve such temporary alterations of internal and external forces that no system A can be defined during the period t_1 to t_2. Said more formally, in the course of interactions, the constituents of a system may not be separable from the environment or, if they are, the states of the system may be correlated with the states of other systems. Nevertheless, at the end of the process, the system becomes again well defined, and its state is again uncorrelated.[1]

1.2.3 Energy and Energy Balance

Energy is a concept that underlies our understanding of all physical phenomena, yet its meaning is subtle and difficult to grasp. It emerges from a fundamental principle known as the first law of thermodynamics.

The *first law* asserts that *any two states of a system may always be interconnected by means of a weight process*[2] *and, for a given weight subject to a constant gravitational acceleration, that the change in elevation during such a process is fixed uniquely by the two states of the system.*

The main consequence of this law is that every system A in any state A_1 has a property called *energy*, denoted by the symbol E_1. The energy E_1 of any state A_1 can be evaluated by means of an auxiliary weight process that interconnects state A_1 and a reference state A_o to which is assigned a fixed reference value E_o, and the expression

$$E_1 - E_o = -Mg\,(z_1 - z_o)\,, \tag{1.1}$$

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[1] We say that a system is well defined and its constituents are *separable from the environment* if the forces exerted on the constituents by a body not included in the system do not depend explicitly on the coordinates of constituents of that body. We say that a state is *uncorrelated* from the state of the environment if none of the values of the properties of the system depends on the values of properties of systems in the environment. All statements and conclusions in this chapter refer to well-defined systems in uncorrelated states.

[2] Other processes equivalent to a weight process are discussed in Chap. 3 of [10].

where M is the mass of the weight, g is the gravitational constant, and z is the elevation of the weight. The energy E_2 of another state A_2 can be evaluated by a similar procedure so that

$$E_2 - E_o = -Mg\,(z_2 - z_o)\,. \tag{1.2}$$

Moreover, subtracting Eq. (1.1) from Eq. (1.2), we find

$$E_2 - E_1 = -Mg\,(z_2 - z_1)\,, \tag{1.3}$$

where we keep the negative sign in front of $Mg\,(z_2 - z_1)$ in order to emphasize that, the larger value of z_2, the smaller value of E_2, and vice versa.

Energy is an *additive* property, namely, the energy of a system consisting of two or more subsystems equals the sum of the energies of the subsystems, and this holds for all combinations of states of the subsystems. Moreover, energy has the same value at the final time as at the initial time whenever the system experiences a zero-net-effect weight process, or remains invariant in time whenever the process is spontaneous. In either of these two processes, $z_2 = z_1$ and $E\,(t_2) = E\,(t_1)$ for time t_2 greater than t_1, that is, energy is *conserved.*

Because of additivity, and because any process of a system can always be thought of as part of a zero-net-effect weight process of a composite system consisting of all the interacting systems, the conclusion that, as a function of time, energy is invariant is known as the *principle of energy conservation.*

Energy can be transferred between systems by means of interactions. Denoting by $E^{A\leftarrow}$ the net amount of energy transferred from the environment to system A as a result of all the interactions involved in a process that changes the state of A from A_1 to A_2, we derive an extremely important analytical tool, the *energy-balance equation* or, simply, the *energy balance.* This equation is based on the additivity of energy and on the principle of energy conservation. It requires that, as a result of a process, the change in the energy of the system from E_1 to E_2 must be equal to the net amount of energy $E^{A\leftarrow}$ transferred into the system, namely,

$$E_2 - E_1 = E^{A\leftarrow}. \tag{1.4}$$

For all applications of thermodynamics, relativistic affects are negligible, and the mass of a system satisfies a *mass balance* of the form

$$m_2 - m_1 = m^{A\leftarrow}, \tag{1.5}$$

where m_1 and m_2 are the masses of states A_1 and A_2, respectively, and $m^{A\leftarrow}$ is the mass flow into system A from other systems in the environment.

1.2.4 Types of States

Because the number of independent properties of a system is infinite even for a system consisting of a single particle with a single translational degree of freedom – a single variable that fixes the configuration of the system in space – and because most properties can vary over a range of values, the number of possible states of a system is infinite.

To facilitate the discussion of these states, we classify them into different categories according to their evolutions in time. This classification brings forth many important aspects of physics, and provides a readily understandable motivation for the introduction of the second law of thermodynamics. We consider four types of states: unsteady, steady, nonequilibrium, and equilibrium. Moreover, we further classify equilibrium states into three types: unstable, metastable, and stable.

An *unsteady state* is one that changes as a function of time because of interactions of the system with other systems. A *steady state* is one that does not change as a function of time, despite interactions of the system with other systems in the environment. A *nonequilibrium state* is one that changes spontaneously as a function of time, that is, a state that evolves in time without any effects on or interactions with any other systems. An *equilibrium state* is one that does not change as a function of time while the system is isolated. An *unstable equilibrium state* is an equilibrium state that may be caused to proceed spontaneously to a sequence of entirely different states by means of a minute and short-lived interaction that has only an infinitesimal temporary effect on the state of the environment. A *metastable equilibrium state* is an equilibrium state that may be changed to an entirely different but compatible state without leaving net effects in the environment of the system, but this can be done only by means of interactions that have a finite temporary effect on the state of the environment. A *stable equilibrium state* is an equilibrium state that can be altered to a different but compatible state only by interactions that leave net effects in the environment of the system.

Starting either from a nonequilibrium state or from an equilibrium state that is not stable, a system can be made to raise a weight without leaving any other net changes in the state of the environment. In contrast, experience shows that from some other types of states – they turn out to be stable equilibrium states – such a raise of a weight is impossible. This impossibility is one of the most striking consequences of the first and the second laws of thermodynamics.

1.2.5 Stable Equilibrium States

The existence of stable equilibrium states is not self-evident. It is the essence of the second law first proposed by Hatsopoulos and Keenan [13]. In the absence of internal mechanisms, such as chemical reactions or internal interconnections, capable of causing spontaneous changes in the values of the amounts of constituents and the parameters, the *second law* asserts that, *among all the states of a system with given values of the energy, the amounts of constituents, and the parameters, there exists one and only one stable equilibrium state.* A more general statement of the second law is this: *Among all the states of a system that have a given value E of the energy and are compatible with a given set of values* $\mathbf{n}$ *of the amounts of constituents and* $\boldsymbol{\beta}$ *of the parameters, there exists one and only one stable equilibrium state. Moreover, starting from any state of a system, it is always possible to reach a stable equilibrium state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process.*

The existence of stable equilibrium states for various conditions of matter has many theoretical and practical consequences. One consequence is that, starting from any stable equilibrium state of any system, no energy can be transferred to a weight in a weight process in which the values of amounts of constituents and parameters of the system experience no net changes. This consequence is often referred to as the *impossibility of a perpetual-motion machine of the second kind*. In some expositions of thermodynamics, it is taken as the statement of the second law. In this chapter, it is only one aspect of the first and the second laws.

Other consequences are discussed immediately below.

1.2.6 Reservoir and Generalized Available Energy

We define a *reservoir* as an idealized kind of system with a behavior that approaches the following three limiting conditions:

1. It passes through stable equilibrium states only.
2. In the course of finite changes of state, it remains in mutual stable equilibrium with a duplicate of itself that experiences no such changes.
3. At constant values of amounts of constituents and parameters of each of two reservoirs initially in mutual stable equilibrium, energy can be transferred reversibly from one reservoir to the other with no net effects on any other system.

Two systems are in *mutual stable equilibrium* if their composite system is in a stable equilibrium state.

Given a system A in state A_1 and a reservoir R with fixed values of amounts of constituents and parameters, we consider the composite of A and R and evaluate the largest amount of energy that can be transferred to a weight in a weight process for the composite of A and R. This amount is called *available energy* and is denoted by Ω_1^R. After Ω_1^R is transferred out of the composite, A and R are in mutual stable equilibrium, that is, the composite of A and R is in a stable equilibrium state.

The first scientist who raised the question about the largest amount of energy that can be transferred to a weight in a weight process for the composite of a system A and a reservoir R was Carnot [14]. He restricted his investigation, however, to A, which was also a reservoir. His results constitute the seminal ideas – the conception event – of the science of thermodynamics. The disclosure of the available energy Ω_1^R as a property is a generalization of the results of Carnot in that system A need not be a reservoir and state A_1 need not be a stable equilibrium state. Available energy can be assigned to any system in any state.

Another property, the *generalized available energy*, may also be defined as a property of a system A in any state A_1. Its definition is identical to that of available energy except that the final state A_2 of system A corresponds to arbitrarily assigned values of the amounts of constituents and parameters that differ in general from those of state A_1. Said differently, generalized available energy involves exchanges of constituents and changes in parameters in addition to other interactions. The generalized available energy of state A_1 is defined with respect to a reservoir R and the arbitrarily assigned values of the amounts of constituents and parameters. For simplicity, we denote it by the same symbol, Ω_1^R, as that of the available energy. We distinguish it from the available energy of state A_1 with respect to reservoir R by name and context.

The difference between the generalized available energies, $\Omega_1^R - \Omega_2^R$, of two states A_1 and A_2 is equal to the energy that can be exchanged with a weight in a reversible weight process of the composite AR of system A and reservoir R as system

A goes from state A_1 to state A_2. On denoting the energy exchanged with the weight by $(W_{12}^{AR\rightarrow})_{\text{rev}}$, we have

$$(W_{12}^{AR\rightarrow})_{\text{rev}} = \Omega_1^R - \Omega_2^R. \tag{1.6}$$

The value of $(W_{12}^{AR\rightarrow})_{\text{rev}}$ is positive if energy is transferred from the composite AR to the weight, and then it is the largest energy transfer to the weight that can be achieved as system A goes from state A_1 to state A_2. It is negative if energy is transferred from the weight to the composite AR, and then it is the least energy transfer that is required for achieving the change of A from state A_1 to state A_2.

