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Development of generalized (rate dependent) availability

Stanislaw Sieniutycz *

Warsaw University of Technology, Faculty of Chemical and Process Engineering, Department of Process Separation, 1 Waryńskiego Street (Room 232), 00-645 Warsaw, Poland

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Abstract

We treat the irreversible extension of the classical problem of maximum mechanical work that may be obtained from a system composed of: a resource fluid at flow, a set of sequentially arranged engines, and an infinite bath. In the engine mode the fluid's temperature T decreases along the path, thus tending to the bath temperature T^e, and the system delivers work. In a related classical problem the process rates vanish due to the reversibility; here, however, finite rates and consistent losses of the work potential are admitted. The variational calculus leads to a finite-rate generalization of the maximum-work potential called the finite-rate exergy. This finite-rate exergy is a function of the usual thermal coordinates and the overall number of transfer units τ or a rate index h, which is, in fact the Hamiltonian of optimal, active (energy-generating) relaxation process to equilibrium. The resulting bounds on the work delivered or supplied are stronger than the classical reversible bounds.

Keywords: Thermodynamic imperfection; Efficiency; Optimal paths; Generalized exergy

1. Introduction

The classical available energy, which describes the maximum work yield for a system approaching the thermodynamic equilibrium with the environment, refers to the reversible evolution. In fact, the thermal availability may be obtained by integration of the product of the Carnot efficiency and the heat differential. When rates of the system's approach to the equilibrium are finite, irreversible processes produce the entropy, and the system's efficiency drops below that of Carnot. For evolutions with finite rates, generalized availabilities may be defined that incorporate non-Carnot efficiencies associated with an inevitable minimum of the entropy production. We outline main rules serving to model the efficiency decrease caused by the finite rates. In particular, we discuss mathematical modeling of radiation engines as rate systems governed by nonlinear laws of thermodynamics and transport. A general formula linking the converter's efficiency with the entropy production is derived to estimate an irreversible limit for power yield and to define a finite-rate extension of the classical work potential. The work produced is the cumulative effect obtained from a resource fluid at flow, a set of sequentially arranged engines, and an infinite bath. The use of optimal control methods leads to maximum work or a finite-rate generalization of the classical available energy.

The generalized availability is a function of usual thermal coordinates and a factor quantifying the effect of system's finite rates. Resulting bounds on the real work delivery or supply are stronger than the classical reversible bounds. The restrictive nature of traditional (thermostatic) bounds implies that bounds associated with finite rates of state change can be at least equally suitable. Generalized available energy of the fluid implies decreased (in comparison with Carnot) efficiencies of energy generators. Mathematical theory and economical aspects of decreased efficiencies and generalized availabilities are essential.

The classical exergy defines bounds on the common work delivered from (or supplied to) slow, reversible

* Fax: +48 22 251440.
E-mail address: sieniutycz@ichip.pw.edu.pl

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Nomenclature

A^{∞}	generalized exergy density of a continuous process (J m^{-3})
A^{class}	classical available energy or exergy (J m^{-3})
a_v	total area of heat exchange per unit volume (m^2 m^{-3})
c	constant specific heat referred to unit volume (J m^{-3} K^{-1})
$c_v(T)$	variable specific heat referred to unit volume (J m^{-3} K^{-1})
F	cross-sectional area perpendicular to the fluid flow (m^2)
$\dot{G}$	fluid mass flux (kg s^{-1})
g_1, g	partial and overall conductance (J s^{-1} K^{-1})
H_{TU}	height of transfer unit (m)
h	Hamiltonian in energy units (J m^{-3})
h_σ	Hamiltonian in entropy units (J m^{-3} K^{-1})
L_σ	Lagrangian of the problem in entropy units (J m^{-3} K^{-1})
N	total number of stages (–)
n	stage number (–)
P, p	total and local power output (J s^{-1})
Q_1	heat delivered from the first reservoir (J)
q_1	driving heat power or dQ_1/dt (J s^{-1})
$q_{1'}$	heat flux at state 1′ (Fig. 1) (J s^{-1})
r	overall resistance (J^{-1} s K)
S	total entropy of the system (J K^{-1})
S_σ	entropy produced in the system (J K^{-1})
$S_\sigma = \sigma_s/V$	entropy source per unit volume (J K^{-1} m^{-3})
$\Delta S_{1'}$	entropy change in circulating fluid along T_1, (J K^{-1})
T	variable temperature of resource fluid (K)
T_1, T_2	bulk temperatures of reservoirs 1 and 2 (K)
$T_{1'}, T_{2'}$	temperatures of circulating fluid (Fig. 1) (K)
T^{i}, T^{f}	initial and final temperature of fluid 1 in dynamical (finite-resource) problem (K)
$T_0 = T^{\text{e}}$	constant temperature of environment (K)
T'	Carnot temperature control (K)
$\dot{T} = \mathrm{d}T/\mathrm{d}\tau$	rate of control of T in time τ (K)
t	physical time (s)
$\dot{W}$	mechanical power (J s^{-1})
w	specific work of the fluid at flow, power per unit mass flux (J kg^{-1})
x	transfer area coordinate (m)
α	overall heat transfer coefficient (J m^{-2} s^{-1} K^{-1})
γ	cumulative conductance (J s^{-1} K^{-1})
ε_σ	Legendre transform of Lagrangian L_σ (J m^{-3} K^{-1})
χ	time constant (–)
$\eta = p/q_1$	first-law efficiency (–)
Φ	factor of internal irreversibility (–)
τ	non-dimensional time (x/H_{TU}) (–)

