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An Unified Approach to Thermodynamics of Power Yield in Thermal, Chemical and Electrochemical Systems

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***Abstract*—**This paper unifies power optimization approaches in various energy converters, such as: thermal, solar, chemical, and electrochemical engines, in particular fuel cells. Thermodynamics leads to converter's efficiency and limiting power. Efficiency equations serve to solve problems of upgrading and downgrading of resources. While optimization of steady systems applies the differential calculus and Lagrange multipliers, dynamic optimization involves variational calculus and dynamic programming. In reacting systems chemical affinity constitutes a prevailing component of an overall efficiency, thus the power is analyzed in terms of an active part of chemical affinity. The main novelty of the present paper in the energy yield context consists in showing that the generalized heat flux Q (involving the traditional heat flux q plus the product of temperature and the sum products of partial entropies and fluxes of species) plays in complex cases (solar, chemical and electrochemical) the same role as the traditional heat q in pure heat engines.

The presented methodology is also applied to power limits in fuel cells as to systems which are electrochemical flow engines propelled by chemical reactions. The performance of fuel cells is determined by magnitudes and directions of participating streams and mechanism of electric current generation. Voltage lowering below the reversible voltage is a proper measure of cells imperfection. The voltage losses, called polarization, include the contributions of three main sources: activation, ohmic and concentration. Examples show power maxima in fuel cells and prove the relevance of the extension of the thermal machine theory to chemical and electrochemical systems. The main novelty of the present paper in the *FC* context consists in introducing an effective or reduced Gibbs free energy change between products p and reactants s which take into account the decrease of voltage and power caused by the incomplete conversion of the overall reaction.

***Keywords*—** Power yield, entropy production, chemical engines, fuel cells, exergy.

I. Introduction

In a previous work [1] we have analyzed models of power production and power optimization towards energy limits in purely thermal systems with finite rates. In particular, radiation engines were treated as important nonlinear systems governed by laws of thermodynamics and transport phenomena. Temperatures T of participating media were sole necessary variables to describe these systems. In the present work we treat generalized power yield problems systems in which both temperatures T and chemical potentials μ_k are essential. This is associated with engines propelled by fluxes of both energy and substance. In a process of power production shown in Fig. 1 two subsystems differing in values of T and μ interact through the set of power generators (engines). The production process is propelled by diffusive and/or convective fluxes of heat and mass transferred through 'conductances' or boundary layers. The energy flux (power) is created in each generator located between the resource stream ('upper' fluid 1) and, say, an waste stream ('lower' fluid, 2).

Basically, both transfer mechanisms, flows and values of conductances of boundary layers influence the rate of power generation [2-5]. Local fluxes of heat and power do not change along the steady process path only when both streams (reservoirs) in Fig.1 are infinite. Whenever one, say, upper, stream is finite, its thermal potential decreases along the path, which is the consequence of the energy balance. Any finite stream is thus a resource reservoir. It is the resource property or the finiteness of amount or flow of a valuable substance or energy which changes the upper fluid properties along its path. For the engine mode of the system and a very large 'lower' stream (sometimes the stream of the environmental fluid), one observes stage-wise relaxation of the upper stream S to the equilibrium with an infinite lower reservoir. This is a cumulative effect obtained for a resource fluid at flow, a set of sequentially arranged engines, and an infinite bath [6]. An inverse process, which needs a supply of an external power, may be referred to the upgrading of the resource in a heat pump [7]. Studies of resource downgrading or upgrading apply methods of dynamical optimization [8]. Indeed, the developments shown in Fig.1 may be regarded as dynamical processes since they evolve through sequence of states, either in the chronological time or in holdup (spatial) time.

Fuel cells working in the power production mode are also engine-type systems. In fact, they are electrochemical flow engines propelled by chemical reactions. Downgrading or upgrading of resources may also occur in the systems of the fuel cell type. The performance of fuel cells is determined by magnitudes and directions of participating streams and by mechanism of electric current generation. Voltage lowering in fuel cells below the reversible value is a good measure of their

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imperfection which influences the downgrading and upgrading of reagents. Yet, in this paper we restrict to the steady-state fuel cell systems.

Section II of the present paper derives relevant controls in power systems, the so called Carnot variables. These results are common for all processes considered here. Energy driven systems are treated in Sects III-VIII of this paper. Role of chemical affinities for chemical conversion is pointed out in Sec. X. Electrochemical systems (fuel cells) are analyzed in Sect XI. Sections XII and XIII present, respectively, final remarks and basic conclusions.

II. Development of Controls in Power Systems.

Here we shall recall and then use definitions of Carnot control variables (Carnot temperature and chemical potential) whose derivations and applications were originated in our previous work [9, 10]. Since diverse control variables of heat and mass transfer can accomplish the task of a sustainable energy conversion, alternative (more traditional) controls are also possible. However, the mathematical formulas are the simplest in terms of Carnot controls.

We begin with the simplest case of no mass transfer, i.e. we shall consider a steady, internally reversible ('endoreversible') engine with perfect internal power generators characterized at each stage by temperatures of circulating fluid $T_{1'}$ and $T_{2'}$, Fig.1.

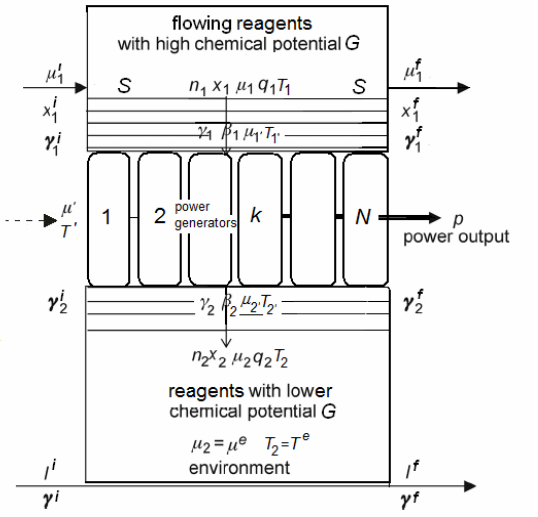

Fig.1. A discrete scheme of chemical and/or thermal engine. G is the flux of Gibbs thermodynamic function (flux G in Eqs. (11) and (12)).

The stream temperatures, attributed to the bulk o each fluid are T_1 and T_2. The inequalities $T_1>T_{1'}>T_{2'}>T_2$ are valid for the engine mode of the system. The internal entropy balance of a perfect engine at an arbitrary stage yields

$$\frac{q_2}{T_{2'}} = \frac{q_1}{T_{1'}} \tag{1}$$

Continuity of pure heat fluxes through each boundary layer (each conductor) is assumed at each stage ($q_1=q_{1'}$ and $q_2= q_{2'}$), the property which does not hold in the case when heat transfer is coupled with transfer of substances.

As a flux can be normalized by dividing it by a constant resource mass flux we neglect dots over symbols of fluxes.

Total entropy balance of a system's stage leads to total entropy source σ_s as the difference of outlet and inlet entropy fluxes

$$\sigma_s = \frac{q_2}{T_2} - \frac{q_1}{T_1} = \frac{q_1}{T_2}\frac{T_{2'}}{T_{1'}} - \frac{q_1}{T_1} = \frac{q_1}{T_2}\left(\frac{T_{2'}}{T_{1'}} - \frac{T_2}{T_1}\right). \tag{2}$$

With an effective temperature called Carnot temperature

$$T' \equiv T_2 \frac{T_{1'}}{T_{2'}} \tag{3}$$

entropy production of the endoreversible process, Eq. (2), takes the following simple form

$$\sigma_s = q_1\left(\frac{1}{T'} - \frac{1}{T_1}\right) \tag{4}$$

This form is identical with the familiar expression obtained for processes of purely dissipative heat exchange between two bodies with temperatures T_1 and T'.

From the entropy and energy balances of an internally reversible process the "endoreversible" thermal efficiency follows in terms of temperatures of the circulating fluid

$$\frac{p}{q_1} = \eta = 1 - \frac{T_{2'}}{T_{1'}} \tag{5}$$

In terms of temperature T' of Eq. (3) this efficiency assumes the classical Carnot form containing the temperature in the bulk of the second reservoir and temperature T'.

$$\eta = 1 - \frac{T_2}{T'} \tag{6}$$

This property substantiates the name "Carnot temperature" for the control variable T'. When a control action takes place, the superiority of Eq. (6) over Eq. (5) consists in using in (6) single, free control T', instead of two constrained controls of Eq. (5) (linked by an internal balance of the entropy). Moreover, the endoreversible power is also of classical form

$$p = \eta q_1 = \left(1 - \frac{T_2}{T'}\right) q_1 \tag{7}$$

In terms of T' description of thermal endoreversible cycles is broken down to formally "classical" equations which contain T' in place of T_1. Importantly, the derivation of Eqs. (1) - (7) does not require any specific assumptions on the nature of heat transfer. In irreversible situations Carnot temperature T' efficiently represents temperature of the upper reservoir, T_1. Yet,

at the reversible Carnot point, where $T_{1'} = T_1$ and $T_{2'} = T_2$, Eq. (3) yields $T' = T_1$, thus returning to the classical reversible theory. These properties of Carnot temperature render descriptions of endoreversible and reversible cycles similar. They also make the variable T' a suitable control in both static and dynamic cases [9, 10].

For the purpose of this paper it is worth knowing that in terms of Carnot temperature T' the linear (Newtonian) heat transfer is described by a simple kinetic equation

$$q_1 = g(T_1 - T'), \tag{8}$$

where g is overall heat transfer conductance i.e. the product of a total exchange area and an overall heat transfer coefficient [8].