Two important relations exist between the energies E_1 and E_2 and the generalized available energies Ω_1^R and Ω_2^R of any two given states A_1 and A_2 of a system A. By virtue of the first law, the two states can always be interconnected by means of a weight process for system A alone. But the first law determines neither the direction of the weight process nor its reversibility. By contrast, a comparison between the difference in energies and the difference in generalized available energies of the two states determines both the direction and the reversibility of the process. Specifically, if

$$\Omega_1^R - \Omega_2^R = E_1 - E_2, \tag{1.7}$$

then a weight process for A alone is possible both from A_1 to A_2 and from A_2 to A_1 and is reversible. However, if

$$\Omega_1^R - \Omega_2^R > E_1 - E_2, \tag{1.8}$$

then a weight process for A alone is possible only from A_1 to A_2 and is irreversible.

For spontaneous or zero-net-effect weight processes, energy conservation implies that $E_2 = E_1$ or, emphasizing the time dependence, $E(t_2) = E(t_1)$ for $t_2 > t_1$. If applied to these processes, Eq. (1.7) and relation (1.8) reveal the following results. If the process is reversible, then $\Omega_2^R = \Omega_1^R$ or, emphasizing the time dependence, $\Omega^R(t_2) = \Omega^R(t_1)$ for $t_2 > t_1$, namely, the generalized available energy is conserved. If the spontaneous or zero-net-effect weight process is irreversible, then $\Omega_2^R < \Omega_1^R$ or $\Omega^R(t_2) < \Omega^R(t_1)$ for $t_2 > t_1$, namely, the generalized available energy is not conserved. Said differently, in the course of an irreversible, zero-net-effect weight process a system loses some of its potential ability to transfer energy to a weight. Whereas energy is conserved, the amount of energy that can be transferred to a weight in a weight process – the potential of a system to perform useful tasks – is not conserved. This potential cannot be created but may be dissipated to a lesser or larger degree, depending on whether the process is a little or a lot irreversible. A quantitative measure of irreversibility can be expressed in terms of the property entropy discussed in the next section.

A noteworthy feature of E and Ω^R is that both are defined for any state of any system, regardless of whether the state is unsteady, steady, nonequilibrium, equilibrium, metastable equilibrium, or stable equilibrium, and regardless of whether the system has many degrees of freedom or one degree of freedom, or whether its size is large or small.

A disadvantage of Ω^R is that it depends both on the state of the system and on the reservoir R. As discussed in the next section, we gain independence of the reservoir, without losing additivity, by considering the difference between energy and generalized available energy.

1.2.7 Entropy and Entropy Balance

An important consequence of the two laws of thermodynamics is that every system A in any state A_1, with energy E_1 and generalized available energy Ω_1^R with respect to an auxiliary reservoir R, has a property called *entropy*, denoted by the symbol S_1. Entropy is a property in the same sense that energy is a property or momentum is a property. It can be evaluated by means of the auxiliary reservoir R, a reference state A_o, with energy E_o and generalized available energy Ω_o^R, to which is assigned a fixed reference value S_o and the expression

$$S_1 = S_o + \frac{1}{c_R}\left[(E_1 - E_o) - \left(\Omega_1^R - \Omega_o^R\right)\right], \tag{1.9}$$

where c_R is a well-defined positive constant. For the given auxiliary reservoir R, c_R is selected in such a way that the values of entropy found by means of Eq. (1.9) are independent of the reservoir.[3] In other words, despite the dependence of the value of the difference of generalized available energies, $\Omega_1^R - \Omega_o^R$, on the selection of the reservoir R, we can show that there is a constant property c_R of reservoir R that makes the right-hand side of Eq. (1.9) independent of R. Thus S is a property of system A only, in the same sense as energy E is a property of system A only. In due course, the concept of temperature is defined as a property of stable equilibrium states. Then we show that the temperature of a reservoir is constant and that c_R is equal to the constant temperature of the reservoir R.

The entropy S_2 of a state A_2 is given by an expression similar to that of A_1, namely,

$$S_2 = S_o + \frac{1}{c_R}\left[(E_2 - E_o) - \left(\Omega_2^R - \Omega_o^R\right)\right]. \tag{1.10}$$

Moreover, subtracting Eq. (1.9) from (1.10), we find

$$S_2 = S_1 + \frac{1}{c_R}\left[(E_2 - E_1) - \left(\Omega_2^R - \Omega_1^R\right)\right], \tag{1.11}$$

or, equivalently,

$$\Omega_2^R - \Omega_1^R = E_2 - E_1 - c_R(S_2 - S_1). \tag{1.12}$$

Like energy, entropy is an additive property, namely, the entropy of a system consisting of two or more subsystems equals the sum of the entropies of the subsystems and this holds for all combinations of states of the subsystems. Whereas energy remains constant in time whenever the system experiences either a spontaneous process or a zero-net-effect weight process, Eqs. (1.7) and (1.11) show that the entropy remains constant in time if the process is reversible. In the course of an irreversible either spontaneous or zero-net-effect weight process, relation (1.8) and Eq. (1.11) show that the entropy increases in time, and part of the potential ability of the system

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[3] The precise definition of c_R and the proof that S_1 is independent of the reservoir are not summarized here for brevity. They are given in [10].

to transfer energy to a weight is destroyed. Because of additivity and because any process of a system can always be thought of as part of a spontaneous process of a composite system consisting of all the interacting systems, the conclusion that, as time proceeds, entropy can either be created, if the process is irreversible, or remain constant, if the process is reversible, but can never be destroyed is of great generality and practical importance. It is known as the *principle of entropy nondecrease.* The entropy created as time proceeds during an irreversible process is called *entropy generated by irreversibility* or *entropy production due to irreversibility*. It is positive.

Like energy, entropy can be transferred between systems by means of interactions. Denoting by $S^{A\leftarrow}$ the net amount of entropy transferred from systems in the environment to a system A as a result of all the interactions involved in a process in which the state of A changes from A_1 to A_2, we derive another extremely important analytical tool, the *entropy-balance* equation. This equation is based on the additivity of entropy and on the principle of entropy nondecrease. It requires that the change in the entropy of the system from S_1 to S_2 be equal to the net amount of entropy $S^{A\leftarrow}$ transferred into the system, plus the positive amount of entropy S_{irr} generated by irreversibility inside A in the course of the process, that is,

$$S_2 - S_1 = S^{A\leftarrow} + S_{\mathrm{irr}}. \tag{1.13}$$

The value of $S^{A\leftarrow}$ is positive if entropy is transferred into A and negative if entropy is transferred out of A.

It is worth repeating that S is defined for any state of any system because energy E and generalized available energy Ω^R are defined for any state of any system. Thus, like energy, entropy is defined for all states, that is, unsteady, steady, nonequilibrium, equilibrium, metastable equilibrium, and stable equilibrium, and for all systems, that is, systems with many degrees of freedom and systems with few degrees of freedom, including a single particle with a single translational degree of freedom or a single spin because both energy and generalized available energy are defined for all these systems, and for all these states.

The dimensions of entropy are determined by the dimensions of both energy and the property c_R of the auxiliary reservoir. We can show that the dimension c_R is independent of the dimensions of mass, length, and time, but the same as the dimension of temperature (defined later). The unit of c_R chosen in the International System of units is the Kelvin, denoted by K. Another unit is the Rankine, denoted by R, where 1 R = (5/9) K. Entropy values are expressed in many different units such as joules per Kelvin (J/K), kilocalorie per Kelvin (kcal/K), and British thermal unit per Rankine (Btu/R). In particular, it turns out that 1 Btu/lb R = 1 kcal/kg K.

1.2.8 The Fundamental Relation

In the absence of internal mechanisms capable of altering the values of the amounts of constituents and the parameters, that is, in the absence of chemical reactions, nuclear reactions, and other types of internal interconnections, a system admits an indefinite number of states that have given values of the energy E, the amounts of constituents $n_1, n_2, \ldots, n_r$, and the parameters $\beta_1, \beta_2, \ldots, \beta_s$. Most of these states are nonequilibrium, metastable equilibrium, and equilibrium, and, according to the second law, only one is a stable equilibrium state. It follows that the value of any property P of the system in a stable equilibrium state is uniquely determined by the values of $E, n_1, n_2, \ldots, n_r$ and $\beta_1, \beta_2, \ldots, \beta_s$, that is, can be written as a function of the form

$$P = P(E, n_1, n_2, \ldots, n_r, \beta_1, \beta_2, \ldots, \beta_s) . \tag{1.14}$$

This result, known as the *stable-equilibrium-state principle* or simply the *state principle*, expresses a fundamental physical feature of the stable equilibrium states of the system and implies the existence of interrelations among the properties at each of these states.

A system in general has a very large number of independent properties. When we focus on the special family of states that are stable equilibrium, however, the state principle asserts that the value of each of these properties is uniquely determined by the values of $E, \boldsymbol{n}, \boldsymbol{\beta}$. In contrast, for states that are not stable equilibrium, the values of $E, \boldsymbol{n}, \boldsymbol{\beta}$ are not sufficient to specify the values of all the independent properties.

When written for the entropy S of stable equilibrium states, Eq. (1.14) becomes

$$S = S(E, n_1, n_2, \ldots, n_r, \beta_1, \beta_2, \ldots, \beta_s) \tag{1.15}$$

and is known as the *fundamental stable-equilibrium-state relation for entropy* or simply the *fundamental relation*. We can show that the function $S(E, \boldsymbol{n}, \boldsymbol{\beta})$ admits partial derivatives of all orders and therefore that any difference between the entropies of two stable equilibrium states may be expressed in the form of a Taylor series in terms of the partial derivatives of $S(E, \boldsymbol{n}, \boldsymbol{\beta})$ at one stable equilibrium state, and differences in the values of the energy, amounts of constituents, and parameters of the two stable equilibrium states.