Subscripts

i	ith state variable
1, 2	first and second fluid

Superscripts

e	environment, equilibrium
f	final state
i	initial state
k or n	number of kth or nth stage
N	total number of stages
′	effective quantity modified by presence of Φ

processes [4]. Such bounds are reversible; the magnitude of the work delivered during the reversible approach to equilibrium is equal to the one of the work supplied, after the initial and final states are after the initial and final states are inverted, i.e. when the second process reverses to the initial state of the first. Our research is towards generalization of the classical exergy for finite rates. During the approach to the equilibrium the so-called engine mode of the system takes place in which the work is released, during the departure-the so-called heat-pump mode occurs in which the work is supplied. The work W delivered in the engine mode is positive by assumption. In the heat-pump mode W is negative, which means that the positive work ($-W$) must be supplied to the system. To find a generalized exergy, optimization problems are considered, for the maximum of the work delivered (max W) and for the minimum of the work supplied (min ($-W$)). We show that while the reversibility property is lost for such exergy, its (kinetic) bounds are stronger and hence more useful than classical thermostatic bounds. This substantiates role of the extended exergy for evaluation of energy limits in practical systems.

With functionals of power generation (consumption) and variational calculus [5] we can calculate the extended exergy and related extremum work. Our problem of generalized exergy falls into the category of finite-time potentials, an important problem of contemporary thermodynamics [2]. In this paper we solve the problem of extremum work by using the concept of multistage energy production or consumption, where each stage is the so-called Curzon–Ahlborn–Chambadal–Novikov process [2,3]. The concept of single irreversible stage is illustrated in Fig. 1 depicting the temperature-entropy diagram of the stage. Each stage can work either in the heat-pump mode (larger, external loop in Fig. 1) or in the engine mode (smaller, internal loop in Fig. 1).

Our analysis here extends the previous analyses of the problem [2,3,1] by taking into account internal irreversibilities within the thermal machines at each stage of the operation following the recent method that applies the factor of

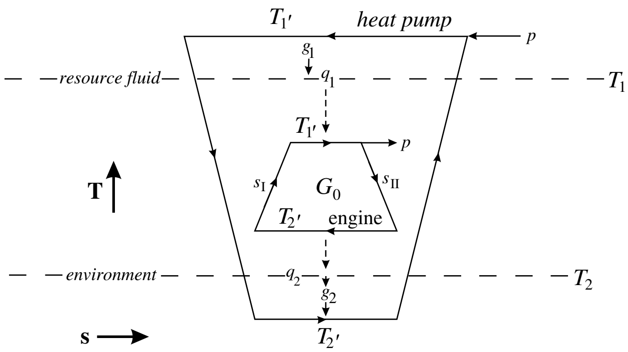

Fig. 1. Principle of designations for two basic modes with internal and external dissipation: power yield in an engine and power consumption in a heat pump. The internal dissipation is characterized by the coefficient $\Phi = \Delta S_{2'}/\Delta S_{1'}$; where $\Delta S_{1'}$, and $\Delta S_{2'}$, are the respective the entropy changes of the circulating fluid.

internal irreversibilities, Φ [7]. By definition, $\Phi = \Delta S_{2'}/\Delta S_{1'}$ (where $\Delta S_{1'}$ and $\Delta S_{2'}$ are respectively the entropy changes of the circulating fluid along the two isotherms $T_{1'}$ and $T_{2'}$ in Fig. 1) equals the ratio of the entropy fluxes across the thermal machine, $\Phi = J_{S_{2'}}/J_{S_{1'}}$. Due to the second law inequality at the steady state the following inequalities are valid: $J_{S_{2'}}/J_{S_1} > 1$ for engines and $J_{S_{2'}}/J_{S_1} < 1$ for heat pumps; thus the considered ratio Φ measures the process irreversibility. In fact, Φ is a synthetic measure of the machine's imperfection. The quantity Φ satisfies inequality $\Phi > 1$ for engine mode and $\Phi < 1$ for heat-pump mode of the system. Our purpose is to derive a generalized exergy in terms of Φ.