For a linear resource relaxing to the thermodynamic equilibrium along the stationary Lagrangian path or for an unsteady relaxation, the kinetics related to Eq. (8) has the linear form

$$\frac{dT_1}{d\tau} = T' - T_1 , \tag{9}$$

where the non-dimensional time τ satisfies Eq. (38) below and is related to the overall conductance g of Eq. (8). Subscript 1 is neglected in equations describing dynamical paths.

The resource (or a finite "upper stream") is upgraded whenever Carnot temperature T' is higher than resource's temperature T_1. Whereas the resource is downgraded (relaxes to the thermodynamic equilibrium with an infinite "lower stream" or the environment of temperature T_2) whenever Carnot temperature T' is lower than resource's temperature T_1. In linear systems, power-maximizing T' is proportional to the resource's temperature T_1 at each time instant [6]. For more details and, in particular, the case of two finite streams with constant heat capacities see a book by Sieniutycz and Jeżowski [11].

The notion of Carnot temperature can be extended to chemical systems where also the Carnot chemical potential emerges [10]. We shall also make some remarks here.

The structure of Eq. (1) also holds to systems with mass transfer provided that instead of pure heat flux q the so called total heat flux (mass transfer involving heat flux) Q is introduced satisfying an equation

$$Q \equiv q + Ts_1 n_1 + ...Ts_k n_k .. + Ts_m n_m \tag{10}$$

or, since the heat flux equals the difference between total energy flux ε and flux of enthalpies of transferred components, $q=\varepsilon-h$,

$$Q \equiv \varepsilon - \mu_1 n_1 ... \mu_k n_k ... - \mu_m n_m . \equiv \varepsilon - G \tag{11}$$

where G is the flux of Gibbs thermodynamic function (Gibbs flux). The equality

$$\varepsilon = Q + G \tag{12}$$

is fundamental in the theory of chemical engines; it indicates that power can be generated by two propelling fluxes: heat flux Q and Gibbs flux G, each generation having its own efficiency (thermal and chemical efficiencies). The related driving forces are the temperature difference and chemical affinity.

When mass transfer is included the internal entropy balance of the perfect engine has in terms of total heat flux Q the same structure as Eq. (1) in terms of q, i.e.

$$\frac{Q_2}{T_{2'}} = \frac{Q_1}{T_{1'}} \tag{13}$$

The continuity of energy and mass fluxes through the resistive layers leads to 'primed' fluxes in terms of those for the bulk. Assuming a complete conversion we restrict to power yield by a simple reaction $A_1+A_2=0$ (isomerisation or phase change of A_1 into A_2). The energy balance

$$\varepsilon_1 = \varepsilon_2 + p \tag{14}$$

and the mass balance in terms of conserved fluxes through cross-sections 1' and 1 as well as 2' and 2

$$n_1 = n_2 \tag{15}$$

are combined with Eq. (13) describing the continuity of the entropy flux in the reversible part of the system. This yields

$$\frac{\varepsilon_1 - \mu_{1'} n_1}{T_{1'}} = \frac{\varepsilon_2 - \mu_{2'} n_2}{T_{2'}} \tag{16}$$

Eliminating ε_2 and n_2 from these equations yields

$$\frac{\varepsilon_1 - \mu_{1'} n_1}{T_{1'}} = \frac{\varepsilon_1 - p - \mu_{2'} n_1}{T_{2'}} \tag{17}$$

whence

$$\frac{p}{T_{2'}} = \frac{\varepsilon_1 - \mu_{2'} n_1}{T_{2'}} - \frac{\varepsilon_1 - \mu_{1'} n_1}{T_{1'}} . \tag{18}$$

which leads to a power expression

$$p = \varepsilon_1 - \varepsilon_2 = \varepsilon_1 (1 - \frac{T_{2'}}{T_{1'}}) + T_{2'} (\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}}) n_1 \tag{19}$$

In Eq. (19) power p is expressed in terms of fluxes continuous through the conductors. To proceed further we need consider quantitatively the entropy produced in the system.

The entropy production in the system follows from the balance of fluxes in the bulks of the streams

$$\sigma_s = \frac{q_2}{T_2} - \frac{q_1}{T_1} + (s_2 - s_1) n_1 \tag{20}$$

Eliminating q_2 from this result with the help of the energy balance (14) we obtain

$$\sigma_s = (q_1 + h_1 n_1)(\frac{1}{T_2} - \frac{1}{T_1}) + (\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2})n_1 - \frac{p}{T_2}. \quad (21)$$

An equivalent form of this equation is the formula

$$p = \varepsilon_1(1 - \frac{T_2}{T_1}) + T_2(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2})n_1 - T_2\sigma_s \quad (22)$$

which may be compared with the same power evaluated for the endoreversible part of the system

$$p = \varepsilon_1(1 - \frac{T_{2'}}{T_{1'}}) + T_{2'}(\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}})n_1 \ . \quad (23)$$

The comparison of Eqs (22) and (23) yields an equality

$$\varepsilon_1(1 - \frac{T_2}{T_1}) + T_2(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2})n_1 - T_2\sigma_s = \varepsilon_1(1 - \frac{T_{2'}}{T_{1'}}) + T_{2'}(\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}})n_1 \quad (24)$$

from which the entropy production can be expressed in terms of bulk driving forces and active driving forces (measures of process efficiencies). We finally obtain

$$\sigma_s = \frac{\varepsilon_1}{T_2}(\frac{T_{2'}}{T_{1'}} - \frac{T_2}{T_1}) + n_1(\frac{\mu_1}{T_1} - \frac{T_{2'}}{T_2}(\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}}) - \frac{\mu_2}{T_2}) \quad (25)$$

This expression generalizes Eq. (3) for the case when a single reaction $A_1+A_2=0$ undergoes in the system. Equation (25) leads again to the definition of Carnot temperature in agreement with Eq. (3) and to Carnot chemical potential of the (first) component

$$\frac{\mu'}{T'} = \frac{\mu_2}{T_2} + \frac{T_{2'}}{T_2}(\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}}) \ . \quad (26)$$

In a special case of an isothermal process the above formula yields a chemical control variable

$$\mu' = \mu_2 + \mu_{1'} - \mu_{2'} \quad (27)$$

which has been used earlier to study an isothermal engine [12]. After introducing the Carnot temperature in accordance with Eq. (3), total entropy production of the endoreversible power generation by the simple reaction $A_1+A_2=0$ (isomerisation or phase change of A_1 into A_2), takes the following simple form

$$\sigma_s = \varepsilon_1(\frac{1}{T'} - \frac{1}{T_1}) + (\frac{\mu_1}{T_1} - \frac{\mu'}{T'})n_1 \ . \quad (28)$$

Introducing into the above formula total heat Q_1 satisfying $Q_1 \equiv \varepsilon_1 - \mu_1 n_1$ we finally obtain

$$\sigma_s = Q_1(\frac{1}{T'} - \frac{1}{T_1}) + n_1\frac{\mu_1 - \mu'}{T'}, \quad (29)$$

where $Q_1=q_1+T_1s_1n_1$ is the total heat flux propelling the power generation in the system.

Carnot variables T' and μ' are two free, independent control variables applied in power maximization of steady and dynamical generators. The resulting equation (29) is formally equivalent with a formula obtained for the purely dissipative exchange of energy and matter between two bodies with temperatures T_1 and T' and chemical potentials μ_1 and μ'.

III. Internal Imperfections in Energy Systems

The ideas referring to endoreversible systems may be generalized to those with internal dissipation. In such cases a single irreversible unit can be characterized by two loops shown in Fig. 2 which presents the temperature–entropy diagram of an arbitrary irreversible stage. Each stage can work either in the heat-pump mode (larger, external loop in Fig. 2) or in the engine mode (smaller, internal loop in Fig. 2).

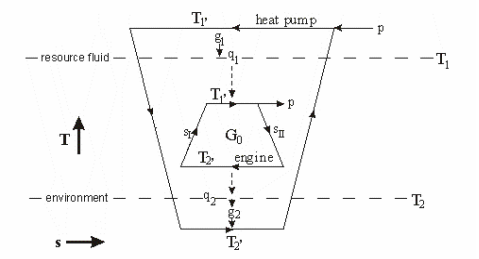

Fig. 2. Two basic modes with internal and external dissipation: power yield in an engine and power consumption in a heat pump. Primed temperatures characterize the circulating fluid.

The related analysis follows the earlier analyses of the problem which take into account internal irreversibilities by applying the factor of internal irreversibilities, Φ [11]. 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. 2) equals the ratio of the entropy fluxes across the thermal machine, $\Phi = J_{s2'}/J_{s1'}$. Because of the second law inequality at the steady state, the following inequalities are valid: $J_{s2'}/J_{s1} > 1$ for engines and $J_{s2'}/J_{s1} < 1$ for heat pumps; thus the considered ratio Φ measures the internal irreversibility. In fact, Φ is a synthetic measure of the machine's imperfection. Φ satisfies inequality $\Phi > 1$ for engine mode and $\Phi < 1$ for heat pump mode of the system. A typical goal is to derive efficiency, entropy production and power limits in terms of Φ. Applications of this quantity are discussed in the book by Sieniutycz and Jeżowski [11].

We shall now present an exposition of the formulas describing efficiencies, power yield and entropy production in systems with internal imperfections. This presentation corresponds with the assumption that it is an average value of Φ, evaluated within the boundaries of operative parameters of interest which is used in most of analyses of thermal machines.