The function $S(E, \boldsymbol{n}, \boldsymbol{\beta})$ is concave in each of the variables $E, n_1, n_2, \ldots, n_r$. It is concave in each of the parameters $\beta_1, \beta_2, \ldots, \beta_s$, which are additive, like volume, and it is also concave collectively with respect to all the variables $E, n_1, n_2, \ldots, n_r$, and the parameters $\beta_1, \beta_2, \ldots, \beta_s$, which are additive. Concavity implies that $(\partial^2 S/\partial E^2)_{n,\beta} \leq 0$, $(\partial^2 S/\partial n_i^2)_{E,n,\beta} \leq 0$ for each i, $(\partial^2 S/\partial \beta_j^2)_{E,n,\beta} \leq 0$ for each additive β_j, and some other necessary conditions on all the second-order derivatives of the fundamental relation.

Using the second law, we assert that the entropy of each unique stable equilibrium state is larger than that of any other state with the same values of $E, n_1, n_2, \ldots, n_r$, and $\beta_1, \beta_2, \ldots, \beta_s$. This assertion is known as the *highest-entropy principle*. This principle is extremely useful in establishing conditions that must be satisfied by properties of systems in stable equilibrium states.

Equation (1.15) may be solved for E as a function of $S, n_1, n_2, \ldots, n_r$ and $\beta_1, \beta_2, \ldots, \beta_s$ so that

$$E = E(S, n_1, n_2, \ldots, n_{\mathrm{r}}, \beta_1, \beta_2, \ldots, \beta_s) . \tag{1.16}$$

The function $E(S, \boldsymbol{n}, \boldsymbol{\beta})$ admits partial derivatives of all orders, and therefore any difference between the energies of two stable equilibrium states may be expressed in the form of a Taylor series in terms of the partial derivatives of $E(S, \boldsymbol{n}, \boldsymbol{\beta})$ at one of the stable equilibrium states, and differences in the values of the entropy, amounts of constituents, and parameters of the two stable equilibrium states.

Among all the partial derivatives, each first-order partial derivative of either the function $S(E, \boldsymbol{n}, \boldsymbol{\beta})$ or the function $E(S, \boldsymbol{n}, \boldsymbol{\beta})$ represents an important and practical property of the family of stable equilibrium states of a system. It is important because each such property enters a condition for mutual stable equilibrium with other systems, and practical because it can be relatively easily related to simple measurements. It should be emphasized that each such property is defined only for the stable equilibrium states of the system.

1.2.9 Temperature

The partial derivative of $E(S, \boldsymbol{n}, \boldsymbol{\beta})$ with respect to entropy, or the inverse of the partial derivative of $S(E, \boldsymbol{n}, \boldsymbol{\beta})$ with respect to energy, that is,

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{n},\boldsymbol{\beta}} = \frac{1}{(\partial S/\partial E)_{\boldsymbol{n},\boldsymbol{\beta}}}, \tag{1.17}$$

is defined as the *absolute temperature* or, simply, the *temperature*. The first of Eqs. (1.17) defines T as a function of $E, \boldsymbol{n}, \boldsymbol{\beta}$ and the second as a function of $S, \boldsymbol{n}, \boldsymbol{\beta}$. Two units of temperature are the Kelvin and the Rankine, denoted by K and R, respectively.

If two systems A and B in states A_0 and B_0 are in mutual stable equilibrium, then the temperature T_0^A of system A must be equal to the temperature T_0^B of system B. Said differently, equality of temperatures of the two systems is a necessary condition for the two systems to be in mutual stable equilibrium.

By virtue of the definition of a reservoir, it follows that all its states have the same temperature T_R, and this temperature is equal to the constant c_R.

1.2.10 Total Potentials

The *total potential of the ith constituent*, μ_i, is defined by either of the two relations

$$\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,\boldsymbol{n},\boldsymbol{\beta}} = -T\left(\frac{\partial S}{\partial n_i}\right)_{E,\boldsymbol{n},\boldsymbol{\beta}}. \tag{1.18}$$

The dimensions of total potential are energy per unit of amount. The first of Eqs. (1.18) defines μ_i as a function of $S, \boldsymbol{n}, \boldsymbol{\beta}$ and the second as a function of $E, \boldsymbol{n}, \boldsymbol{\beta}$. If volume is the only parameter, each total potential is called a *chemical potential.*

If two systems A and B in states A_0 and B_0 are in mutual stable equilibrium, both contain the ith type of constituent for $i = 1, 2, \ldots, r$, and the amount of that constituent may both increase and decrease in each system, then the total potential $(\mu_\mathrm{i})_0^A$ of the ith constituent of A must be equal to the total potential $(\mu_\mathrm{i})_0^B$ of the ith constituent of B. Said differently, in addition to temperature equality, equality of total potentials for every constituent is a necessary condition for two systems to be in mutual stable equilibrium.

1.2.11 Pressure

The *generalized force conjugated to the jth parameter*, f_j, is defined by either of the two relations

$$f_{\mathrm{j}} = \left(\frac{\partial E}{\partial \beta_{\mathrm{j}}}\right)_{S,\boldsymbol{n},\boldsymbol{\beta}} = -T\left(\frac{\partial S}{\partial \beta_j}\right)_{E,\boldsymbol{n},\boldsymbol{\beta}} . \tag{1.19}$$

If volume V is a parameter, the negative of the generalized force conjugated to V is called *pressure*, denoted by p, and given by either of the two relations

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,\boldsymbol{n},\boldsymbol{\beta}} = T\left(\frac{\partial S}{\partial V}\right)_{E,\boldsymbol{n},\boldsymbol{\beta}} , \tag{1.20}$$

where here $\boldsymbol{\beta} = \{V, \beta_2, \beta_3, \ldots, \beta_s\}$. The first of Eqs. (1.20) defines p as a function of $S, \boldsymbol{n}, \boldsymbol{\beta}$ and the second as a function of $E, \boldsymbol{n}, \boldsymbol{\beta}$. The dimensions of p are energy per unit volume and, as is any other generalized conjugated force, it is a property of stable equilibrium states only. Pressure can also be thought of as force per unit area. However, force per unit area is not pressure if the state is not a stable equilibrium state [10].

1.2.11.1 First-Order Taylor Series Expansions

In terms of $T_0, p_0, (\mu_{\mathrm{i}})_0$, and $(f_{\mathrm{j}})_0$ of an arbitrary stable equilibrium state A_0 of a system A, small differences in energy, $dE = E_1 - E_0$, entropy, $dS = S_1 - S_0$, volume $dV = V_1 - V_0$, other parameters, $d\beta_2 = (\beta_2)_1 - (\beta_2)_0, d\beta_3 = (\beta_3)_1 - (\beta_3)_0, \ldots, d\beta_s = (\beta_s)_1 - (\beta_s)_0$, and amounts of constituents, $dn_1 = (n_1)_1 - (n_1)_0$, $dn_2 = (n_2)_1 - (n_2)_0, \ldots, dn_{\mathrm{r}} = (n_{\mathrm{r}})_1 - (n_{\mathrm{r}})_0$ between two neighboring stable equilibrium states are related by a first-order Taylor series expansion or differential energy relation

$$dE = T_0 dS - p_0 dV + \sum_{i=1}^{r} (\mu_i)_0 dn_i + \sum_{j=2}^{s} (f_{\mathrm{j}})_0 d\beta_j . \tag{1.21}$$

On solving Eq. (1.21) for dS, and writing dS as a first-order Taylor series expansion in terms of dE, dV, dn_i, and d_j, we find

$$dS = \frac{1}{T_0}dE + \frac{p_0}{T_0}dV - \sum_{i=1}^{r}\frac{(\mu_i)_0}{T_0}dn_i - \sum_{j=2}^{s}\frac{(f_j)_0}{T_0}d\beta_j \tag{1.22a}$$

$$= \left[\left(\frac{\partial S}{\partial E}\right)_{V,\boldsymbol{n},\boldsymbol{\beta}}\right]_0 dE + \left[\left(\frac{\partial S}{\partial V}\right)_{E,\boldsymbol{n},\boldsymbol{\beta}}\right]_0 dV + \sum_{i=1}^{r}\left[\left(\frac{\partial S}{\partial n_i}\right)_{E,V,\boldsymbol{n},\boldsymbol{\beta}}\right]_0 dn_i$$

$$+ \sum_{j=2}^{\mathrm{s}}\left[\left(\frac{\partial S}{\partial \beta_j}\right)_{E,V,\boldsymbol{n},\boldsymbol{\beta}}\right]_0 d\beta_j . \tag{1.22b}$$

On comparing the coefficients of dE, dV, dn_i, and $d\beta_j$ in (1.22a) and (1.22b), we find

$$\left(\frac{\partial S}{\partial E}\right)_{V,\boldsymbol{n},\boldsymbol{\beta}} = \frac{1}{T}, \tag{1.23}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,\boldsymbol{n},\boldsymbol{\beta}} = \frac{p}{T}, \tag{1.24}$$

$$\left(\frac{\partial S}{\partial n_\mathrm{i}}\right)_{E,V,\boldsymbol{n},\boldsymbol{\beta}} = -\frac{\mu_i}{T} \quad \text{for } i = 1, 2, \ldots, r, \tag{1.25}$$

$$\left(\frac{\partial S}{\partial \beta_j}\right)_{E,V,\boldsymbol{n},\boldsymbol{\beta}} = -\frac{f_j}{T} \quad \text{for } j = 2, 3, \ldots, s, \tag{1.26}$$

where, in writing these equalities, we simplify them by dropping the subscript 0, which specifies the particular stable equilibrium state about which we make the Taylor series expansion and at which we evaluate the partial derivatives. Each of Eqs. (1.23), (1.24), (1.25), and (1.26) proves the second of Eqs. (1.17), (1.20), (1.18), and (1.19), respectively.