In this paper, we assume the constancy of Φ. Note, however, that whereas one can always handle the effect of internal dissipation in the form described by Eq. (3) below, one may treat Φ as a constant coefficient only in the first approximation. In general, Φ may be a complicated function of the machine's operating variables. Referring to the variability of Φ, Sieniutycz and Szwast [7] presented in Appendix of their paper an analysis that allows to exploit data of the internal entropy production σ_s^{int} to calculate an averaged value of coefficient Φ. Such mean Φ is next used in analyses within the boundaries of operative parameters of interest. An alternative analysis which uses σ_s^{int} instead of Φ in modeling is not easier since the quantity σ_s^{int} may also be a complicated function of the machine's operating variables; in the description of thermal machines the use of Φ is often more suitable than the use of σ_s^{int}. Clearly, applying a variable Φ or σ_s^{int} will ensure more exact modeling at the expense of much more complicated formulas. Yet, in this latter case, due to the resulting complication, the results universality is lost and one is usually forced to use numerical approaches instead of analytical ones, achieved for constant Φ.

The second issue requiring at least a brief comment is the use of the thermodynamic entropy in the theory presented. If the working body is far from equilibrium then the notion of thermodynamic entropy for it is no longer applicable. Such entropy only exists and can be calculated subject to the assumption of internal equilibrium. This is why in finite time thermodynamics it is usually assumed that the significant irreversibilities are concentrated at contact points between internally equilibrium subsystems. For highly non-equilibrium systems statistical approaches involving probability distributions and master equations may be more fruitful.

In our mathematical formalism the so-called Carnot temperature T' appears, defined by Eq. (6) below. The origin and role of T' was discussed in detail earlier [6] for steady endoreversible processes ($\Phi = 1$) associated with infinite (constant temperature) reservoirs. In the present work, in its part two, Carnot temperature is applied for dynamic (unsteady) evolutions associated with the decay of the thermal potential (temperature) of a finite reservoir in time. Moreover, the endoreversibility assumption is abandoned (arbitrary Φ different than unity). It is just the finiteness of the upper reservoir that is consistent with the notion of exergy, in our case generalized or rate dependent exergy.

2. Entropy production and efficiency

We shall present here a shortest possible proof of the formula describing the real work by using the so-called Gouy–Stodola law that links the lost work with the entropy production [4]. By evaluating *total* entropy produced at an infinitesimal stage (the sum of external and internal parts) as the difference between the outlet and inlet entropy flows we find in terms of the first-law efficiency η

$$\mathrm{d}S_\sigma = \frac{\mathrm{d}Q_2}{T_2} - \frac{\mathrm{d}Q_1}{T_1} = \frac{\mathrm{d}Q_1(1-\eta)}{T_2} - \frac{\mathrm{d}Q_1}{T_1} = \frac{\mathrm{d}Q_1}{T_2}(1 - \eta - T_2/T_1). \quad (1)$$

This is a general equation as there was no special assumptions involved in its derivation. It states that the entropy production in an arbitrary thermal engine is directly related to the deviation of the engine's efficiency from the corresponding Carnot efficiency. This conclusion will lead us to an important analytical formula for the total entropy source that will enable its direct optimization. To derive such a formula we note that the thermal efficiency of any real thermal engine can always be written in the form

$$\eta = 1 - \frac{\mathrm{d}Q_2}{\mathrm{d}Q_1}. \quad (2)$$

The entropy balance of the thermal machine contains the internal entropy production σ_s^{int} as a source term. In terms of internal irreversibility factor $\Phi = 1 + T_{1'}\mathrm{d}\sigma_s^{int}/\mathrm{d}Q_1$ the entropy balance of the internal part takes the form usually applied for thermal machines

$$\Phi \frac{\mathrm{d}Q_1}{T_{1'}} = \frac{\mathrm{d}Q_2}{T_{2'}}. \quad (3)$$

One can evaluate Φ from the internal entropy production within the thermal machine. As in many cases Φ is a complicated function of the machine's operating variables an averaged value of Φ over the cycle is found. Next this average Φ is treated as the process constant. The efficiency η follows in terms of Φ in the form

$$\eta = 1 - \frac{dQ_2}{dQ_1} = 1 - \Phi \frac{T_{2'}}{T_{1'}}. \tag{4}$$

This equation simplifies, of course, to the Carnot formula in terms of both primed T when the internal entropy source vanishes which is the case of so-called endoreversible operation. Note that no special assumptions were made to derive Eqs. (1) and (4), yet Φ can be a variable quantity dependent of all state coordinates.