In the analysis we shall make use of the fact that, in agreement with Eq. (13), the thermal efficiency component of any endoreversible thermal or chemical engine can always by written in the form η=1-Q_2/Q_1. By evaluating *total* rate of entropy production σ_s (the sum of external and internal parts) as the difference between the outlet and inlet entropy fluxes we find in terms of the first-law efficiency η

$$\sigma_s = \frac{Q_1(1-\eta)}{T_2} - \frac{Q_1}{T_1} = \frac{Q_1}{T_2}(1-\eta-\frac{T_2}{T_1}) \tag{30}$$

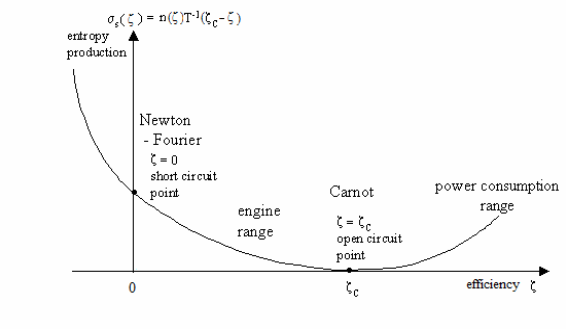

Fig. 3. Qualitative sketch illustrating entropy production in chemical engines versus chemical efficiency ζ in a flow operation with simultaneous mass transfer and power production. For thermal engines the picture is qualitatively similar provided that the chemical efficiency ζ is replaced by the thermal efficiency η.

Equation (30) is a general relationship as no special assumptions are involved in its derivation. It states that the entropy production in an arbitrary engine is directly related to the deviation of the thermal efficiency from the corresponding Carnot efficiency. This conclusion leads to an important analytical formula for the total entropy source that will enable its direct optimization. The entropy balance of an irreversible machine contains internal entropy production σ_s^{int} as a source term in the expression

$$\frac{Q_2}{T_{2'}} - \frac{Q_1}{T_{1'}} = \sigma_s^{\text{int}} \tag{31}$$

After defining the coefficient

$$\Phi = 1 + T_{1'}\sigma_s^{\text{int}} / Q_1 \tag{32}$$

called the internal irreversibility factor the internal entropy balance takes the form usually applied for thermal machines

$$\Phi\frac{Q_1}{T_{1'}} = \frac{Q_2}{T_{2'}} \tag{33}$$

We have already stressed that one can evaluate Φ from the averaged value of the internal entropy production, that describes the effect of irreversible processes within the thermal machine. Clearly, in many cases Φ is a complicated function of the machine's operating variables. In those complex cases one applies the data of $\sigma_s^{\text{int}} = dS_\sigma^{\text{int}} / dt$ to calculate averaged values of the coefficient Φ. In our analysis the quantity Φ is treated as the process constant. For chillers and energy generators experimental data of $\sigma_s^{\text{int}} = dS_\sigma^{\text{int}} / dt$ are available that allow the calculation of Φ. For more information, see the book by Sieniutycz and Jeżowski [11] and many references therein.

Consequently, thermal efficiency η can be evaluated in terms of suitable parameters characterizing the imperfect machine

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - (1 + T_{1'}\frac{\sigma_s^{\text{int}}}{Q_1})\frac{T_{2'}}{T_{1'}} = 1 - \Phi\frac{T_{2'}}{T_{1'}}. \tag{34}$$

After eliminating η from Eqs. (30) and (34) we conclude that, quite generally, total entropy production rate can be written as

$$\sigma_S = \frac{Q_1}{T_2}(\Phi\frac{T_{2'}}{T_{1'}} - \frac{T_2}{T_1}) = Q_1\left(\frac{(\Phi-1)}{T'} + (\frac{1}{T'} - \frac{1}{T_1})\right). \tag{35}$$

The first term in the resulting expression the describes the internal entropy source (within the thermal machine) and the second one the external entropy source (within the reservoirs).

Equivalently, after using the definition of the internal irreversibility factor (32) we obtain for the entropy generation

$$\sigma_s = \frac{T_{1'}}{T'} dS_\sigma^{\text{int}} + dQ_1(\frac{1}{T'} - \frac{1}{T_1}). \tag{36}$$

In the last two equations the Carnot temperature T' was introduced that satisfies the thermodynamic definition (3)

$$T' \equiv T_2 T_{1'} / T_{2'} \tag{3}$$

In terms of the Carnot temperature T' and factor Φ the efficiency η , Eq. (33), assumes the simple, pseudo-Carnot form

$$\eta = 1 - \Phi\frac{T_2}{T'}. \tag{37}$$

which is quite useful and general enough to describe thermal, radiative and chemical engines.

A particularly interesting role of the above formulas is observed for radiation engines which are energy systems driven by the black radiation. In these systems Gibbs flux G = 0, whereas total heat flux Q is identical with the energy flux ε,

i.e. $Q = \varepsilon$. Their power of entropy production follows from Eqs. (35) and (36) as

$$\sigma_s = \varepsilon_1\left(\frac{(\Phi-1)}{T'} + (\frac{1}{T'} - \frac{1}{T_1})\right) \quad (38)$$

or

$$\sigma_s = \frac{T_{1'}}{T'}\sigma_s^{\text{int}} + \varepsilon_1(\frac{1}{T'} - \frac{1}{T_1}). \quad (39)$$

The first of these equations can be applied immediately; the second calls for a function $T_{1'}(T_1, \varepsilon_1)$ as the one shown below of Eq. (40).

When the energy exchange in both reservoirs depends on the difference of temperatures in power a (a=4 for the radiative energy exchange and 1 for the Newtonian one), i.e. for

$$Q_1 = \varepsilon_1 = g_1(T_1^a - T_1^a) \quad (40)$$

then, since $T_{1'} = (T_1^a - \varepsilon_1 / g_1)^{1/a}$, from the radiation law, the following formula describes the power of entropy generation

$$\sigma_s = \frac{(T_1^a - \varepsilon_1 / g_1)^{1/a}}{T'}\sigma_s^{\text{int}} + \varepsilon_1(\frac{1}{T'} - \frac{1}{T_1}). \quad (41)$$

This means that only in the "endoreversible" case, i.e. when the power of internal entropy production vanishes, the external entropy production is simply related to the product of energy flux ε_1 and the suitable difference of temperature reciprocals, $(T')^{-1}$- $(T_1)^{-1}$, as in the two-body contact. In the general case of a finite internal entropy production the external part of σ_s follows in terms of its internal part in the form

$$\sigma_s^{ext} = \left(\frac{(T_1^a - \varepsilon_1 / g_1)^{1/a} - T'}{T'}\right)\sigma_s^{\text{int}} + \varepsilon_1(\frac{1}{T'} - \frac{1}{T_1}), \quad (42)$$

or the sum of both parts of the entropy production agrees with Eq. (42). Therefore, the analytical description of thermal converters in terms of the Carnot temperature is particularly simple.

The efficiency worsening caused by the dissipation is described in a general way by the inverted formula (30)

$$\eta = \eta_C - T_2\sigma_s / \varepsilon_1 \quad (43)$$

Of course, the pseudo-Carnot formula, Eq. (37), also belongs to the class of imperfect efficiencies since it can be expressed in the form

$$\eta = \eta_C - T_2(\frac{\Phi}{T'} - \frac{1}{T_1}). \quad (44)$$

This result implies the ratio σ_s/ε_1 consistent with Eqs. (35) and (38). Equations for entropy production σ_s, presented above, are helpful in definite situations when one wants to evaluate the efficiency worsening. Yet, the knowledge of the entropy production σ_s is also necessary in calculations of generalized exergies [11]. In the dynamical cases essential is also the best time behavior of σ_s.

The majority of research papers on power limits published to date deals with systems in which there are two infinite reservoirs. To this case refer steady-state analyses of the Chambadal-Novikov-Curzon-Ahlborn engine (CNCA engine) in which energy exchange is described by Newtonian law of cooling [2], or of the Stefan-Boltzmann engine, a system with the radiation fluids and energy exchange governed by the Stefan-Boltzmann law [3]. Entropy production characteristic for these systems is shown in Fig. 3.

In a CNCA engine the maximum power point may be related to the optimum value of a single, free (unconstrained) control variable which may be efficiency η, heat flux q_1, or Carnot temperature T'. When the internal irreversibilities within the power generator play a role, the pseudo-Carnot formula (37) applies in place of Eq. (6), where Φ is the internal irreversibility factor [5].

In terms of bulk temperatures T_1, T_2 and Φ one finds for linear systems at the maximum power point

$$T'_{opt} = (T_1\Phi T_2)^{1/2}. \quad (45)$$

For the Stefan-Boltzmann engine exact expression for the optimal point cannot be determined analytically, yet, this temperature can be found graphically from the chart $p=f(T')$. A pseudo-Newtonian model, [5, 7], which treats the state dependent energy exchange with coefficient $\alpha(T^3)$, omits to a considerable extent analytical difficulties associated with the use of the Stefan-Boltzmann equation. The results stemming from this model show that the formula (45) is a good approximation also in nonlinear cases.

IV. A Theory for Dynamical Energy Production

Whenever the resources are finite the previous (steady) analysis is replaced by a dynamic one, and the mathematical formalism is transferred from the realm of functions to the realm of functionals. This refers to the case when the propelling fluid flows at a finite rate; in this case the Carnot temperature and the resource temperature decrease along the process path. Here the optimization task is to find an optimal profile of the Carnot temperature T' along the resource fluid path that assures an extremum of the work consumed or delivered and – simultaneously – the minimum of the integral entropy production. Figure 4 below illustrates the evaluation idea of the dynamic work limit for a system of a resource and infinite bath. This idea leads to a generalized exergy, for a finite duration of the state change and a minimal irreversibility.

Dynamical energy yield requires the knowledge of an extremal curve rather than an extremum point. This leads to variational metods (to handle extrema of functionals) in place of static optimization methods (to handle extrema of functions). For example, the use of a pseudo-Newtonian model to quantify the dynamic power yield from radiation, gives rise to a non-exponential optimal curve describing the radiation

relaxation to the equilibrium. The non-exponential shape of the relaxation curve is the consequence of nonlinear properties of the radiation fluid. Non-exponential are also other curves describing the radiation relaxation, e.g. those following from exact models involving the Stefan-Boltzmann equation [4, 5, 7]. Optimal (e.g. power-maximizing) temperature of the resource, $T(t)$, is accompanied by the optimal control $T'(t)$; they both are components of the dynamic optimization solution.