1.2.12 Energy Relation of a Reservoir

We recall that a reservoir is an idealized kind of system that passes through stable equilibrium states only and remains in mutual stable equilibrium with a duplicate of itself that experiences no changes of state. If reservoir R has only volume as a parameter, the specifications just cited imply that all states of R have the same value of the temperature T_R, the same value of the pressure p_R, and the same values of the chemical potentials of the r constituents, $\mu_{1R}, \mu_{2R}, \ldots, \mu_{rR}$, so that the necessary conditions of temperature equality, pressure equality, and chemical potential equality for all constituents are satisfied. It follows that, for a reservoir, Eq. (1.21) may be stated in terms of differences – large or small – between properties of any two states R_1 and R_2 so that

$$E_2^R - E_1^R = T_R\left(S_2^R - S_1^R\right) - p_R\left(V_2^R - V_1^R\right) + \sum_{i=1}^{r} \mu_{iR}\left[(n_i)_2^R - (n_i)_1^R\right]. \tag{1.27}$$

1.2.13 Work and Heat Interactions

Interactions result in the exchange of properties across the boundaries of the interacting systems. Various combinations of exchanges are used to classify interactions into different categories. An interaction between two systems that results in a transfer of energy only between two systems is classified as a *work interaction*. The amount of energy exchanged as a result of such an interaction is called *work*. All interactions that result in the exchange of energy and at least one more property, for example entropy, between the interacting systems are called *nonwork interactions*. A process of a system experiencing only work interactions is called an *adiabatic process*. Any process that involves nonwork interactions is called a *nonadiabatic process*.

In the course of an adiabatic process, system A changes from state A_1 to state A_2, the energy exchange $E_{12}^{A\leftarrow}$ is work, that is, $E_{12}^{A\leftarrow} = -W_{12}^{A\rightarrow}$, where $W_{12}^{A\rightarrow}$ denotes the *work done* by system A on systems in its surroundings with which it interacts.

In the course of an adiabatic process, the entropy exchange $S_{12}^{A\leftarrow} = 0$. Therefore the energy and entropy balances are

$$E_2 - E_1 = -W_{12}^{A\rightarrow}, \tag{1.28}$$

$$S_2 - S_1 = S_{\text{irr}}, \tag{1.29}$$

where S_{irr} denotes the entropy generated by irreversibility inside A during the process.

A special example of nonwork interaction entirely distinguishable from work is one between two systems initially differing infinitesimally in temperature. It results in no other effects except a transfer of energy and a transfer of entropy between the two systems such that the ratio of the amount of energy transferred and the amount of entropy transferred equals the almost common temperature of the interacting systems. It is called a *heat interaction*. The amount of energy transferred as a result of such an interaction is called *heat*.

Often, in applications, system A consists of many subsystems, one of which, A', is in a stable equilibrium state at a temperature T_Q. Similarly, system B consists of many subsystems, one of which, B', is in a stable equilibrium state at temperature almost equal to T_Q. If the two subsystems A' and B' experience a heat interaction, we say that systems A and B experience a heat interaction at temperature T_Q, even though A and B are not necessarily in stable equilibrium states.

In the course of a process that involves only a heat interaction at temperature T_Q, system A changes from state A_1 to state A_2, the energy exchange $E_{12}^{A\leftarrow}$ is heat and is denoted by $Q_{12}^{A\leftarrow}$, that is, $E_{12}^{A\leftarrow} = Q_{12}^{A\leftarrow}$, and the entropy exchange is $Q_{12}^{A\leftarrow}/T_Q$. So the two balances are

$$E_2 - E_1 = Q_{12}^{A\leftarrow}, \tag{1.30}$$

$$S_2 - S_1 = \frac{Q_{12}^{A\leftarrow}}{T_Q} + S_{\text{irr}}, \tag{1.31}$$

where S_{irr} is the entropy generated by irreversibility inside A during the process. It is noteworthy that $Q_{12}^{A\leftarrow}$ is not a function of T_Q.

If a process of a system A involves both work and heat but no other interactions, the energy exchange is $E_{12}^{A\leftarrow} = Q_{12}^{A\leftarrow} - W_{12}^{A\rightarrow}$, the entropy exchange $S_{12}^{A\leftarrow} = Q_{12}^{A\leftarrow}/T_Q$, and

$$E_2 - E_1 = Q_{12}^{A\leftarrow} - W_{12}^{A\rightarrow} \tag{1.32}$$

$$S_2 - S_1 = \frac{Q_{12}^{A\leftarrow}}{T_Q} + S_{\text{irr}} \tag{1.33}$$

where S_{irr} is the entropy generated by irreversibility inside A during the process. On dropping some self-evident subscripts and superscripts, we may rewrite Eqs. (1.32) and (1.33) in the form

$$E_2 - E_1 = Q^{\leftarrow} - W^{\rightarrow}, \tag{1.34}$$

$$S_2 - S_1 = \frac{Q^{\leftarrow}}{T_Q} + S_{\text{irr}}, \tag{1.35}$$

or, for differential changes,

$$dE = \delta Q^{\leftarrow} - \delta W^{\rightarrow}, \tag{1.36}$$

$$dS = \frac{\delta Q^{\leftarrow}}{T_Q} + \delta S_{\mathrm{irr}}. \tag{1.37}$$

It is noteworthy that the prefix d denotes infinitesimal differences between the values of a property at two different states of the system, whereas the prefix δ denotes infinitesimal amounts of quantities that are not properties, such as work, heat, and entropy generation by irreversibility.

For processes in which the end states of the system are stable equilibrium states, energy and entropy changes, and therefore work, heat, and entropy generation by irreversibility may be related to changes of other properties and variables, such as temperature, pressure, and volume.

Work and heat interactions are most frequently encountered in engineering applications. Other interactions, involving transfers of energy, entropy, and amounts of constituents, are discussed later.

1.3 Availability Functions

1.3.1 General Remarks

To accomplish almost every practical task, we exploit resources in our natural environment. Some resources are used as energy sources, others as raw materials. *Energy sources* are substances not in permanent mutual stable equilibrium with the environment that can be used to power the energy-conversion systems required by various tasks. Typical sources are coal, oil, natural gas, uranium, and solar energy. Typical tasks are locomotion; motive power and process heat for manufacturing; space conditioning, such as heating, cooling, and ventilation; and electric power for communication devices, computers, industrial machines, home appliances, and lighting. *Raw materials* are substances used as feedstocks in manufacturing tasks – in materials-processing installations that produce different products. Examples of manufacturing tasks are the making of steel out of iron ore and the making of aluminum out of bauxite. Most raw materials are in mutual stable equilibrium with the environment. They are reduced to desired products at the expense of energy sources. Other raw materials are in only partial mutual stable equilibrium with the environment and remain so if prevented from chemical (or nuclear) interactions with other environmental materials. Also, these raw materials are reduced to desired products at the expense of energy sources, such as in a refinery where crude oil is processed to yield petroleum products that are subsequently used as energy sources, or in an enrichment plant where natural uranium is processed to yield fissile uranium that is subsequently used as an energy source.

Each task is accomplished by means of an arrangement of devices, materials-processing systems, and energy-conversion systems interacting with each other, with resources, and with the natural environment. The selection, evaluation, and adoption of a particular arrangement involves the resolution and reconciliation of many complex and conflicting scientific, technical, economical, environmental, social, and safety questions. A complete discussion of these issues is of decisive importance but beyond the scope of this chapter, except for the following questions that are related to thermodynamics:

1. What are the actual inlet, outlet, and end states of both the task and the energy sources used in a particular arrangement?
2. What are the optimum interactions required by the specified inlet, outlet, and end states of the task?
3. What are the optimum interactions that could be supplied by the energy sources employed if these sources were used in the best way physically possible?
4. If the answers to questions 2 and 3 differ, what aspects of the arrangement are the causes of the difference?
5. What can be done to change the difference between the answers to questions 2 and 3?
6. What is a universal measure of such a difference that characterizes how effectively the task is accomplished by a given arrangement?

It is clear that the concept of optimum that we use here is delimited only by the laws of physics, not by restrictions imposed either by economic, social, and environmental considerations or by current technology. As such, it may well be secondary to all the other concerns. Nevertheless, it does provide a limit that cannot be exceeded under any circumstances.

1.3.2 The Environment as a Reservoir

It is shown [10] that, for given inlet, outlet, and end states of a system, a process is optimum if it is reversible. Accordingly, if the inlet, outlet, and end states are not matched so as to yield zero net differences in entropy, the entropy balance must be achieved by exchange of entropy with another system; otherwise the process cannot be carried out reversibly. The only system that is readily available and can exchange large amounts of entropy at no cost is the environment. Similarly, the environment is a readily available, no-cost[4] source of certain substances, such as the air we breathe, the water we drink, and the air intake of our automobile engines. It is also an easy-access sink of substances, such as from automobile engines and energy-conversion systems and many wastes from residential, commercial, and industrial activities.

For analyses of optimum processes, we model all substances in our natural environment, except energy sources, as a system behaving as a reservoir. We call it the *environmental reservoir* and denote it by R^*. Depending on the application, to focus our attention on the phenomena that are most prevalent, we find it convenient to impose different restrictions on the values of the amounts of constituents and the volume of the environmental reservoir.

For example, in applications in which the system and the environment exchange entropy and energy but neither amounts of constituents nor volume, we model the environment as a reservoir R^* with fixed values of amounts of constituents and

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[4] The recent decades of heavy exploitation of our natural environment show that an unregulated use of the environment may cause a variety of serious alterations that result in enormous costs to our society and impacts on the quality of our lives. Thus the cost-free use of the environment should be allowed only for purposes that are unavoidable.

volume and denote its constant temperature by T_{R^*}. Under these restrictions, the relation between entropy and energy differences [Eq. (1.27) for $E = U$] becomes

$$S_2^{R^*} - S_1^{R^*} = \frac{1}{T_{R^*}} \left(U_2^{R^*} - U_1^{R^*} \right), \tag{1.38}$$

where R_1^* and R_2^* are any two stable equilibrium states of R^*.