After eliminating η from Eqs. (1) and (4) we conclude that, quite generally, the total entropy produced at an infinitesimal stage can be written in the form

$$dS_\sigma = \frac{dQ_1}{T_2}\left(\Phi \frac{T_{2'}}{T_{1'}} - \frac{T_2}{T_1}\right) = dQ_1\left(\frac{1}{T'} - \frac{1}{T_1}\right) + dQ_1 \frac{(\Phi - 1)}{T'}. \tag{5}$$

In the last expression of this equation the structural quantity called the Carnot temperature T' was introduced that satisfies the thermodynamic relation

$$T' \equiv T_2 T_{1'} / T_{2'}. \tag{6}$$

In terms of T' the thermal efficiency η assumes the simple, pseudo-Carnot form

$$\eta = 1 - \Phi \frac{T_2}{T'}. \tag{7}$$

The resulting expression (5) describes the sum of the external entropy source (in the reservoirs) and the internal entropy source (within the thermal machine). We observe a remarkable simplicity of the analytical description in terms of the Carnot temperature.

3. Steady heat flux and power production

An expression describing the heat flux propelling the thermal machine can also be obtained. To get an explicit analytical formula we must apply some special models of the heat exchange. Here the Newtonian model with conductances g_1 and g_2 is used. The corresponding heat transfer coefficients are α_1 and α_2. Since the entropy balance (3) holds, temperatures $T_{1'}$ and $T_{2'}$ are not independent but linked by

$$\frac{g_2(T_{2'} - T_2)}{T_{2'}} - \Phi \frac{g_1(T_1 - T_{1'})}{T_{1'}} = 0. \tag{8}$$

This means that the system has only one degree of freedom (one independent control). We use (6) to substitute into (8). We then obtain $T_{1'}$ in terms of Carnot T'

$$T_{1'} = \frac{\Phi g_1 T_1 + g_2 T'}{\Phi g_1 + g_2}, \tag{9}$$

and the corresponding equation for temperature $T_{2'} \equiv T_{1'} T_2 / T'$. The fluxes of heat are

$$q_1 \equiv \frac{d^2 Q_1}{\alpha_1 dt\, dA_1} g_1 = (T_1 - T_{1'}) g_1 = \frac{g_1 g_2 (T_1 - T')}{\Phi g_1 + g_2} \equiv g'(\Phi)(T_1 - T'), \tag{10}$$

and $q_2 = q_1(1-\eta)$, where η is defined by the pseudo-Carnot expression (7). In (10) an operational overall conductance has been defined as follows:

$$g'(\Phi) \equiv \frac{g_2 g_1}{\Phi g_1 + g_2} = \left(g_1^{-1} + \Phi g_2^{-1}\right)^{-1}. \tag{11}$$

This is, in fact, the suitably modified *overall* conductance of an inactive heat transfer in which the use of the operative (Φ dependent) heat conductance, g' is required.

In terms of the Carnot temperature the work flux or power p follows in the form

$$p = q_1 \eta = g'(\Phi)(T_1 - T')\left(1 - \Phi \frac{T_2}{T'}\right). \tag{12}$$

Under the assumption of a constant Φ, the maximum power of the engine is found by differentiation of p with respect to free control T'. The efficiency at maximum power is

$$\eta_{mp} = 1 - \Phi T_2 / \sqrt{\Phi T_1 T_2} = 1 - \sqrt{\Phi T_2 / T_1}. \tag{13}$$

This formula generalizes the well-known result of Curzon–Ahlborn–Chambadal–Novikov ([3], Berry et al., 2000) for the case of imperfect thermal machine. Rigorously, it applies to fluids with a constant heat capacity. However, it is valid only for constant Φ and under the assumption of infinite reservoirs. This needs to be improved in the case of a finite reservoir or a finite flow of fluid, as shown in the corresponding analysis below.