Energy limits of dynamical processes are inherently connected with exergies, the classical exergy and its rate-dependent extensions. To obtain the classical exergy from work functionals it suffices to assume that the thermal efficiency of the system is identical with the Carnot efficiency. On the other hand, non-Carnot efficiencies, influenced by rates, lead to 'generalized exergies'. The benefit from generalized exergies is that they define stronger energy limits than those predicted by classical exergies [1,8,9,11].

The classical exergy defines bounds on the common work delivered from (or supplied to) slow, reversible processes [8]. Such bounds are reversible since 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 inverted, i.e. when the second process reverses to the initial state of the first. Our approach leads to the 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 work is supplied. Work W delivered in the engine mode is positive by assumption. In the heat-pump mode W is negative, or the positive work ($-W$) must be supplied to the system. To find a generalized exergy, optimization problems are set, for the maximum of the work delivered [max W] and for the minimum of the work supplied [min ($-W$)], e.g. [12]. While the reversibility property is lost for such exergy, its (kinetic) bounds are stronger and more useful than classical thermostatic bounds. This substantiates role of the extended exergy for evaluation of energy limits in practical systems.

With the functionals of power generation (consumption) at disposal one can formulate the Hamilton-Jacobi-Bellman theory (HJB theory) for the extended exergy and related extremum work. The HJB theory is the basic ingredient in variational calculus and optimal control [8,11]. A HJB equation extends the classical Hamilton-Jacobi equation by the addition of extremum conditions, and it is essential to develop numerical methods in complex cases (with state dependent coefficients) when the problem cannot be solved analytically. Due to the direct link between the HJB theory and dynamic programming the associated numerical methods make use Bellman's recurrence equation [13]. These methods are complementary with respect of the Pontryagin's principle [8], as both are effective seeking methods of functional extrema. Yet, in spite of its power, Pontriagin's principle does not yield the principal function V which is a general work potential describing the change of the extended exergy, the main result being sought. Otherwise, when a HJB equation is known, the exergy (or work) is explicit, and the discrete numerical problem leads to Bellman's recurrence equation, solvable by the method of the dynamic programming [13]. The problem of generalized exergy falls into the category of finite-time potentials, an important issue of contemporary thermodynamics [8]. This problem is solved with the concept of multistage energy production or consumption, where each stage represents the standard Curzon-Ahlborn-Novikov operation [3], as in Fig.1.

V. Dynamical Energy Generation from Radiation

Energy transfer rates in reservoirs (streams) with nonlinear media can be described by various models. As an example of the above theory we consider the radiation engines which are thermal machines driven by the radiation fluid, a medium exhibiting nonlinear properties. Usually one assumes that the energy transfer in a reservoir is proportional to the difference of absolute temperatures in certain power, a. The case of a =4 refers to the radiation, a=-1 to the Onsagerian kinetics and a=1 to the Fourier law of heat exchange. (In the Onsagerian case the quantities g_i are negative in the common formalism considered.)

As the first case of the radiation engine modeling we consider a "symmetric nonlinear case" in which the the energy exchange process in the energy exchange in each reservoir satisfies the Stefan-Boltzmann equation. Next we consider "hybrid nonlinear case" in which the upper-temperature fluid is still governed by the kinetics proportional to the difference of $(T^4)_i$, whereas the kinetics in the lower reservoir is Newtonian.

Here are the equations of the *symmetric nonlinear case*. The energy exchange process in the upper reservoir satisfies Eq. (40), and an equation of the same type and with the same coefficient a is valid for the energy exchange in the lower reservoir, namely

$$\varepsilon_2 = Q_2 = g_2(T_{2'}^a - T_2^a) \tag{46}$$

To express the internal balance equation for the entropy

$$\Phi\, g_1(T_1^a - T_{1'}^a)/T_{1'} = g_2(T_{2'}^a - T_2^a)/T_{2'} \tag{47}$$

in terms of T' and $T_{1'}$ we substitute $T_{2'} \equiv T_{1'}T_2/T'$ into (47). Next we solve the result obtained with respect to $T_{1'}$. This leads to an equation describing (in terms of T') the upper temperature of the circulating fluid $T_{1'}$

$$T_{1'} = \left(T_1^a - g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2} \right)^{1/a}. \tag{48}$$

.

From this expression and Eq. (40) the energy flux ε_1 follows in terms of T'. This flux is obtained in the form

$$\varepsilon_1 = g_1 g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2} \tag{49}$$

which represents "thermal characteristics" of the system. An expression for $T_{2'}$ corresponding with (48) follows from the thermodynamic definition of Carnot temperature, $T_{2'} \equiv T_{1'}T_2 / T'$. Also, $\varepsilon_2 = \varepsilon_1(1-\eta)$, where η is defined by the pseudo-Carnot expression, Eq. (37). Thus all necessary quantities are known.

For a=1 the kinetics of heat exchange depends on the difference of two temperatures $T_1 - T'$, as in the case of the direct two-body contact. Yet, in nonlinear processes the heat flux (49) emerges as function of three (not merely two) temperatures, T', T_1 and T_2. This means that the modeling rule involving the formalism of the two-body contact (satisfied when a=1) is invalid in the case of nonlinear processes. Still we can evaluate power limits by maximizing the power p related to equation (49) with respect to the free Carnot control, T'; see Eq. (52) below.

For a=4 the model describes the radiation engine usually called the Stefan-Boltzmann engine. In spite of the model's simplicity, its two "resistive parts" take rigorously into account the entropy generation caused by simultaneous emission and absorption of black-body radiation, the model's property which some of FTT adversaries seem not to be aware of. This entropy generation is just the external part of the total entropy production that follows as the "classical" sum:

$$\sigma_s^{ext} = \varepsilon_1(T_{1'}^{-1} - T_1^{-1}) + \varepsilon_2(T_2^{-1} - T_{2'}^{-1}), \qquad (50)$$

where each ε_i is determined by the Stefan-Boltzmann law. For the "symmetric"kinetics", governed by the differences in T^a, the Carnot representation of the total entropy production follows from equations (38) and (49)

$$\sigma_s = g_1 g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2}\left(\frac{(\Phi-1)}{T'} + (\frac{1}{T'} - \frac{1}{T_1})\right). \qquad (51)$$

Superiority of Carnot control T' over the energy flux control ε_1 may be noted. Since the energy flux expression (49) cannot be inverted to get an explicit function $T'(\varepsilon_1)$, analytical expressions for the energy-flux representation of the entropy production or the associated mechanical power p cannot generally be found in an analytical form. Still we can express the entropy production and power p in terms of Carnot control, T', and then evaluate the work limit by maximizing work W with respect to the free Carnot control, T'. The work expression to be minimized is

$$W = \int_{t^i}^{t^f} \varepsilon_1 \eta dt = \int_{t^i}^{t^f} g_1 g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2}\left(1 - \Phi\frac{T_2}{T'}\right)dt \qquad (52)$$

Whenever analytical difficulties occur (for a different from the unity), the maximization can be performed numerically by dynamic programming using Carnot T' as the free control.

We consider now *hybrid nonlinear case* in which the radiation law governs the energy flow only in the upper reservoir, whereas the lower one is governed by the Newtonian model

$$\varepsilon_2 = g_2(T_{2'} - T_2) \ . \qquad (53)$$

The efficiency of an imperfect unit is still satisfied by expression $\eta = 1 - \Phi T_{2'}/T_{1'}$, Eq. (37). To express the internal balance equation for the entropy

$$\Phi\, g_1(T_1^4 - T_{1'}^4)/T_{1'} = g_2(T_{2'} - T_2)/T_{2'} \qquad (54)$$

in terms of T' and $T_{1'}$ we substitute $T_{2'} \equiv T_{1'}T_2 / T'$ into (54). This leads to T' in terms of $T_{1'}$

$$\Phi g_1(T_1^4 - T_{1'}^4) = g_2(T_{1'} - T') \qquad (55)$$

and whence to the mechanical power p in terms of $T_{1'}$. The thermal efficiency of the engine can be obtained in the form

$$\eta = 1 - \Phi\frac{T_2}{T'} = 1 - \frac{\Phi T_2}{T_{1'} - \Phi g_1(T_1^4 - T_{1'}^4)/g_2} \qquad (56)$$

which contains the temperature $T_{1'}$ as an effective control variable. This result leads to the mechanical power expression with the explicit control $T_{1'}$

$$W = \int_{t^i}^{t^f} \varepsilon_1 \eta dt = \int_{t^i}^{t^f} g_1(T_1^4 - T_{1'}^4)\left(1 - \frac{\Phi T_2}{T_{1'} - \Phi g_1(T_1^4 - T_{1'}^4)/g_2}\right)dt \qquad (57)$$

Since from Eq. (40), $T_{1'} = (T_1^a - \varepsilon_1/g_1)^{1/a}$, the energy flux representation of Eq. (57) is obtained in the form

$$W = \int_{t^i}^{t^f} \varepsilon_1 \eta dt = \varepsilon_1\left(1 - \frac{\Phi T_2}{(T_1^a - \varepsilon_1/g_1)^{1/a} - \Phi\varepsilon_1/g_2}\right). \qquad (58)$$

Equations (57) or (58) allow analytical or graphical maximization of work with respect to a single control variable, $T_{1'}$or ε_1. This leads to the limits on work production in imperfect units. A suitable control may be the Carnot temperature itself, its function or an operator in terms of the process variables. Operator structure of T' is frequent in dynamical problems.