Again, in applications in which the system and the environment exchange entropy, energy, and volume but no amounts of constituents, we model the environment as a reservoir R^* with variable volume and fixed values of the amounts of constituents, and we denote its constant temperature by T_{R^*} and its constant pressure by p_{R^*}. Under these restrictions, the relation among differences in values of energy, entropy, and the volume of any two stable equilibrium states R_1^* and R_2^* is

$$S_2^{R^*} - S_1^{R^*} = \frac{1}{T_{R^*}} \left(U_2^{R^*} - U_1^{R^*} \right) + \frac{p_{R^*}}{T_{R^*}} \left(V_2^{R^*} - V_1^{R^*} \right). \tag{1.39}$$

Finally, in applications in which the system and the environment exchange entropy, energy, volume, and amounts of constituents, we model the environment as a reservoir R^* with variable volume and variable amounts of constituents, and we denote its constant temperature by T_{R^*}, its constant pressure by p_{R^*}, and the constant chemical potentials by $\mu_{1R^*}, \mu_{2R^*}, \ldots, \mu, \mu_{\mathrm{r}R^*}$. Here the relation among differences in values of energy, entropy, volume and amounts of constituents of any two stable equilibrium states R_1^* and R_2^* becomes

$$S_2^{R^*} - S_1^{R^*} = \frac{1}{T_{R^*}} \left[U_2^{R^*} - U_1^{R^*} \right] + \frac{p_{R^*}}{T_{R^*}} \left[V_2^{R^*} - V_1^{R^*} \right] - \sum_{i=1}^{r} \frac{\mu_{iR^*}}{T_{R^*}} \left[(n_i)_2^{R^*} - (n_i)_1^{R^*} \right]. \tag{1.40}$$

Any state of the environmental reservoir is sometimes called a *passive* or *dead state* because, starting from such a state and using no energy sources, we can accomplish no useful task. Indeed, we cannot build a perpetual-motion machine of any kind using the environmental reservoir as a system.

In addition, the state of any system A in mutual stable equilibrium with R^* is sometimes called a passive or dead state and is denoted by A_{0^*} because, once in such a state, system A is useless as well. In particular, if the environmental reservoir R^* is modeled as having variable volume and variable amounts of constituents, the dead state A_{0^*} of system A has the same values of temperature, pressure, and chemical potentials as the respective values of R^*, that is, $T_{0^*} = T_{R^*}$, $p_{0^*} = p_{R^*}$, and $\mu_{i0^*} = \mu_{iR^*}$ for $i = 1, 2, \ldots, r$. Again, if R^* is modeled as having fixed values of the volume and the amounts of constituents, the dead state A_{0^*} of A has temperature $T_{0^*} = T_{R^*}$, but values of pressure and chemical potentials not necessarily equal to the corresponding values of R^*.

Given a composite of system A and the environmental reservoir R^*, spontaneous changes of state can occur only until A reaches mutual stable equilibrium with R^*, that is, only until A is in state A_{0^*}. After state A_{0^*} is reached, no further change in the state of the composite of A and R^* is possible without expenditure of an energy source because A_{0^*} has null available energy with respect to R^*, and no reservoir other than the environmental is readily available.

In principle, it is always possible to create a reservoir at conditions of temperature, pressure, and chemical potentials different from those of the natural environment. But the creation of such a reservoir requires the expenditure of energy sources, and any benefit that could result would be at best equal to, but usually less than, the expenditure.

1.3.3 Availability or Exergy

In previous discussions, we encountered some answers to questions related to optimum interactions. For example, it was shown that, in changing the state of system A from state A_1 to state A_2 while the system is in combination with a reservoir R that has fixed amounts of constituents and parameters and the composite AR experiences a weight process, the optimum work done on the weight is

$$(W_{12}^{AR\rightarrow})_{\text{optimum}} = \Omega_1^R - \Omega_2^R, \tag{1.41}$$

where Ω_1^R and Ω_2^R are the generalized available energies of the two states of A with respect to R and to some reference values $\boldsymbol{n}$ and $\boldsymbol{\beta}$ of the amounts of constituents and the parameters of A. Hence, if $\Omega_1^R > \Omega_2^R$, then $(W_{12}^{AR\rightarrow})_{\text{optimum}}$ is the largest work that the composite of A and R could do in a weight process under the specified conditions, whereas if $\Omega_2^R > \Omega_1^R$, then $-(W_{12}^{AR\rightarrow})_{\text{optimum}} = (W_{12}^{AR\leftarrow})_{\text{optimum}}$ is the least work required in a weight process for the composite of A and R to change the state of A from A_1 to A_2, again under the specified conditions.

If the system is simple[5] and the reservoir environmental, Eq. (1.41) may be expressed in terms of energy and entropy in the form

$$(W_{12}^{AR*\rightarrow})_{\text{optimum}} = (U_1 - T_{R^*}S_1) - (U_2 - T_{R^*}S_2)\,, \tag{1.42}$$

where U and S represent the internal energy and the entropy of system A, respectively, and in writing the equation we use the relation between energy, generalized available energy, and entropy introduced in Section 1.2. Moreover, under the specified conditions, we recall that the available energy is zero if A and R^* have the same temperature and conclude that

$$\Omega_1^{R^*} = (W_{10^*}^{AR^*\rightarrow})_{\text{rev}} = (U_1 - T_{R^*}S_1) - (U_{0^*} - T_{R^*}S_{0^*})\,, \tag{1.43}$$

where U_{0^*} and S_{0^*} are the energy and entropy of system A in the dead state A_{0^*}, respectively, with temperature $T_{0^*} = T_{R^*}$, and the values of the amounts of constituents and the parameters are equal to the respective reference values $\boldsymbol{n}$ and $\boldsymbol{\beta}$.

The expression $U - T_{R^*}S$ is called an *availability function* or *exergy function*. As Eq. (1.42) indicates, for the specified conditions the difference in the values of this function at two states yields the optimum work in a weight process for the composite of A and R^*.

The expression $(U_1 - T_{R^*}S_1) - (U_{0^*} - T_{R^*}S_{0^*})$, that is, the generalized available energy of state A_1, is also called the *availability* or *exergy* of state A_1. Under the specified conditions, it represents the optimum work that can be done as a result of the state of system A changing from A_1 to the state A_{0^*} with the reference values

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[5] The definition of a *simple system* is given in Chap. 17 of [10].

$\boldsymbol{n}$ and $\boldsymbol{\beta}$ and temperature T_{0^*} equal to that of the environmental reservoir. It turns out that this work is not sign definite, namely, it can be either positive or negative.

Expressions analogous to Eqs. (1.42) and (1.43) can be derived for conditions other than those involved in the definition of generalized available energy. Ideally, we should define a distinct name for each set of conditions and the corresponding function and its differences. Because there are innumerable conditions that we must examine, we would then have so many names that it would be questionable whether the richness of the vocabulary would be of any help. To avoid this linguistic pileup, we proceed as follows.

First, we consider a system A and the environmental reservoir R^* with given specifications regarding whether the values of their respective amounts of constituents and volume are variable or fixed. We define as the *availability function* or *exergy function* corresponding to the given specifications that expression the differences of which yield the optimum work in a weight process for the composite of A and R^* as system A changes from a given state A_1 to another given state A_2. Moreover, we define as the *availability* or *exergy* corresponding to the given specifications and to state A_1 that expression which yields the optimum work in a weight process for the composite of A and R^* as system A changes from state A_1 to state A_{0^*} in which A and R^* are in mutual stable equilibrium. For example, for the conditions discussed at the beginning of this section, we summarize the results by writing, in addition to Eq. (1.42)

$$\text{availability function} = U - T_{R^*} S, \tag{1.44}$$

$$\begin{aligned}\text{availability or exergy} &= (U - U_{0^*}) - T_{R^*}(S - S_{0^*}) \\ &= (U - T_{R^*} S) - (U_{0^*} - T_{R^*} S_{0^*}) .\end{aligned} \tag{1.45}$$

Other examples are discussed in the following subsection.

Next, we consider a given type of interaction, such as work, heat, or bulk flow, and the environmental reservoir R^* with given specifications regarding whether the values of its amounts of constituents and volume are variable or fixed. We define as the *availability rate function* or *exergy rate function* corresponding to the given specifications that expression whose differences yield the optimum work rate in a process for the composite of reservoir R^* and a system A maintained in a steady state by two given interactions of the same type. Moreover, we define as the *availability rate* or *exergy rate* corresponding to the given specifications and associated with a given interaction that expression which yields the optimum work rate in a process for the composite of reservoir R^* and a system A maintained in a steady state by the given interaction and an interaction of the same type with the reservoir R^*. A discussion of availability rate functions is given in [10, Chap. 22].

1.3.4 Different Availabilities or Exergies

Here we consider a simple system A, changing from state A_1 with volume V_1 to state A_2 with a different volume V_2, and surrounded by the environmental reservoir R^*, modeled as having variable volume but fixed values of the amounts of constituents, so that the reservoir experiences an equal and opposite change in volume.