4. Finite resources and dynamical optimization

When resources become finite or the propelling fluid flows at a finite rate the driving temperature and other intense parameters decrease along the process path. The above analysis needs to be generalized to take into account the decay of the thermal potential in time or space. A dynamic analysis replaces the previous (steady) analysis, and the formalism is transferred from the realm of functions to the realm of functionals. Here the optimization task is to find an optimal profile of the driving temperature along the resource fluid path that assures the minimum of the integral entropy production and—simultaneously—the extremum of the work, consumed or delivered. The idea of a sequential dynamical process leading to the generalized exergy is illustrated in Fig. 2.

Let us outline derivations leading to functionals describing generalized work and exergy. From the pseudo-Carnot equation (7) the efficiency representation of the Carnot temperature follows in the form $T' = \Phi T_2/(1-\eta)$. Eq. (10) then reads in terms of the differentials of cumulative heat flux and the cumulative conductance γ',

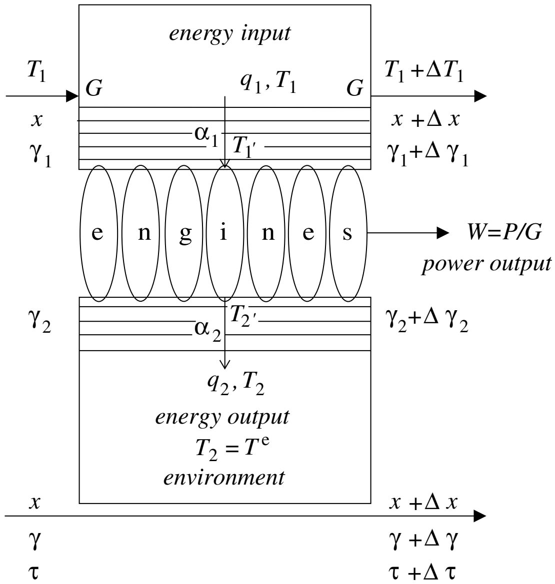

Fig. 2. A multistage CACN operation as a sequential model of active heat exchange between two fluids that leads to the notion of generalized exergy (in the engine mode $\Delta T_1 \leqslant 0$; in the heat-pump mode $\Delta T_1 < 0$).

$$d\dot{Q}_1 \equiv d\gamma'(T_1 - \Phi T_2/(1-\eta)). \tag{14}$$

This can be solved with respect to η to yield a suitable formula describing the instantaneous efficiency in terms of the local heat flux density or the derivative $d\dot{Q}_1/dA$

$$\eta = 1 - \Phi\frac{T_0}{T - d\dot{Q}_1/d\gamma'} = 1 - \Phi\frac{T_0}{T - d\dot{Q}_1/(\alpha' dA)}. \tag{15}$$

The derivative term $\upsilon = d\dot{Q}_1/d\gamma'$ is a process control that has units of the temperature itself. It is essential that it is proportional to the derivative of T with respect to the resource contact time t with engines' fluid or dimensionless time τ. This property follows from the differential balance of the driving fluid given below in the form of several alternative expressions

$$\begin{aligned} d\dot{Q}/d\gamma' &\equiv \upsilon = -\dot{G}c\,dT/(\alpha' a_v F\,dx) = -\rho c\,dT/(\alpha' a_v\,dt) \\ &= -\chi\,dT/dt = -dT/d\tau \end{aligned} \tag{16}$$

of which the two last ones are the most suitable. In Eq. (16), $\chi = c/(\alpha' a_v)$ is a time constant for the energy exchange process. Two other useful quantities can also be selected in Eq. (16). The first one is a spatial scale for the overall transfer, H_{TU},

$$\frac{\dot{G}c}{\alpha' a_v F} = H_{TU}, \tag{17}$$

whereas the second is a non-dimensional time, τ

$$\tau \equiv \frac{x}{H_{TU}} = \frac{\alpha' a_v F}{\dot{G}c}x. \tag{18}$$

H_{TU} has the units of length and is known as the 'height of the heat transfer unit'. In the above formula H_{TU} is referred to the fluid at state 1. The independent variable τ is a non-dimensional length called the 'number of transfer units'. Clearly, the variables τ, x and t measure the system's extent. The fluid residence time, t, is proportional to this extent. Even in nonlinear fluids the time constant $\chi = c/(\alpha' a_v)$, linking t and τ, is practically temperature independent due to the similar type of dependence of α' and c on T. This property substantiates the usefulness of the non-dimensional variable τ that absorbs into its definition the time constant χ. With Eq. (16) the local pseudo-Carnot efficiency (15) takes a suitable form

$$\eta = 1 - \Phi\frac{T_2}{T + \chi\,dT/dt} = 1 - \Phi\frac{T_2}{T + dT/d\tau}. \tag{19}$$