In dynamical systems differential forms of expressions are necessary. For a suitably defined time τ (associated with the resource fluid; see Eq. (32) below) and for an arbitrary heat transfer (Newtonian or not) the internal entropy production is

$$S_\sigma^{\text{int}} = -\int_{\tau^i}^{\tau^f} c(T)\frac{\Phi - 1}{T'(T_1, \dot{T})}\dot{T}_1 d\tau_1 \qquad (59)$$

whereas its external part

$$S_\sigma^{ext} = -\int_{\tau^i}^{\tau^f} c(T)\left(\frac{1}{T'(T_1,\dot{T}_1)} - \frac{1}{T_1}\right)\dot{T}_1 d\tau_1 . \quad (60)$$

The minimization must involve total entropy production as the quantity which determines the lost work in thermal equations of availabilities. The sum of Eqs. (59) and (60) is the integral

$$S_\sigma = -\int_{\tau^i}^{\tau^f} c(T)\left(\frac{\Phi}{T'} - \frac{1}{T_1}\right)\dot{T}_1 d\tau_1 . \quad (61)$$

The limiting production or consumption of mechanical energy is associated with extremum work (52) or (57) or minimum of overall entropy production (31). Often is possible to determine explicit form of functions describing Carnot temperature T' in terms of the current fluid's temperature T and its time derivative. Such functional structure allows to apply the variational calculus in the optimization analysis. If this function is difficult to find in an explicit form then equations (59) and (60) should be written in the form in which T' and T_1 are two variables in the Pontryagin's algorithm of the optimal control. In that case a differential constraint must be added which links rate dT_1/dt with state variable T_1 and control T' (Eq. (63) below).

We shall again specialize with what we called *symmetric nonlinear case*. It involves the radiative heat transfer (a=4) in both upper and lower reservoirs and corresponds with the form (51) of the intensity of total entropy production.

We shall define the nondimensional time τ_1 by the equality

$$\varepsilon_1 / g_1 = -G_1 c(T_1) dT_1 / (\alpha_1 a_v F_1 dx) \equiv -dT_1 / d\tau_1 \quad (62)$$

which means that the driving energy flux can be measured in terms of the temperature drop of the propelling fluid per unit of the nondimensional time. Comparing the result obtained with ε_1 of Eq. (49) we obtain the basic differential equation

$$dT_1 / d\tau_1 = -g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2} . \quad (63)$$

This formula constitutes the differential constraint in the problem of minimization of the total entropy production (61) by Pontryagin's maximum principle. This is particularly important in view of the fact that the method of variational calculus cannot effectively be used (as opposed to the case considered below).

We shall now specialize to what we called the *hybrid nonlinear case*. It involves the radiative heat transfer (a=4) in the upper reservoir and a convective one in the lower one. In terms of the rate $\dot{T}_1 \equiv dT_1 / d\tau_1$ we obtain

$$S_\sigma^{\text{int}} = -\int_{\tau^i}^{\tau^f} c(T_1) \frac{\Phi - 1}{\left(T_1^a + \dot{T}_1^a\right)^{\frac{1}{a}} + \dot{T}_1 \Phi g_1 / g_2} \dot{T}_1 d\tau_1 \quad (64)$$

and

$$S_\sigma^{ext} = -\int_{\tau^i}^{\tau^f} c(T_1)\left(\frac{1}{\left(T_1^a + \dot{T}_1^a\right)^{\frac{1}{a}} + \dot{T}_1 \Phi g_1 / g_2} - \frac{1}{T_1}\right)\dot{T}_1 d\tau_1 . \quad (65)$$

To obtain an optimal path associated with the limiting production or consumption of mechanical energy the sum of the above functionals i.e. the overall entropy production

$$S_\sigma = -\int_{\tau^i}^{\tau^f} c(T_1)\left(\frac{\Phi}{\left(T_1^a + \dot{T}_1^a\right)^{\frac{1}{a}} + \dot{T}_1 \Phi g_1 / g_2} - \frac{1}{T_1}\right)\dot{T}_1 d\tau_1 \quad (66)$$

has to be minimized for a fixed duration and defined end states of the radiation fluid. The most typical way to do accomplish the minimization is to write down and then solve the Euler-Lagrange equation of the variational problem. Analytical solution is very difficult to obtain, thus one has to rest on numerical approaches. For Eqs. (61) or (66) these approaches involve the dynamic programming algorithms (Bellman's equations; [8, 13]) which are, in fact, discrete representations of the HJB equations of the variational problem. Analytical aspects of HJB equations are analyzed throughout the Sects. 6-9 of the present paper.

VI. Finite Resources and Finite Rate Exergies

Two different kinds of work, first associated with the resource downgrading during its relaxation to the equilibrium and the second – with the reverse process of resource upgrading, are essential. During the engine mode work is released, during heat-pump mode work is supplied. The optimal work follows in the form of a generalized potential which depends on the end states and duration. For appropriate boundary conditions the principal function of the variational problem of extremum work at flow coincides with the exergy as the function that characterizes quality of resources.

We are now in position to formulate the HJB theory for systems propelled by energy flux ε. Total power obtained from an infinite number of infinitesimal stages representing the resource relaxation is determined as the Lagrange functional of the following structure

$$\dot{W}[\mathbf{T}^i, \mathbf{T}^f] = \int_{t^i}^{t^f} f_0(T, T')dt = -\int_{t^i}^{t^f} \dot{G} c(T) \eta(T, T') \dot{T} dt \quad (67)$$

where f_0 is power generation intensity, $\dot{G}$ - resource flux, $c(T)$-specific heat, $\eta(T, T')$ - efficiency in terms of state T and control T', further $\mathbf{T}$ – enlarged state vector comprising state and time, t – time variable (residence time or holdup time) for a resource contacting with energy transfer surface. For a

constant mass flux of a resource stream, one can extremize power per unit mass flux, i.e. the quantity of specific work dimension called 'work at flow'. A non-dimensional time τ is often used in the description

$$\tau \equiv \frac{x}{H_{TU}} = \frac{\alpha' a_v F}{\dot{G}c} x = \frac{\alpha' a_v F v}{\dot{G}c} t = \frac{t}{\chi} \ . \qquad (68)$$

This definition assures that τ is identical with the number of the energy transfer units, and related to system's time constants, χ and H_{TU} (relaxation constant and height of the transfer unit). Equation (68), which links non-dimensional and physical times, contains resource's flow $\dot{G}$, stream velocity v through cross-section $A^{\perp}$, and heat transfer exchange surface per unit volume a_v [5].

The function f_0 in Eq. (67) contains thermal efficiency, η, described by a practical counterpart of the Carnot formula. When $T > T^e$, efficiency η decreases in the engine mode below η_C and increases in the heat-pump mode above η_C. At the limit of vanishing rates $dT/dt = 0$ and $T' \to T$. Work of each mode simplifies then to the classical exergy.

Solutions to work extremum problems can be obtained by variational methods, i.e. via Euler-Lagrange equation of variational calculus. However, such solutions do not contain direct information about the optimal work function $V = \max(\dot{W} / \dot{G})$. Yet, V can be obtained by solving the related Hamilton-Jacobi-Bellman equation (HJB equation: [8,13]).

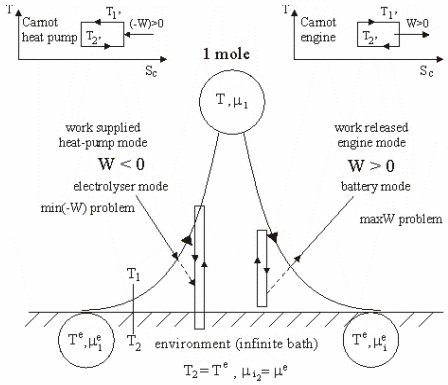

Fig. 4. In finite-rate processes limiting work produced and consumed differ in both process modes.

For the Newtonian energy transfer (linear kinetics)

$$\frac{\partial V}{\partial \tau} - \max_{T'} \left\{ \left(-\frac{\partial V}{\partial T} - c\left(1 - \frac{T^e}{T'}\right) \right) (T' - T) \right\} = 0 \qquad (69)$$

Extremum work function $V = \max(\dot{W} / \dot{G})$ contained in equations of this type is a function of the final state and total duration.

After the evaluation of optimal control and its substitution to Eq. (69) one obtains a nonlinear equation

$$\frac{\partial V}{\partial \tau} - c\left\{ \sqrt{T^e} - \sqrt{T(1 + c^{-1} \partial V / \partial T)} \right\}^2 = 0 \qquad (70)$$

which is the Hamilton-Jacobi equation of the problem. Its solution can be found by the integration of work intensity along an optimal path, between limits T^i and T^f. A reversible (path independent) part of V is the classical exergy $A(T, T^e, 0)$.

Whenever analytical difficulties are serious method of dynamic programming is applied to solve a discrete HJB equation which is in, fact, Bellman's equation of dynamic programming for a multistage cascade process [13].

Details of modeling of multistage power production in sequences of engines are discussed in the previous publications [5, 9, 11].

VII. Examples of HJB Equations in Power Systems

In this section we shall display some Hamilton-Jacobi-Bellman equations for the power systems with radiation. A suitable example is a radiation engine whose power integral is approximated by a pseudo-Newtonian model of radiative energy exchange.

The model is associated with an optimal function

$$V(T^i, t^i, T^f, t^f) \equiv \max_{T'(t)} \left(-\int_{t^i}^{t^f} \dot{G}_m c_m (1 - \Phi' \frac{T^e}{T'}) \upsilon(T', T) dt \right), \qquad (71)$$

where $\upsilon = \alpha(T^3)(T' - T)$. Alternative forms use expressions of Carnot temperature T' in terms of other control variables [5]. Optimal power (71) can be referred to a pseudolinear kinetics $dT/dt = f(T, T')$ consistent with rate $\upsilon = \alpha(T^3)(T' - T)$. A general form of HJB equation for work function V is

$$-\frac{\partial V}{\partial t} + \max_{T'(t)} \left(f_0(T, T') - \frac{\partial V}{\partial T} f(T, T') \right) = 0 \ , \qquad (72)$$

where f_0 is defined as the integrand in Eq. (71).