At the moving boundary between A and R^*, a volume exchange occurs according to

$$V_2^{R^*} - V_1^{R^*} = -(V_2 - V_1)\,. \tag{1.46}$$

The motion of the boundary against the constant reservoir pressure p_{R^*} results in a work interaction between A and R^*, and the work done by A on R^* is $p_{R^*}(V_2 - V_1)$. In a weight process for the composite of A and R^*, the work $p_{R^*}(V_2 - V_1)$ represents just an internal exchange between A and R^* and not work $W_{12}^{AR^*\rightarrow}$ done on the weight. To evaluate the optimum work $(W_{12}^{AR\rightarrow})_{\text{optimum}}$ done on the weight under the specified conditions, we begin by writing the energy and entropy balances:

$$\left(U_2 + U_2^{R^*}\right) - \left(U_1 + U_1^{R^*}\right) = -\left(W_{12}^{AR*\rightarrow}\right), \tag{1.47}$$

$$\left(S_2 + S_2^{R^*}\right) - \left(S_1 + S_1^{R^*}\right) = S_{\text{irr}}. \tag{1.48}$$

On combining (1.46)–(1.48) with (1.38) and setting $S_{\text{irr}} = 0$ for optimality, we find that

$$(W_{12}^{AR^*\rightarrow})_{\text{optimum}} = (U_1 - T_{R^*}S_1 + p_{R^*}V_1) - (U_2 - T_{R^*}S_2 + p_{R^*}V_2)\,, \tag{1.49}$$

$$\text{availability function} = U - T_{R^*}S + p_{R^*}V, \tag{1.50}$$

$$\begin{aligned}\text{availability or exergy} &= (U - U_{0^*}) - T_{R^*}(S - S_{0^*}) + p_{R^*}(V - V_{0^*})\\ &= (U - T_{R^*}S + p_{R^*}V) - (U_{0^*} - T_{R^*}S_{0^*} + p_{R^*}V_{0^*})\,,\end{aligned} \tag{1.51}$$

where U_{0^*}, S_{0^*}, and V_{0^*} are the energy, entropy, and volume, respectively, of A in mutual stable equilibrium with the reservoir and therefore in state A_{0^*} with temperature $T_{0^*} = T_{R^*}$ and pressure $p_{0^*} = p_{R^*}$. Although the value of $U_{0^*} + p_{R^*}V_{0^*} - T_{R^*}S_{0^*}$ equals that of the Gibbs free energy of state A_{0^*} because $T_{0^*} = T_{R^*}$ and $p_{0^*} = p_{R^*}$, it is noteworthy that $U + p_{0^*}V - T_{0^*}S$ is not a Gibbs free energy because U, S, V, T_{0^*}, and p_{0^*} are not all associated with the same state of system A.

Here we consider a simple system A, changing from state A_1 with values V_1 and $(\boldsymbol{n})_1$ of the volume and the amounts of constituents to state A_2 with values V_2 and $(\boldsymbol{n})_2$ and surrounded by the environmental reservoir R^*. The reservoir is modeled as having variable values of volume and amounts of constituents, so that it experiences changes in values of volume and in each of the amounts of constituents equal and opposite to the respective changes in values of A. Thus Eq. (1.46) also holds here and, in addition, we have

$$(n_i)_2^{R^*} - (n_i)_1^{R^*} = -\left[(n_i)_2 - (n_i)_1\right] \quad \text{for } i = 1, 2, \ldots, r, \tag{1.52}$$

where $(n_i)_1^{R^*}$ and $(n_i)_2^{R^*}$ are the values of the amount of the ith constituent of R^* at states R_1^* and R_2^*, respectively, and $(n_i)_1$ and $(n_i)_2$ are the values of the amount of the same constituent at states A_1 and A_2 of A, respectively.

The energy and entropy balances for a weight process of the composite of A and R^* under the specified conditions are still given by Eqs. (1.47) and (1.48).

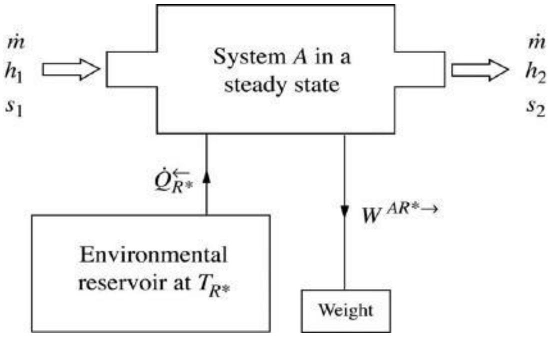

Figure 1.1. Schematic of system A maintained in steady state by two bulk-flow interactions, shaft work, and heat with the environmental reservoir.

Combining Eqs. (1.39), (1.46–1.48), and (1.52) and setting $S_{\text{irr}} = 0$ for optimality, we find that

$$\begin{aligned}(W_{12}^{AR^*\rightarrow})_{\text{optimum}} &= \left[U_1 - T_{R^*}S_1 + p_{R^*}V_1 - \sum_{i=1}^{r}\mu_{i\,R^*}\,(n_i)_1\right] \\ &\quad - \left[U_2 - T_{R^*}S_2 + p_{R^*}V_2 - \sum_{i=1}^{r}\mu_{i\,R^*}\,(n_i)_2\right], \qquad (1.53)\end{aligned}$$

$$\text{availability function} = U - T_{R^*}S + p_{R^*}V - \sum_{i=1}^{r}\mu_{i\,R^*}n_i, \qquad (1.54)$$

$$\begin{aligned}\text{availability or exergy} &= (U - U_{0^*}) - T_{R^*}\,(S - S_{0^*}) + p_{R^*}\,(V - V_{0^*}) \\ &\quad - \sum_{i=1}^{r}\mu_{i\,R^*}\,[n_i - (n_i)_{0^*}] \\ &= \left[U - T_{R^*}S + p_{R^*}V - \sum_{i=1}^{r}\mu_{i\,R^*}n_i\right] \\ &\quad - \left[U_{0^*} - T_{R^*}S_{0^*} + p_{R^*}V_{0^*} - \sum_{i=1}^{r}\mu_{i\,R^*}\,(n_i)_{0^*}\right]. \qquad (1.55)\end{aligned}$$

As a third example, we consider system A maintained at steady state by two bulk-flow interactions and the environmental reservoir R^* modeled as having variable volume and amounts of constituents. We assume no changes in mass flow rate and composition and negligible changes in kinetic and potential energies between the bulk-flow states of the inlet and outlet streams. For example, for the arrangement shown in Fig. 1.1, bulk-flow states 1 and 2 are the states of the inlet and outlet streams of a steady-state device A that, in addition to these two bulk-flow interactions, is surrounded by the environmental reservoir and connected to a weight.

For the conditions just specified for the composite of the device A and the reservoir R^*, we find that

$$(W_{12}^{AR^*\rightarrow})_{\text{optimum}} = \dot{m}\,(h_1 - T_{R^*}s_1) - \dot{m}\,(h_2 - T_{R^*}s_2)\,, \qquad (1.56)$$

$$\text{availability rate function} = \dot{m}\,(h - T_{R^*}s)\,, \qquad (1.57)$$

$$\text{availability rate or exergy rate} = \dot{m}\,(h - T_{R^*}s) - \dot{m}\,(h_{0^*} - T_{R^*}s_{0^*})\,, \qquad (1.58)$$

where h_{0^*} and s_{0^*} are the specific enthalpy and the specific entropy, respectively, of a bulk-flow state O^* at temperature $T_{0^*} = T_{R^*}$ and pressure $p_{0^*} = p_{R^*}$. It is noteworthy that the stream in bulk-flow state O^* is not in mutual stable equilibrium with R^*. The reason is that a bulk-flow state is not stable equilibrium unless the kinetic and potential energies are zero, and even if these energies are zero, the condition of chemical potential equality cannot be met because of the specification that no changes in compositions can occur. In other words, the bulk-flow interaction at state O^* introduces into the environment substances that do not correspond to the environmental composition and therefore cause a subsequent irreversible mixing. This irreversibility is built into the system specifications we are considering. If the specifications are different, such as when chemical reactions are allowed, the availability rate has a different expression.

In processes involving many streams, the availability rate function and the availability rate are given by expressions similar to Eqs. (1.57) and (1.58) except that here each rate is a sum over many streams. Specifically,

$$(\dot{W}_{12}^{AR^*\rightarrow})_{\text{optimum}} = [\dot{H}_{\text{in}} - T_{R^*}\dot{S}_{\text{in}}] - [\dot{H}_{\text{out}} - T_{R^*}\dot{S}_{\text{out}}], \tag{1.59}$$

$$\text{availability rate function} = \dot{H} - T_{R^*}\dot{S}, \tag{1.60}$$

$$\text{availability rate or exergy rate} = [\dot{H} - T_{R^*}\dot{S}] - [\dot{H}(T_{R^*}, p_{R^*}) - T_{R^*}\dot{S}(T_{R^*}, p_{R^*})] \tag{1.61}$$

where $\dot{H}$ and $\dot{S}$ represent summations of flow rates of enthalpies and entropies over many streams. For details see [10, Chap. 22].

Under the same conditions as specified in Subsection 1.3.4.3, except that the changes in kinetic and potential energies of the bulk-flow streams are not negligible, Eqs. (1.56)–(1.58) become

$$\begin{aligned}(\dot{W}_{12}^{AR^*\rightarrow})_{\text{optimum}} &= \dot{m}\left[h_1 - T_{R^*}s_1 + \frac{\xi_1^2}{2} + gz_1\right]\\ &\quad - \dot{m}\left[h_2 - T_{R^*}s_2 + \frac{\xi_2^2}{2} + gz_2\right],\end{aligned} \tag{1.62}$$

$$\text{availability rate function} = \dot{m}\left[h - T_{R*}s + \frac{\xi^2}{2} + gz\right] \tag{1.63}$$

$$\begin{aligned}\text{availability rate or exergy rate} &= \dot{m}\left[(h - h_{0^*}) - T_{R^*}(s - s_{0^*}) + \frac{\xi^2}{2} + g(z - z_{0^*})\right]\\ &= \dot{m}\left[h - T_{R^*}s + \frac{\xi^2}{2} + gz\right] - \dot{m}(h_{0^*} - T_{R^*}s_{0^*} + gz_{0^*}),\end{aligned} \tag{1.64}$$

where h_{0^*}, s_{0^*}, and z_{0^*} refer to a bulk-flow state with temperature $T_{0^*} = T_{R^*}$, pressure $p_{0^*} = p_{R^*}$, bulk-flow speed $\xi_{0^*} = 0$, and the lowest elevation z_{0^*} in the environment.