Note the presence of the Carnot temperature operators in the denominators of these expressions. The suitability of Eq. (19) follows from the presence of T itself and the time derivative of T, the property that renders the cumulative work W a well-defined functional. With Eq. (19), the cumulative power per unit fluid flow, $\dot{W}/\dot{G}$, can be obtained for any process mode by integration of the product of Eq. (19) and the associated heat differential $c\,dT$ between an arbitrary initial temperature T^i to an arbitrary final temperature T^f of the fluid. This integration leads to a finite-rate generalization of the specific work of the *flowing* fluid

$$\begin{aligned} w \equiv \dot{W}/\dot{G} &= -\int_{\tau^i}^{\tau^f} c\left(1 - \frac{\Phi T_2}{T + \chi\,dT/dt}\right)dT \\ &= -\int_{\tau^i}^{\tau^f} c\left(1 - \frac{\Phi T_2}{T + \dot{T}}\right)\dot{T}\,d\tau, \end{aligned} \tag{20}$$

where the dots in the last expression refer to the derivatives with respect to the non-dimensional time τ rather than t.

The specific work expression (20) can be transformed into the functional

$$\begin{aligned} w = &-\int_{\tau^i}^{\tau^f} c\left(1 - \frac{T_2}{T}\right)dT \\ &- T_2\int_{\tau^i}^{\tau^f} c\left(\frac{\dot{T}}{T(T + \dot{T})} - \frac{\Phi - 1}{T + \dot{T}}\right)\dot{T}\,d\tau, \end{aligned} \tag{21}$$

where the first (classical) part is path-independent and describes the reversible work.

From Eq. (5) an integral describing the specific entropy production in the dynamical problem follows as

$$s_\sigma = \dot{S}_\sigma/\dot{G} = \int_{\tau^i}^{\tau^f} c\left(\frac{T}{T(T + \dot{T})} - \frac{\Phi - 1}{T + \dot{T}}\right)\dot{T}\,d\tau. \tag{22}$$

Its two additive parts take into account the external and internal dissipation. The presence of integral (22) in Eq. (21) proves that Eq. (21) is consistent with the Gouy–Stodola law whenever the second reservoir is infinite and has the temperature of the environment, $T_2 = T^e$. For the fixed end states T^i and T^f (initial and final temperatures of the resource fluid) the extremum trajectories of functionals (21) and (22) are the same because the first integral in Eq. (21) is path independent. Of course, this is associated with the potential properties of classical (reversible) work.

5. Extremum dynamical path from the first integral

The variational calculus applied to Eq. (21) or (22) leads to the Euler–Lagrange equation of the optimization problem in which either work or entropy production are extremized. As temperature T is the only dynamical variable, the state dimensionality is one, and instead of solving the Euler–Lagrange equation one may write down the Legendre transform of the integrand of (21) or (22) as the first integral of the problem (an energy-like integral). The obtained first integral is the constant of the extremal path, say, h for the work functional or h_σ for the entropy production functional. It follows that $h = T_2 h_\sigma$, i.e. both approaches result in the same path whenever the second reservoir is infinite, i.e. whenever T_2 is constant.

We shall now describe some insightful details of the derivation leading to the Legendre transform of the thermodynamic Lagrangian, L_σ. For the integrand of the entropy production integral, Eq. (22), taken in a slightly generalized form which allows the state dependent heat capacity

$$L_\sigma(T,\dot{T}) = c_v(T)\left(\frac{\dot{T}^2}{T(T+\dot{T})} + (1-\Phi)\frac{\dot{T}}{T+\dot{T}}\right) \tag{23}$$

we calculate the derivative

$$\partial L_\sigma/\partial\dot{T} = c_v(T)\left(\frac{2\dot{T}T+\dot{T}^2}{T(T+\dot{T})^2} + (1-\Phi)\frac{T}{(T+\dot{T}^2)}\right) \tag{24}$$

and then substitute the expression

$$\dot{T}\partial L_\sigma/\partial\dot{T} = c_v(T)\left(\frac{2\dot{T}^2T+\dot{T}^3}{T(T+\dot{T})^2} + (1-\Phi)\frac{T\dot{T}}{(T+\dot{T})^2}\right), \tag{25}$$

into the formula for the Legendre transform of L_σ. After simplification of the expression