A more exact model or radiation conversion relaxes the assumption of the pseudo-Newtonian transfer and applies the Stefan-Boltzmann law. For the *symmetric* model of radiation conversion (both reservoirs composed of radiation we obtain

$$\dot{W} = \int_{t^i}^{t^f} \dot{G} c(T) \left(1 - \frac{\Phi T^e}{T'} \right) \beta \frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1} + 1) T^{a-1}} dt \cdot \qquad (73)$$

Here $\Phi' \equiv \Phi g_1/g_2$ and coefficient $\beta = \sigma a_v c_h^{-1} (p_m^0)^{-1}$ is related to molar constant of photons density p_m^0 and Stefan-Boltzmann constant σ. In the physical space, power exponent a=4 for radiation and a=1 for a linear resource. With a dynamical state equation following from Eq. (63)

$$\frac{dT}{dt} = -\beta \frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1} + 1) T^{a-1}} \qquad (74)$$

applied in general Eq. (72) we obtain a HJB equation

$$\frac{\partial V}{\partial t}=\max_{T'(t)}\left\{\left(\dot{G}_c(1-\Phi\frac{T^e}{T'})+\partial V/\partial T\right)\beta\frac{T^a-T'^a}{(\Phi'(T'/T_2)^{a-1}+1)T^{a-1}}\right\} \quad (75)$$

[5]. Dynamics (74) is the characteristic equation to Eq. (75).

For *a hybrid model* of the radiation conversion (upper reservoir composed of the radiation and lower reservoir of a Newtonian fluid), the power production expression has the form

$$\dot{W}=-\int_{\tau^i}^{t^f}G_C(T)\left(1-\frac{\Phi T^e}{T'}\right)udt \quad (76)$$

whereas the related Hamilton-Jacobi-Bellman equation is

$$-\frac{\partial V}{\partial t^f}+\max_{T'(t)}\left\{-\left(\dot{G}_c(T)(1-\frac{\Phi T^e}{T'})+\frac{\partial V}{\partial T^f}\right)u\right\}=0 \quad (77)$$

where by definition:

$$T'\equiv(T^a+\beta^{-1}T^{a-1}u)^{1/a}+\Phi\beta^{-1}T^{a-1}ug_1/g_2$$

is the Carnot temperature of this particular problem [5].

The HJB approach can also be applied when one is using the general equations of nonlinear macrokinetics [11]. In this case one may consider coupled transfer of mass (*m*) and energy (*e*). On this ground one can develop the nonlinear theory in which thermal conductances are variable i.e. are state functions

VIII. Solutions of HJB Equations in Energy Systems

By applying the feedback control, either optimal temperature *T*' or some other optimal control is implemented as the quantity maximizing the hamiltonian with respect to Carnot temperature at each point of the path. The Pontryagin's variable for the energy problem is $z = -\partial V/\partial T$. Expressions extremized in HJB equations are some Hamiltonians, *H*. The maximization of *H* leads to two equations. The first expresses optimal control *T*' in terms of *T* and $z = -\partial V/\partial T$. For the linear kinetics of Eq. (69) we obtain

$$\frac{\partial V}{\partial T}-\frac{\partial f_0(T,T')}{\partial T'}=\frac{\partial V}{\partial T}+c(1-\frac{T^eT}{T'^2})=0 \quad (78)$$

whereas the second is the original equation (69) without maximizing operation

$$\frac{\partial V}{\partial\tau}+\frac{\partial V}{\partial T}(T'-T)+c(1-\frac{T^e}{T'})(T'-T)=0\ . \quad (79)$$

To obtain optimal control function $T(z, T)$ one should solve the second equality in Eq. (78) in terms of *T*'. The result is optimal Carnot control *T*' in terms of *T* and $z = -\partial V/\partial T$,

$$T'=\left(\frac{T^eT}{1+c^{-1}\partial V/\partial T}\right)^{1/2}. \quad (80)$$

This expression is next substituted into Eq. (79); the result is the nonlinear Hamilton-Jacobi equation

$$-\frac{\partial V}{\partial\tau}+cT\left(\sqrt{1+c^{-1}\partial V/\partial T}-\sqrt{T^e/T}\right)^2=0 \quad (81)$$

which contains the energy-like (extremum) Hamiltonian

$$H(T,\frac{\partial V}{\partial T})=cT\left(\sqrt{1+c^{-1}\partial V/\partial T}-\sqrt{T^e/T}\right)^2. \quad (82)$$

Expressing extremum Hamiltonian (82) in terms of state variable *T* and Carnot control *T* ' yields an energy-like function satisfying the following relation

$$E(T,u)=f_0-u\frac{\partial f_0}{\partial u}=cT^e\frac{(T'-T)^2}{T'^2}. \quad (83)$$

E is the Legendre transform of the work lagrangian $l_0 = -f_0$ with respect to the rate $u = \mathrm{d}T/\mathrm{d}\tau$.

Assuming a numerical value of the Hamiltonian, say *h*, one can exploit the constancy of *H* to eliminate $\partial V/\partial T$. Next combining equation $H=h$ with optimal control (80), or with an equivalent result for heat flow control $u=T'-T$

$$u=\left(\frac{T^eT}{1+c^{-1}\partial V/\partial T}\right)^{1/2}-T \quad (84)$$

yields optimal rate $u=\dot{T}$ in terms of temperature *T* and the Hamiltonian constant *h*

$$\dot{T}=\{\pm\sqrt{h/cT^e}(1-\pm\sqrt{h/cT^e})^{-1}\}T. \quad (85)$$

A more general form of this result which applies to systems with internal dissipation (factor Φ) and applies to the pseudo-Newtonian model of radiation is

$$\dot{T}=\left(\pm\sqrt{\frac{h_\sigma}{\Phi c_v(T)}}\left(1-\pm\sqrt{\frac{h_\sigma}{\Phi c_v(T)}}\right)^{-1}\right)T\equiv\xi(h_\sigma,\Phi,T)T. \quad (86)$$

The coefficient ξ, defined in the above equation, is an intensity index and $h_\sigma=h/T$. The result is valid the temperature dependent heat capacity $c_v(T)=4a_0T^3$. Positive ξ refer to heating of the resource fluid in the heat-pump mode, and the negative - to cooling of this fluid in the engine mode. Therefore pseudo-Newtonian systems produce power relaxing with the optimal rate

$$\dot{T}=\xi(h_\sigma,T,\Phi)T \quad (87)$$

Equations (86) and (87) describe the optimal trajectory in terms of state variable T and constant h_σ. The corresponding optimal control (Carnot control) is

$$T' = \left(1 + \xi(h_\sigma, \Phi, T)\right)T \,. \tag{88}$$

In comparison with the linear systems, the pseudo-Newtonian relaxation curve is not exponential. Kuran [7] has illustrated the optimal temperature of radiation downgraded in engine mode or upgraded in the heat-pump mode, see also [4] and [5].

HJB theory of energy systems can also be based on properties of entropy production. Equations (64)-(66) contain expressions representing Carnot temperature T' in terms of the upper reservoir temperature T_1 and the time derivative of this quantity. They prove that the success in achieving Lagrange functionals (necessary when one wants to apply the method of calculus of variations) is crucially dependent on the possibility of getting Carnot temperature T' in the form of an explicit analytical function of T' and dT'/dt. For the symmetric nonlinear model of the engine such explicit function is impossible to find, yet the possibility exists in the case of the hybrid nonlinear model. For the latter model one can therefore write down explicit Euler-Lagrange equations of the variational problem and perform the minimization of the entropy production.

IX. Rate Dependent Exergies as Generalized Work Potentials

Let us begin with linear systems. Substituting temperature control (88) with a constant ξ into work functional (67) and integrating along an optimal path yields an extremal work function

$$\begin{aligned} V(T^i, T^f, h) &= c(T^i - T^f) - cT^e \ln\frac{T^i}{T^f} \\ &- cT^e\sqrt{\frac{h}{cT^e}}\ln\frac{T^i}{T^f} \end{aligned} \tag{89}$$

This expression is valid for every process mode. Integration of Eq. (86) subject to end conditions $T(\tau^i)=T^i$ and $T(\tau^f)=T^f$ leads to V in terms of the process duration.

For radiation $c_v(T)=4a_0T^3$, where a_0 is the radiation constant. The optimal path consistent with Eqs. (87) and (89) has the form

$$\begin{aligned} &\pm(4/3)a_0{}^{1/2}\Phi^{1/2}h_\sigma{}^{-1/2}\left(T^{3/2} - T^{i\,3/2}\right) \,. \\ &-\ln(T/T^i) = \tau - \tau^i \end{aligned} \tag{90}$$

The integration limits refer to the initial state (i) and a current state of the radiation fluid, i.e. temperatures T^i and T corresponding with τ^i and τ. Optimal curve (90) refers to the case when the radiation relaxation is subject to a constraint resulting from Eq. (87).

The corresponding extremal work function per unit volume of flowing radiation is

$$\begin{aligned} V &\equiv h_v^i - h_v^f - T^e(s_v^i - s_v^f) \\ &-(4/3)a_0{}^{1/2}h_\sigma^{1/2}\Phi^{1/2}T^e(T^{i\,3/2} - T^{f\,3/2}) \\ &+(4/3)a_0T^e(1-\Phi)(T^{i\,3} - T^{f\,3}). \end{aligned} \tag{91}$$

Generalized exergy change V prohibits processes from operating below the heat-pump mode (lower bound for work supplied) and above the engine mode line (upper bound for work produced). The so-called endoreversible limits correspond with Φ=1; weaker limits of classical exergy are represented by the straight line $A = A^{\text{class}}$. The classical availability is potential or state function whose change between two arbitrary states describes the reversible work. On the other hand, generalized availability functions are irreversible extensions of this classical function including minimally irreversible processes.