It is clear that many more availability (availability rate) or exergy (exergy rate) functions can be defined, each associated with a particular set of conditions.

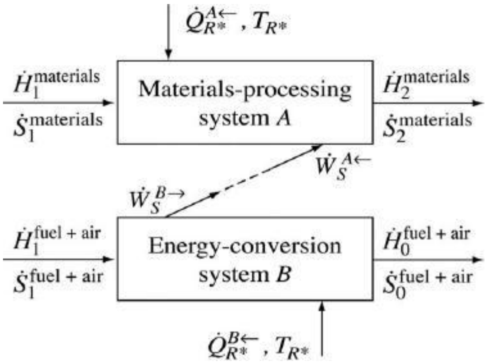

Figure 1.2. The burning of fuel–air mixture in the energy-conversion system provides the work needed to process the bulk-flow stream through the materials-processing system.

1.3.5 Availability or Exergy Analysis

An illustration of the usefulness of Eqs. (1.59) and (1.61) is provided by the bulk-flow processes in Fig. 1.2. Various substances enter a materials-processing system A in various bulk-flow streams with overall enthalpy rate $\dot{H}_1^{\text{materials}}$ and entropy rate $\dot{S}_1^{\text{materials}}$. The plant is designed to operate in steady state and to transform the entering streams into products having overall enthalpy rate $\dot{H}_2^{\text{materials}}$ and overall entropy rate $\dot{S}_2^{\text{materials}}$. The transformation requires shaft work from a power plant at a rate $\dot{W}_s^{A\leftarrow}$ and heat from the natural environment at temperature T_{R^*} at a rate $\dot{Q}_{R^*}^{A\leftarrow}$. The rate balance for the materials-processing system is

$$\dot{W}_s^{A\leftarrow} = \left[\dot{H}_2^{\text{materials}} - \dot{H}_1^{\text{materials}} - T_{R^*}\left(\dot{S}_2^{\text{materials}} - \dot{S}_1^{\text{materials}}\right)\right] + T_{R^*}\dot{S}_{\text{irr}}^{A}, \quad (1.65)$$

where $\dot{S}_{\text{irr}}^{A}$ is the rate of entropy generation by irreversibility in the materials-processing system A. It is noteworthy that $\dot{W}_s^{A\leftarrow}$ is optimum if $\dot{S}_{\text{irr}}^{A} = 0$ and that to each different value of $\dot{W}_s^{A\leftarrow}$ there corresponds a different value of $\dot{Q}_{R^*}^{A\leftarrow}$.

The shaft work is provided by energy-conversion system B (Fig. 1.2), which converts a fuel and air stream into products of combustion. The fuel and air enter the system as bulk-flow streams with overall enthalpy rate $\dot{H}_1^{\text{fuel+air}}$ and overall entropy rate $\dot{S}_1^{\text{fuel+air}}$. The energy conversion system does shaft work at a rate $\dot{W}_{\text{s}}^{B\rightarrow}$ and interacts with the natural environment at T_{R^*} with heat at a rate $\dot{Q}_{R^*}^{B\leftarrow}$. Moreover, we assume that the products of combustion exit in bulk-flow streams at temperature $T_{0^*} = T_{R^*}$ and pressure $p_{0^*} = p_{R^*}$. For these streams, we denote the overall enthalpy rate by $\dot{H}_{0^*}^{\text{fuel+air}}$ and the overall entropy rate by $\dot{S}_{0^*}^{\text{fuel+air}}$. If no entropy is generated by irreversibility in the energy-conversion system, the work rate is given by the availability rate of the fuel–air mixture, Eq. (1.61). However, if entropy is generated by irreversibility, $\dot{W}_s^{B\rightarrow}$ satisfies the relation

$$\dot{W}_s^{B\rightarrow} = \left[\dot{H}_1^{\text{fuel+air}} - \dot{H}_{0^*}^{\text{fuel+air}} - T_{R^*}\left(\dot{S}_1^{\text{fuel+air}} - \dot{S}_{0^*}^{\text{fuel+air}}\right)\right] - T_{R^*}\dot{S}_{\text{irr}}^{B}, \quad (1.66)$$

where $\dot{S}_{\text{irr}}^{B}$ is the rate of entropy generation by irreversibility in the energy-conversion system.

On subtracting Eq. (1.65) from Eq. (1.66), recognizing that $\dot{W}_{\text{s}}^{B\rightarrow} = \dot{W}_{\text{s}}^{A\leftarrow}$, and rearranging terms, we find that

$$\begin{aligned}&\left[\dot{H}_1^{\text{fuel+air}} - \dot{H}_{0^*}^{\text{fuel+air}} - T_{R^*}\left(\dot{S}_1^{\text{fuel+air}} - \dot{S}_{0^*}^{\text{fuel+air}}\right)\right]\\ &\quad = \left[\dot{H}_2^{\text{materials}} - \dot{H}_1^{\text{materials}} - T_{R^*}\left(\dot{S}_2^{\text{materials}} - \dot{S}_1^{\text{materials}}\right)\right] + T_{R^*}\dot{S}_{\text{irr}}, \quad (1.67)\end{aligned}$$

where $\dot{S}_{\text{irr}} = \dot{S}_{\text{irr}}^{A} + \dot{S}_{\text{irr}}^{B}$, that is, the rate of entropy generation by irreversibility in both the materials-conversion and the energy-conversion systems.

The left-hand side of Eq. (1.67) is the availability rate of the fuel–air mixture, that is, the largest rate at which work could possibly be done by processing the mixture in the natural environment under the specified conditions on the types of interactions between the energy-conversion system and the environment. The bracketed term on the right-hand side is the least work rate required for achieving the change of state of the bulk-flow streams processed by the materials-processing system under the specified types of interactions with the environment. The term $T_{R^*}\dot{S}_{\text{irr}}$ is the work rate equivalent of the rate of entropy generation by irreversibility. It represents a loss of availability. It is a partial loss of the ability of the fuel source to perform a useful task. This loss is incurred because the processes in the materials-processing and the energy-conversion systems are not the best achievable under the specified conditions, that is, the processes are not reversible. So, in contrast to energy, availability is not conserved. It is destroyed or consumed by the generation of entropy due to irreversibility.

For the arrangement in Fig. 1.2, Eq. (1.67) provides answers to questions raised in Subsection 1.3.1. Specifically, it includes the inlet and outlet states of the task and the energy sources and therefore answers question 1: “What are the actual inlet, outlet, and end states of both the task and the energy sources used in the arrangement?” It specifies the optimum interactions required by the task and, therefore, answers question 2: “What are the optimum interactions required by the specified inlet, outlet, and end states of the task?” And it specifies the optimum interactions that could be supplied by the energy sources and thus provides an answer to question 3. It is important to emphasize here that the only optimum dictated by the laws of thermodynamics (physics) is reversible processes.

To answer question 4, “What aspects of the arrangement are the causes of the difference between the answers to questions 2 and 3?,” we must look into the detailed design characteristics of the equipment used in the process. The answer to question 4 indicates the difference between the answers to questions 2 and 3 and is suggestive of steps that might be taken to answer question 5.

An analysis of a system based on considering the energy, entropy, and combined balances for each component of the system and computing the availability or exergy consumption, that is, the entropy generation by irreversibility, is called an *availability analysis* or *exergy analysis*.

Availability analyses, as well as energy and other analyses, require that the inlet, outlet, and end states of the task be specified and that the changes in availability or availability rates of feedstocks, products, and energy sources be evaluated. Because of practical considerations related to existing knowledge and technology, the specification of a desired task is very often relative to existing knowledge and technology and not absolute, and therefore availability and other analyses yield results that are relative to existing knowledge and technology.

For example, a common process encountered in industry is the heat treating of alloy steel parts to produce a locally hard surface, such as the surface of a steel ball for a bearing or the surface teeth of a gear. Although only a very small fraction of the material of each part needs to be hardened, conventional technology has required that the entire part be heated to about 900 °C. So the task is defined according to this requirement. Another way to specify the task, however, is to say that only a small fraction near the surface of the material need be hardened. The availability change required by the first task is much larger than that required by the second. Moreover, the results of the two availability analyses are not comparable to each other, just as the task of making pig iron in a blast furnace is not comparable to that of making aluminum in an electrolytic cell.

In the example of steel hardening, the second specification of the task has of course little practical significance if we do not know how to treat just the surface without affecting the bulk of the processed piece. However, the lower availability change required by this specification in the framework of the conventional technology of the task can provide useful guidance for innovative approaches to the problem of metal hardening. In fact, recent developments in high-power lasers and electron-beam accelerators have led to the development of practical processes for localized heat treating. In one carburizing application, for example, electron-beam heat treating reduced the energy needed for a particular part from 1 kWh to only 2 Wh. Thus, by redefining the task, the required availability was lowered well below the level that was previously thought to be optimum.

1.3.6 Thermodynamic Efficiency or Effectiveness

Associated with each task, such as heating a room or making a specified amount of steel out of iron ore, is the least amount of work that must be done to accomplish the task. This least amount of work is equal to the change in availability of the substances processed to achieve the task and is independent of any details of the arrangement of devices and engines used in the task.

In practice, however, each specific arrangement consumes a certain, not necessarily optimum, amount of fuel or energy source to accomplish the task. Associated with this amount of fuel or energy source is the largest amount of work that can be delivered to a weight. This largest amount of work is equal to the availability of the fuel or energy source consumed and is independent of any details of the energy-conversion systems and devices used to convert the fuel or energy source to work.