$$\begin{aligned}\frac{\varepsilon_\sigma}{c_v(T)} &\equiv \frac{\dot{T}\partial L_\sigma/\partial\dot{T} - L_\sigma}{c_v(T)}\\ &= \frac{2\dot{T}^2T+\dot{T}^3}{T(T+\dot{T})^2} + (1-\Phi)\frac{T\dot{T}}{(T+\dot{T})^2} - \frac{\dot{T}^2}{T(T+\dot{T})}\\ &\quad - (1-\Phi)\frac{\dot{T}}{T+\dot{T}}\end{aligned} \tag{26}$$

we obtain the following Legendre transform of the thermodynamic Lagrangian L_σ

$$\dot{T}\partial L_\sigma/\partial\dot{T} - L_\sigma = c_v(T)\left(\frac{\dot{T}^2}{(T+\dot{T})^2} - (1-\Phi)\frac{\dot{T}^2}{(T+\dot{T})^2}\right). \tag{27}$$

The first (Φ-free) component describes the effect of external entropy production, whereas the second one—the effect of internal entropy production. In an "endoreversible" process, where only external dissipation takes place and $\Phi = 1$, the second term vanishes. In a general situation where both external and internal contributions are essential our approximate constant—Φ theory yields the following simple result for the Legendre transform of the total entropy production

$$\varepsilon_\sigma(T,\dot{T}) \equiv \dot{T}\partial L_\sigma/\partial\dot{T} - L_\sigma = c_v(T)\frac{\Phi\dot{T}^2}{(T+\dot{T})^2}. \tag{28}$$

In conclusion, for the entropy Lagrangian L_σ i.e. the integrand of the functional (22), an equation describing the extremal path is obtained from the equation

$$\Phi c\frac{\dot{T}^2}{(T+\dot{T})^2} = h_\sigma. \tag{29}$$

The quantity h_σ is the parameter called the numerical Hamiltonian of the optimization problem in the entropy representation. Solving equality (29) with respect to rate $\dot{T}$ we obtain an optimal trajectory associated with the minimum entropy production or extremum work in our dynamical process.

After introducing the intensity constant of the optimal process, ξ, defined by an equation

$$\xi\left(\frac{h_\sigma}{\Phi c}\right) \equiv \pm\sqrt{\frac{h_\sigma}{\Phi c}}\left(1-\pm\sqrt{\frac{h_\sigma}{\Phi c}}\right)^{-1} = \left(\pm\sqrt{\frac{\Phi c}{h_\sigma}}-1\right)^{-1}, \tag{30}$$

(upper sign refers to the heat-pump mode, lower one to the engine mode) an exponential unconstrained extremal follows for the processes with constant heat capacity

$$\dot{T} = \xi(h_\sigma,\Phi)T. \tag{31}$$

Eq. (31) is the representation of an extremal curve in terms of the "dissipative Hamiltonian" h_σ, which is the rate indicator of the optimal path. In fact, it is a suitable rate indicator because h_σ, is constant along any optimal trajectory. For a vanishing h_σ an extremal correspond with a reversible quasistatic process, with vanishing rate constant ξ, vanishing rate $\dot{T}$ and without entropy production. Finite-rate evolutions correspond with finite values of the quantities $h_\sigma, \xi, \dot{T}, s_\sigma$ and L_σ. For very intense processes the numerical values of these quantities are very high.

Eq. (31) describes the relaxing extremals as a set of curves parametric with respect to h_σ (or h). In such equations the independent variable is the (modified) non-dimensional time τ, or the ratio of pipeline length x and the height of the transfer unit HTU related to g' of Eq. (11). τ is identical with the (Φ dependent) overall number of transfer units. $\xi(\Phi,h_\sigma)$ is the rate indicator positive for the fluid's heating and negative for fluid's cooling. Its use in the optimal trajectory prediction is essential in the problems with given initial conditions for T and $\dot{T}$ (initial value problems in which the specification of T and $\dot{T}$ defines both constants h_σ and ξ. Yet, in the case of the two-point-boundary value problems in which initial and final values of T are prescribed, it suffices to evaluate and then use the (numerical value of) constant ξ. From the boundary conditions applied for the exponential extremal (31) the numerical value of ξ follows in the form

$$\xi = \ln(T^{\mathrm{f}}/T^{\mathrm{i}})/(\tau^{\mathrm{f}} - \tau^{\mathrm{i}}). \tag{32}$$

To express the same extremal in terms of the Carnot temperature $T' = T + \dot{T}$ requires the use of the equation

$$\frac{\mathrm{d}T}{\mathrm{d}\tau} = T' - T \tag{33}$$

consistent with Eqs. (14) and (16), Eq. (33) describes any nonoptimal or optimal heat exchange in our problem; thus it also applies to the optimal situation described by Eq. (31).