Regions of possible improvements are found when imperfect machines are replaced by those with better performance, including limits for Carnot machines. The generalized exergy of radiation at flow, [14], follows in analytical form from Eq. (91) after applying exergy boundary conditions. Yet the classical exergy of radiation at flow resides in the discussed exergy equation in Jeter's 1981 form, [15], rather than in Petela's 1964 form, [14]. The zero-rate limit, i.e. the change of classical thermal availability appears in Eq. (91) in the standard way.

X. Power Systems Driven by Chemical Affinities

The developed approach can be extended to chemical and electrochemical engines. Here we shall make only a few basic remarks. In chemical engines mass transports participate in transformation of chemical affinities into mechanical power [12, 16]. Yet, as opposed to thermal machines, in chemical ones generalized streams or reservoirs are present, capable of providing both heat and substance. Large streams or infinite reservoirs assure constancy of chemical potentials. Problems of extremum power (maximum of power produced and minimum of power consumed) are static optimization problems. For a finite "upper stream", however, amount and chemical potential of an active reactant decrease in time, and considered problems are those of dynamic optimization and variational calculus. Because of the diversity and complexity of chemical systems the area of power producing chemistries is extremely broad.

The simplest model of power producing chemical engine is that with an isothermal isomerization reaction, $A_1+A_2=0$, [3, 12]. Power expression and efficiency formula of a chemical system follow from the entropy conservation and energy balance of a power-producing zone ('active part'). In an 'endoreversible chemical engine' total entropy flux is continuous through the active zone. When a formula describing this continuity is combined with energy balance we find in an isothermal case

$$p = (\mu_{1'} - \mu_{2'})n_1, \tag{92}$$

where the feed flux n_1 equals to n, an invariant molar flux of reagents. Process efficiency ζ is defined as power yield per flux n. This efficiency is identical with the chemical affinity of our reaction in the chemically active part of the system. While ζ is

not dimensionless, it describes correctly the system. In terms of Carnot variable, μ', which satisfies Eq. (27)

$$\zeta = \mu' - \mu_2 \,. \tag{93}$$

For a steady engine the following function describes chemical Carnot control μ' in terms of fuel flux n_1 and its mole fraction x

$$\mu' = \mu_2 + \zeta_0 + RT \ln\left(\frac{x_1 - n_1 g_1^{-1}}{n_1 g_2^{-1} + x_2}\right) \tag{94}$$

Since Eq. (93) is valid, Eq. (94) also characterizes the efficiency control in terms of n and fuel fraction x.

Equation (94) shows that an effective concentration of the reactant in upper reservoir $x_{1\text{eff}} = x_1 - g_1^{-1} n$ is decreased, whereas an effective concentration of the product in lower reservoir $x_{2\text{eff}} = x_2 + g_2^{-1} n$ is increased due to the finite mass flux. Therefore chemical efficiency ζ decreases nonlinearly with n.

When the effect of resistances $(g_k)^{-1}$ is ignorable or flux n is very small, reversible Carnot-like chemical efficiency, ζ_C, is attained. The power function, described by the product $\zeta(n)n$, exhibits a maximum for a finite value of the fuel flux, n.

Application of Eq. (94) to the Lagrangian relaxation path leads to a work functional

$$W = -\int_{\tau_1^i}^{\tau_1^f} \left\{\zeta_0 + RT \ln\left(\frac{X/(1+X) + dX/d\tau_1}{x_2 - j dX/d\tau_1}\right)\right\} \frac{dX}{d\tau_1} d\tau_1 \tag{95}$$

whose maximum describes the dynamical limit of the system. Here X=x/(1-x) and j equals the ratio of upper to lower mass conductance, g_1/g_2.

The path optimality condition may be expressed in terms of the constancy of the following Hamiltonian

$$H(X, \dot{X}) = RT\dot{X}^2 \left(\frac{1+X}{X} + \frac{j}{x_2}\right). \tag{96}$$

For low rates and large concentrations X (mole fractions x_1 close to the unity) optimal relaxation rate of the fuel resource is approximately constant.

Yet, in an arbitrary situation optimal rates are state dependent so as to preserve the constancy of H in Eq. (96). Extensions of Eq. (94) are known for multicomponent, multireaction systems [17].

Power formula which treats the internal imperfections has the form generalizing "endoreversible" Eq. (23)

$$p = \varepsilon_1 (1 - \Phi \frac{T_{2'}}{T_{1'}}) + T_{2'} (\frac{\mu_{1'}}{T_{1'}} - \Psi \frac{\mu_{2'}}{T_{2'}}) n_1 \,, \tag{97}$$

where Ψ is the coefficient of chemical losses which takes into account the imperfections of the species transformations caused by incomplete conversions [17].

This formalism can be generalized to complex, multi-reaction chemical systems [17].

XI. Fuel Cells at Steady State Conditions

To understand the role of electrochemical reactions in the power yield we consider performance bounds of fuel cells. These systems are electrochemical flow engines propelled by chemical reactions, which satisfy requirements imposed by chemical stoichiometry. The performance of fuel cells is determined by magnitudes and directions of all streams and by mechanism of electric current generation. The mode distinction for the work production and consumption units applies here as well. Units which produce power are electrochemical engines whereas those which consume power are electrolyzers. Figure 5 illustrates a solid oxide fuel cell engine (SOFC) and refers to the power yield mode.

A fuel cell is an electrochemical energy converter which directly and continuously transforms a part of chemical energy into electrical energy by consuming fuel and oxidant. Fuel cells have recently attracted great attention by virtue of their inherently clean, efficient, and reliable performance. Their main advantage in comparison to heat engines is that their efficiency is not a major function of device size.

While both electronic and ionic transfers are necessary to sustain power generation, it is the overall chemical reaction which is the source of power, and it is the chemical unit property which constitutes the first major component of the theory of power generation in fuel cell engines. The second major component involves the kinetics of electronic, ionic and thermal transfer phenomena.

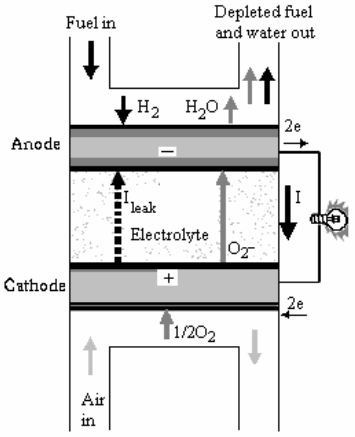

Fig. 5. Principle of a solid oxide fuel cell

The basic structure of fuel cells includes electrolyte layer in contact with a porous anode and cathode on either side. Gaseous fuels are fed continuously to the anode (negative electrode) compartment and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode) compartment. Electrochemical reactions take place at the electrodes to produce an electric current. The reaction is the electrochemical oxidation of fuel, usually hydrogen, and the reduction of the oxidant, usually oxygen. These properties make fuel cells similar to the chemical engine of Fig. 1.

Voltage lowering in fuel cells below the reversible value E^0 is a good measure of their imperfection only when E^0 can be identified with the so-called idle run voltage E_0, see discussion

below and Fig. 6a. With the concept of effective nonlinear resistances operating voltage of a general fuel cell can be represented as the departure from the idle run voltage E_0.

$$V = E_0 - V_{int} = E - V_{act} - V_{conc} - V_{ohm}$$

$$= E_0 - I(R_{act} + R_{conc} + R_{ohm}) \quad (98)$$

The rate dependent losses, which are called polarization, include three main sources: activation polarization (V_{act}), ohmic polarization (V_{ohm}), and concentration polarization (V_{conc}). They refer to the equivalent activation resistance (R_{act}), equivalent ohmic resistance (R_{ohm}), and equivalent concentration resistance (R_{conc}). Large number of approaches for calculating these polarization losses has been reviewed in the literature by Zhao, Ou and Chen, [18].

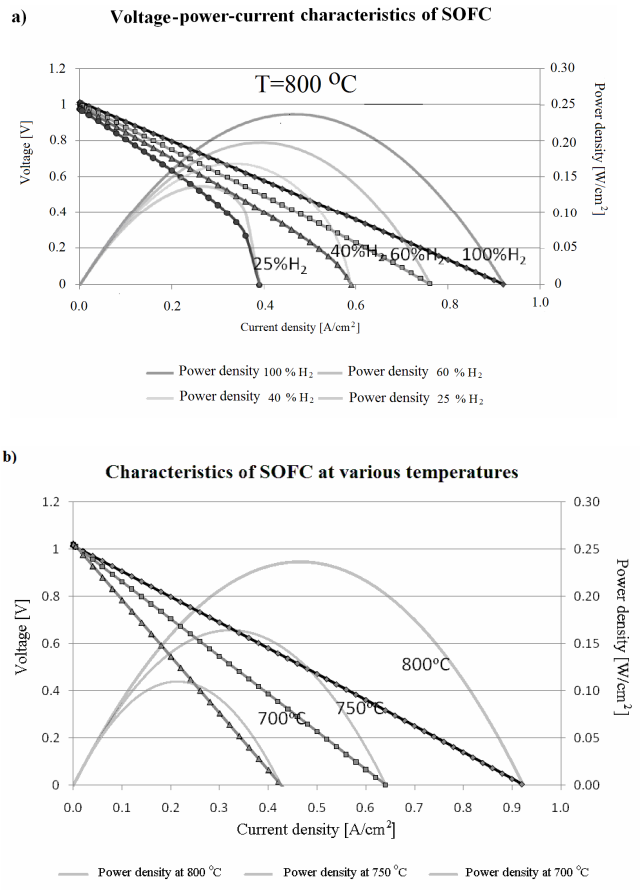

Fig. 6. Voltage-current density and power - current density characteristics of the SOFC for various fuels in temperature 800°C (a) and at various temperatures (b). Continuous lines represent the Aspen Plus™ calculations testing the model consistency with the experiments. These lines were obtained in Wierzbicki's MsD thesis [19], supervised by the present author and J. Jewulski. Points refer to experiments of Wierzbicki and Jewulski in Warsaw Institute of Energetics (Wierzbicki, [19], and his ref. 18).