For emphasis, we denote the least work rate required by a specified task production rate as $\dot{W}^{\leftarrow}_{\text{least}}$ and the largest availability rate of the fuel or energy source consumption as $\dot{W}^{\rightarrow}_{\text{largest}}$, and we define the *thermodynamic efficiency* or *effectiveness*[6] ε of the actual arrangement as the ratio of these two rates, that is,

$$\varepsilon = \frac{\dot{W}^{\leftarrow}_{\text{least}} \text{ required by the actual task production rate}}{\dot{W}^{\rightarrow}_{\text{largest}} \text{of the actual energy source consumption rate}}. \tag{1.68}$$

The effectiveness is a measure of the degree to which the processes involved in carrying out the task and in converting the energy source are reversible. If the processes are reversible, $\varepsilon = 1$. If the processes are irreversible, $\varepsilon < 1$.

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[6] In some literature on this subject, the concept of effectiveness defined here is called second-law efficiency. Such terminology, however, is misleading because the concept is based on not just the second law but on the first law as well, and on many other concepts, such as work, heat, and bulk-flow interactions, and energy and entropy balances. All these concepts are certainly related to but not derivable solely from the second law.

The concept of effectiveness is applicable to any process and can always be expressed in the form

$$\varepsilon = 1 - \frac{T_{R^*}\dot{S}_{\mathrm{irr}}}{\dot{W}^{\rightarrow}_{\mathrm{largest}} \text{ of the actual energy source consumption rate}} \tag{1.69}$$

because the difference between the denominator and the numerator in Eq. (1.68) is always $T_{R^*}\dot{S}_{\mathrm{irr}}$, where $\dot{S}_{\mathrm{irr}}$ is the total rate of entropy generation by irreversibility in the process. For example, the effectiveness of the materials-processing plant discussed in Subsection 1.3.5 is of the form of Eq. (1.69) as we can readily verify by using Eq. (1.67).

The effectiveness may assume even negative values. A negative value signifies that ideally the task can be accomplished while the processed streams transfer energy to a weight rather than consume energy sources, that is, the processed streams can be used as energy sources themselves. Instead, because of large irreversibilities in the actual materials-processing and energy-conversion systems, not only is the contribution from the processed streams wasted but other energy sources are consumed. The term $T_{R^*}\dot{S}_{\mathrm{irr}}$ is sometimes called the *lost work rate*. It represents the work rate that could be produced in the absence or irreversibility, but is not produced because of irreversibility.

We can express the thermodynamic efficiency or effectiveness also in terms of batch quantities rather than rates. Then,

$$\begin{aligned}\varepsilon &= \frac{W^{\leftarrow}_{\mathrm{least}} \text{ required by the actual task production}}{W^{\rightarrow}_{\mathrm{largest}} \text{ of the actual energy source consumption}} \\ &= 1 - \frac{T_{R^*}S_{\mathrm{irr}}}{W^{\rightarrow}_{\mathrm{largest}} \text{ of the actual energy source consumption}}.\end{aligned} \tag{1.70}$$

This effectiveness behaves exactly in the same way as that defined by Eq. (1.68).

Subject to the qualifications discussed in the next subsection, the concept of thermodynamic efficiency or effectiveness is the answer to question 6 posed in Subsection 1.3.1, namely, the universal measure of how effectively the task is accomplished by a given arrangement.

1.3.7 Thermal Efficiency

In practically every textbook, work-delivering engines are analyzed, and the ratio of the work output $W^{\rightarrow}$ over the heat input $Q^{\leftarrow}$ per cycle is evaluated under the assumption that in each cycle all processes are reversible. For example, the cycles that are considered are the Carnot, Rankine, Otto, Diesel, Joule–Brayton, and Stirling. The ratio just cited is called the *thermal efficiency*, is smaller than unity, and, more often than not, its difference from unity is interpreted as indicative of the margin for improvement of the processes involved in the cycle. Such interpretation is faulty because there are no processes that are better than reversible. Said differently, the correct measure of perfect use of the heat from a high-temperature reservoir is the thermodynamic efficiency or effectiveness for every one of the cycles listed earlier, and this efficiency is equal to unity. For example, for the Carnot cycle, the largest thermal efficiency of use of heat from the hot reservoir is

$$\eta_{\text{thermal}} = \frac{W^{\rightarrow}}{Q^{\leftarrow}} = \frac{T_1 - T_2}{T_1}. \tag{1.71}$$

But exergy of $Q^{\leftarrow}$ with respect to the low-temperature reservoir is $Q^{\leftarrow}(T_1 - T_2)/T_1$ so that the effectiveness or thermodynamic efficiency of the Carnot cycle under ideal (reversible) conditions is equal to unity.

Similar conclusions are obtained for all the other types of cycles if the processes of use of heat from the hot reservoir are reversible.

1.3.8 Practical Limitations

The construction of each machine, engine, and device is in itself a task that involves materials-processing and energy-conversion systems and therefore the consumption of energy sources. When it is sizable, this consumption must be accounted for. An important requirement of any installation used in primary energy processing, such as the production of electricity from various energy sources, is that the installation be capable of extracting more availability from the sources than the availability consumed for the construction of the machinery.

In many applications it may be technically impossible to take full advantage of the availability of the energy sources utilized. This may happen because some of the availability is either lost in processes outside the application or remains intact for use in subsequent applications. When this occurs, defining the effectiveness of the application in terms of the availability of the energy sources is misleading.

For example, if the only known method to carry out a process is by means of electrolysis, and electricity is generated from coal, it is hopeless to expect to improve the electrolytic process so as to take full advantage of the fuel availability. Electricity is not available in nature, and its generation entails losses. These losses should not be charged to the imperfections of the electrolytic process because it requires electricity to operate and the losses cannot be recovered no matter how perfect the electrolytic process is. To avoid this difficulty, the reasonable thing to do is to consider the availability of electricity as a source of input and evaluate the effectiveness of the electrolytic process with respect to electricity rather than with respect to coal.

Again, in each stage of a steam turbine, only some of the availability of the flowing steam is consumed. The remaining availability is ready for use in subsequent stages. Hence it is misleading to compute the effectiveness of one stage of the turbine with respect to the full availability of the steam flow.

In some applications, the properties of the materials of the equipment do not permit the full utilization of the fuel availability. For example, in oil-fired power plants, the exhaust combustion gases contain water vapor. If cooled to environmental temperature, the vapor condenses and corrodes the equipment. So exhaust gases are not cooled to such low temperatures. Correspondingly, the availability of the fuel should be evaluated with respect to a final state, not in temperature equality with the environment, but at a temperature such that vapor condensation cannot occur.

1.3.9 Comments

In contrast to other measures of efficiency, each specifically designed for a class of applications, the concept of thermodynamic efficiency or effectiveness is applicable to any task without conceptual modifications. For example, miles per gallon of gasoline is a measure of thermodynamic performance of a transportation task by an automobile, and the larger the value of this measure, the better the performance. Again, equivalent barrels of oil per ton of steel are a measure of thermodynamic performance of a steelmaking task at a steel plant, and the smaller the value of this measure, the better the performance. Clearly these two measures are not interchangeable and have different limiting values. In contrast, the concept of effectiveness can be applied to both an automobile and a steelmaking plant. The result for each of these two tasks would be a number less than unity, with an upper limit equal to unity. The upper limit of unity corresponds to perfect thermodynamic performance, namely, to all processes involved in the task that are reversible, and it is *the only limit imposed by the laws of thermodynamics* or, more generally, *the laws and theorems of nonstatistical quantum thermodynamics*.

Being directly related to irreversibility, the thermodynamic efficiency or effectiveness provides a realistic measure of the degree to which the performance of a task can be improved. Other measures of efficiency may be misleading. To illustrate the last assertion, we consider a perfectly insulated heat exchanger in which all the energy change of the primary stream is transferred to the secondary stream. On defining efficiency as the energy increase of the secondary stream divided by the energy decrease of the primary stream, we would find that this heat exchanger is 100% efficient. Such a result is correct but misleading. It implies that the heat exchanger is perfect and cannot be improved. However, if we define the effectiveness as the ratio of the availability increase of the secondary stream divided by the availability decrease of the primary stream, we find that the best exchanger is less than 100% efficient and subject to improvement by reduction of the temperature differences between the two streams. Clearly the second answer is realistic and, more important, relevant to our concerns about efficient use of resources.

Another important characteristic of thermodynamic efficiency or effectiveness is that it provides a realistic evaluation of tasks with dissimilar outputs. To see this point, we consider a cyclic device that produces work $W^{\rightarrow}$ and heat $Q^{\rightarrow}$ at temperature T_Q, while using heat $Q_1^{\leftarrow}$, from a source at temperature $T_{Q'} > T_Q$. If these are the only interactions, the energy and entropy balances are

$$Q_1^{\leftarrow} = W^{\rightarrow} + Q^{\rightarrow}, \tag{1.72}$$

$$\frac{Q_1^{\leftarrow}}{T_{Q'}} + S_{\text{irr}} = \frac{Q^{\rightarrow}}{T_Q}. \tag{1.73}$$

If efficiency were defined as the energy out divided by the energy in, then this efficiency would be unity here, regardless of whether most of $Q_1^{\leftarrow}$ is provided as work or low-temperature heat $Q^{\rightarrow}$. We know, however, that heat is not equally valuable as work. For example, if T_Q were equal to the environmental temperature T_{R^*}, then $Q^{\rightarrow}$ would be entirely useless and yet the energy ratio would count it as equally useful as work.

These difficulties are eliminated if we compare the availability of the two outputs with the availability of the input, because then all interactions are evaluated on a comparable basis. Specifically, the effectiveness of the cyclic device is

$$\varepsilon = \frac{W^{\rightarrow} + Q^{\rightarrow}(1 - T_{R^*}/T_Q)}{Q_1^{\leftarrow}(1 - T_{R^*}/T_{Q'})} = 1 - \frac{T_{R^*} S_{\mathrm{irr}}}{Q_1^{\leftarrow}(1 - T_{R^*}/T_{Q'})}, \tag{1.74}$$

where, in writing the second form of Eqs. (1.74), we use Eqs. (1.72) and (73).

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