6. Generalized availability

From Eqs. (31) and (32) Carnot-temperature control ensuring the extremum of work is

$$\begin{aligned} T'(\tau) &= T(\tau)(1+\xi) \\ &= T^{\mathrm{i}}(T^{\mathrm{f}}/T^{\mathrm{i}})^{(\tau-\tau^{\mathrm{i}})/(\tau^{\mathrm{f}}-\tau^{\mathrm{i}})} \times (1 + \ln(T^{\mathrm{f}}/T^{\mathrm{i}})/(\tau^{\mathrm{f}} - \tau^{\mathrm{i}})). \end{aligned} \tag{34}$$

It corresponds with the entropy production (14) and the generalized availability

$$\begin{aligned} A^{\infty} &= A^{\mathrm{class}} + c(1-\Phi)T^{\mathrm{e}}\ln(T/T^{\mathrm{e}}) \\ &\quad \pm cT^{\mathrm{e}}\Phi\frac{[\ln(T/T^{\mathrm{e}})]^2}{\tau^{\mathrm{f}} - \tau^{\mathrm{i}} \pm \ln(T/T^{\mathrm{e}})}. \end{aligned} \tag{35}$$

Upper sign refers to the heat-pump mode, lower one to the engine mode. This formula is obtained as the extremum value of the integral (20) or (21) with the help of the extremum conditions (30) and (31) and subject to the standard boundary conditions for the exergy as extremal work. The last term of Eq. (35) may be put in the form in which the mean logarithmic rate associated with the optimal process is the argument of Eq. (35). The classical thermal availability of this equation is defined in the standard way

$$A^{\mathrm{class}} \equiv c(T - T^{\mathrm{e}}) - cT^{\mathrm{e}}\ln(T/T^{\mathrm{e}}). \tag{36}$$

In terms of the entropy-representation Hamiltonian, which is constant rate indicator along every autonomous path the generalized exergy for the fluid at flow reads

$$\begin{aligned} A(T, T^{\mathrm{e}}, h_{\sigma}) &= A^{\mathrm{class}}(T, T^{\mathrm{e}}, 0) \pm T_0 S_{v_{\mathrm{gen}}} \\ &= A^{\mathrm{class}}(T, T^{\mathrm{e}}, 0) \pm T^{\mathrm{e}} c Y(h_{\mathrm{s}}) \ln\left(\frac{T}{T^{\mathrm{e}}}\right), \end{aligned} \tag{37}$$

where the Hamiltonian dependent or, simultaneously, rate dependent coefficient $Y(h_{\sigma})$ is defined by an equation

$$Y(h_{\sigma}) \equiv (h_{\sigma}/(\Phi c))^{1/2} + (1-\Phi)(1 - \pm(h_{\sigma}/(\Phi c))^{1/2}). \tag{38}$$

(Upper sign refers to the heat-pump mode and lower one to the engine mode.) The classical availability is the potential or state function; its change between two states describes the reversible work. On the other hand, generalized availabilities are rate-dependent irreversible extensions of this classical function including minimally irreversible processes. Higher mean rates correspond with larger Hamiltonians h_{σ}, vanishing or quasistatic rates with vanishing Hamiltonians. Note that the mean process efficiency or the ratio A^{∞}/Q_1 is lower than the pseudo-Carnot efficiency (7) due to the finiteness of the resource flow and the corresponding decrease of the resource temperature as the process advances in time.

7. Concluding remarks

The exergy function (35) or (37) is the generalization of the standard exergy for the case of dissipative rates and imperfect power generators. In processes departing from the equilibrium (upper sign) the generalized exergy is larger than in processes approaching the equilibrium (lower sign). This is because one respectively adds or subtracts the product of T^{e} and entropy production in equations of the generalized availability. Importantly, the limits for the mechanical energy yield or consumption provided by exergies A^{∞} are stronger than those defined by the classical exergy. In fact, in both modes, the generalized exergies provide enhanced bounds in comparison with those of classical exergy. Both internal and external dissipation increases the minimum work that must be supplied to the system. Likewise, both sorts of dissipation decrease the maximum work that can be produced by the system. The Carnot temperature application to imperfect dynamical systems (with relaxed endoreversibility assumption), presented here, supplements and generalizes a less general formalism obtained earlier for steady endoreversible systems ($\Phi = 1$; [6]).

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