Activation and concentration polarizations occur at both anode and cathode locations, while the resistive polarization represents ohmic losses throughout the fuel cell. As the voltage losses increase with current, the initially increasing power begins finally decrease for sufficiently large currents, so that maxima of power are observed (Fig. 6b).

The final voltage equation used for the calculation of the fuel cell voltage in Wierzbicki's model is:

$$V = E_0(T, p_{H_2}) - iA_R(p_{H_2})\exp\left(\frac{\Delta E}{RT}\right) + B\ln\left(1 - \frac{i}{i_L(T, p_{H_2})}\right), \quad (99)$$

where the limiting current is

$$i_L = C_1 \frac{\exp(\frac{-E_a}{RT}) p_{H_2}}{T} \quad (100)$$

and C_1 is a experimentally determined parameter. Power density is simply the product of voltage V and current density i. In an ideal situation (no losses) the cell voltage is defined by the Nernst equation. Yet, while the first term of Eq. (99) defines the voltage without load, it nonetheless takes into account losses of the idle run, which are the effect of flaws in electrode constructions and other imperfections which cause that the open circuit voltage will in reality be lower than the theoretical value. Activation polarization V_{act} is neglected in this model. The losses include ohmic polarization and concentration polarization. The second term of Eq. (99) quantifies ohmic losses associated with electric resistance of electrodes and flow resistance of ions through the electrolyte. The third term refers to mass transport losses. Quantity i_L is the particular current arising when the fuel is consumed in the reaction with the maximum possible feed rate. For comparison, the data of Zhao, Ou and Chen, [18], are shown in Fig. 7.

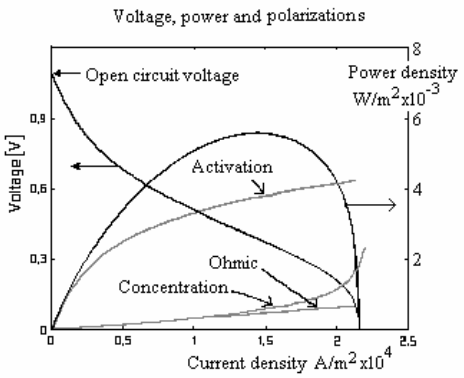

Fig. 7. Data of the cell voltage, polarizations, and power density in terms of current density for a fuel cell using hydrogen (97% H_2 + 3% H_2O) as fuel and air (21% O_2 + 79% N_2) as oxidant (Zhao, Ou and Chen [18]), consistent with the data of Wierzbicki, [19].

XII. Final Remarks

The present paper provides the unifying thermodynamic method for determining power production limits in energy systems. These limits are enhanced in comparison with those

predicted by the classical thermodynamics. As opposed to the classical thermodynamics, these bounds depend not only on changes of the thermodynamic state of participating resources but also on process irreversibilities, ratios of stream flows, stream directions, and mechanism of heat and mass transfer.

To understand the problem of bounds and their distinction for the work production and consumption, recall that the work-producing process is the inverse of the work-consuming process (the final state of the second process is the initial state of the first, and conversely), when durations of the two processes and their end states are fixed to be the same.

In thermostatics the two bounds on the work, the bound on the work produced and that on the work consumed, coincide. However thermostatic bounds are often too far from reality to be really useful. The generalized bounds, obtained here by solving HJB equations, are stronger than those predicted by thermostatics. They do not coincide for processes of work production and work consumption; they are 'thermokinetic' rather than 'thermostatic' bounds. Only for infinitely long durations or for processes with excellent transfer (an infinite number of transfer units) the thermokinetic bounds reduce to the classical thermostatic bounds.

A real process which does not apply the optimal protocol but has the same boundary states and duration as the optimal path, requires a real work supply that can only be larger than the finite-rate bound obtained by the optimization. Similarly, the real work delivered from a nonequilibrium work-producing system (with the same boundary states and duration but with a suboptimal control) can only be lower than the corresponding finite-rate bound. Indeed, the two bounds, for a process and its inverse, which coincide in thermostatics, diverge in thermodynamics, at a rate that grows with any index quantifying the process deviation from the static behavior, e.g. Hamiltonian H. For sufficiently high values of rate indices (large H), work consumed may far exceed the classical work; work produced can be much lower than classical or even vanish.

Functions of optimal work obtained via optimization are generalizations of the classical exergy, [20], for the case of imperfect (dissipation–involving) downgrading and utilization of resources. The generalized exergy in processes departing from the equilibrium (resource relaxation, downgrading) is larger than the one in processes approaching the equilibrium (resource utilization, upgrading). This property emerges because one respectively adds or subtracts the product of T^e and entropy production in equations describing the generalized availability. Limits for mechanical energy yield or consumption provided by exergies A are always stronger than those defined by the classical exergy. Thus, in both modes, generalized exergies provide enhanced bounds in comparison with those predicted by classical exergy.

In the realm of fuel cells these issues are relatively fresh but there is a potential of implementing them especially in connection with control problems [21, 22]. Electrochemical systems and particularly fuel cells are especially important in this context by virtue of their inherently clean, efficient, and reliable performance. The methodology extending that familiar for the classical thermal machines has also been extended to the complex multi-component and multi-reaction chemical engines, [17].

XIII. Conclusion

Clearly, with thermokinetic models, we can confront and surmount the limitations of applying classical thermodynamic bounds to real processes. The consequence are enhanced power limits, stronger than those of classical thermodynamics. This is a direction with many open opportunities, especially for separation and chemical systems. More information related to power limits in energy systems can be found in our earlier papers [9, 23] and in the book [11]. A challenging extension is also the optimization of the fuel cell–heat engine hybrid systems [24].

Nomenclature

A_v generalized exergy per unit volume [Jm^{-3}]
$A^{\perp}$ surface area perpendicular to flow [m^2]
a temperature power exponent in kinetic equation [-]
$a_0=4\sigma/c$ constant related to the Stefan-Boltzmann constant [$Jm^{-3}K^{-4}$]
a_v total area of energy exchange per unit volume [m^{-1}]
E^0, E_0 Nernst ideal voltage and idle run voltage, respectively [V]
$\dot{G}$ resource flux [gs^{-1}, $mols^{-1}$]
g_1, g partial and overall conductance [$Js^{-1}K^{-a}$]
f_0, f_i profit rate and process rates
H Hamiltonian function
H_{TU} height of transfer unit [m]
h numerical value of Hamiltonian [$Jm^{-3}K^{-1}$]
h, h_v specific and volumetric enthalpies [Jg^{-1}, Jm^{-3}]
i-electric current density [Am^{-2}]
n flux of fuel reagents [gs^{-1}, $mols^{-1}$]
$p = \dot{W}$ power output [Js^{-1}]
p_m^0 molar constant of photons density [$molm^{-2}K^{-3}s^{-1}$]
q heat flux between a stream and power generator [Js^{-1}]
Q total heat flux involving transferred entropies [Js^{-1}]
S, S_σ entropy and entropy produced [JK^{-1}]
$\Delta S_{1'}$ entropy change of circulating fluid along isotherm $T_{1'}$,
$\Delta S_{2'}$ entropy change of the circulating fluid along isotherm $T_{2'}$,
s, s_v specific and volumetric entropy [$JK^{-1}g^{-1}$, $J\,K^{-1}m^{-3}$]
T variable temperature of resource [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^e constant temperature of environment [K]
T' Carnot temperature control [K],
$\dot{T} = u$ rate of control of T in non-dimensional time [K]
t physical time [s]
u and υ rate controls, $dT/d\tau$ and dT/dt, [K, Ks^{-1}]
V voltage, maximum work function, resp.[V, $Jmol^{-1}$]
v velocity of resource stream [ms^{-1}]
W work produced, positive in engine mode [J]

w specific work at flow or power per unit flux of a resource [J/mol]
x mass fraction [-], length coordinate [m]
z adjoint variable

Greek symbols
α_1, α' partial and overall heat coefficients referred to respective cross-sections [$Jm^{-2}s^{-1}K^{-1}$]
β effective coefficient of radiation transfer related to molar constant of photons density p_m^0 and Stefan-Boltzmann constant of radiation; $\beta = \sigma a_v c_h^{-1}(p_m^0)^{-1}$ [s^{-1}]
ε total energy flux, conservative along a conductor [Js^{-1}]
$\eta = p/q_1$ first-law thermal efficiency [-]
$\chi = \rho c_v(\alpha' a_v)^{-1}$ time constant assuring the identity of ratio t/χ with number of transfer units [s]
μ chemical potential [$Jmol^{-1}$]
μ' Carnot chemical potential [$Jmol^{-1}$]
Φ factor of internal irreversibility [-]
σ Stefan-Boltzmann constant for radiation [$Jm^{-2}\,s^{-1}K^{-4}$]
σ_s entropy production of the system [$JK^{-1}s^{-1}$]
ξ intensity index [-]
ζ chemical efficiency [-]
τ dimensionless time or number of transfer units [-]

Subscripts
C Carnot point
m molar flow
v per unit volume
1,2 first and second fluid
0 idle run voltage

Superscripts
e environment
i initial state
f initial state
0 ideal (equilibrium) voltage

Abbreviations
CNCA Chambadal-Novikov-Curzon-Ahlborn engine
HJB Hamilton-Jacobi-Bellman
HJ Hamilton Jacobi equation.

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