Dynamical energy limits in traditional and work-driven operations II. Systems with heat and mass transfer

Stanislaw Sieniutycz *, Monika Kubiak

Faculty of Chemical Engineering and Process Engineering, Warsaw Polutechnic, Warsaw University of Technology, 1 Warynskiego Street, 00-645 Warsaw, Poland

Abstract

This is the second part of the work that analyses dynamical energy limits for diverse operations with finite rates important in engineering. Our position is that a dynamic limit of a sufficiently high hierarchy may be helpful in modelling and design of a prescribed operation. In particular, we treat active systems with coupled heat and mass transfer important in separation and biological systems. The operations considered occur in separation units, heat and mass exchangers, energy converters and chemical reactors. The energy limits are expressed in terms of classical exergy and a residual minimum of entropy generated in equipment of a fixed dimension. To ensure physical limits we treat sequential work-driven operations, in particular those of dissolving or evaporation which run jointly with thermal machines (e.g. heat pumps). We also compare structures of optimization criteria describing these limits (in particular "endoreversible limits") in traditional and work-driven operations. Through quantitative analyses we extend to the realm of mass transfer operations the method initiated in Part I that applies "Carnot variables" as suitable controls. Functions of extremum work, which apply a residual minimum entropy production, are found in terms of initial and final states, duration and (in discrete processes) number of stages. Mathematical analogies between entropy production expressions in traditional and work-driven operations are helpful to formulate optimization criteria in both cases.
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1. Introduction

1.1. Dynamic limits and generalized exergies

In Part I of this work [1] we formulated basic principles of integrated physical limits for energy production or consumption applicable to various traditional and work-driven operations of chemical and mechanical engineering. One of major aims of analyses leading to these limits are quantities of definite physical nature that still bound practical or industrial processes. The integrated physical limits may be contrasted with so-called cumulative exergy costs used in thermal engineering or ecology [2]. The latter are defined in terms of total consumption of exergy of natural resources necessary to yield the unit of a definite product. These cumulative exergy costs are, however, burden by sorts, locations and dates of various technologies, variable efficiencies, semiproducts, controls, etc., and, therefore, they do not constitute objective physical measures. In view of their non-objectiveness, mathematical properties of cumulative exergy cost and ecological cost are hardly defined; also corresponding optimal costs remain largely unknown. In fact, cumulative cost [2] provides a way to compare diverse energy-consuming technologies rather than to evaluate energy limits. Yet, technical indicators obtained from cumulative costs may be useful to forecast changes in demand for heat agents caused by

* Corresponding author. Fax: +48-22-8251440.
E-mail address: sieniutycz@ichip.pw.edu.pl (S. Sieniutycz).

Nomenclature

A	available energy (exergy)
C	constraining expression
c	specific heat at the constant pressure,
G	molar mass flux, total flow rate
g_1, g	partial and overall conductances
H_{TU}	heat of transfer unit
$h_{1'}$	partial enthalpy of active component in state $1'$
H^n	enthalpy at stage n
H'	specific enthalpy of controlling phase
N	molar mass flux of active component
n	interface mass flux
P^n, p^n	cumulative power output and power output at nth stage
P'	modified optimization criterion
q_1	driving heat in the engine mode of the stage
R	gas constant
$R^n(\boldsymbol{x}, t)$	optimal work function of cost type in terms of state and time
r_1, r_2	resistances, reciprocals of conductances g_1 and g_2
S	solid entropy, entropy of controlled phase (solid)
$s_{1'}$	partial entropy of active component in state $1'$
s'	specific entropy of controlling phase
S_σ	specific entropy production
T	temperature of controlled phase
T_1, T_2	bulk temperatures of fluids 1 and 2
T_1', T_2'	temperatures of circulating fluid (see Fig. 1)
T^e	constant equilibrium temperature of environment
T'	Carnot temperature, temperature of controlling phase
t	physical time, contact time

u^n	rate of the temperature change as the control variable, $u^n = \Delta T^n / \Delta \tau^n$
V	optimal work function of profit type, max W
W	total specific work or total power per unit mass flux, $W = P/G$
W^n	work at stage n
X_1	bulk concentration in fluid 1 (inert basis)
x	transfer area coordinate

Greek symbols

α'	overall heat transfer coefficient
η	first-law efficiency, $\eta = p/q_1$
ε	interface energy flux
θ^n	free interval of an independent variable or time interval at stage n
μ_1	molar chemical potential of active component in fluid 1
μ'	Carnot chemical potential
τ	nondimensional time, number of the heat transfer units (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

Abbreviations

EGM	entropy generation minimization
FTT	finite-time thermodynamics
OCT	optimal control theory

variations in production size, technology of product yield and changes of heat agents.

Importantly, the integrated power criteria are well-defined functionals of controls and state coordinates, and their optimal counterparts have properties of functions (potentials). The potential properties of these optimal counterparts are ensured due to a well-defined, unique process that follows from the optimization method eliminating effect of controls [3]. This is a constrained optimization method for a benchmark sequential operation in which a single resource is produced with a fixed mean rate from common constituents of the environment [1,4]. The sequential process that leads to the production of a resource resembles the one known from the theory of classical exergy [5,6]. However, there

is one essential difference: the duration of the resource yield process is constrained to a finite value, and thus some residual energy dissipation is admitted [3,4]. The physical limits obtained in this way generalize those stemming from the classical exergy and exhibit significant degree of universality. They are of dynamic nature and, therefore, they are not only stronger than static, but are also more useful in design. Our interest is in revealing and systematising such generic limits. These may, for example, determine lower bound for the amount of the energy supply or amount of a key substance in equipment of a finite investment, for separation units running with a prescribed intensity. In brief, we are interested in "dynamic" bounds of physical origin—usually functions of operational constraints—established under the con-

dition that, in any circumstances, the process will run with a minimum required intensity, yet yielding a desired product. Complex optimization techniques are used to obtain dynamic bounds for various processes, including those for exchange and separation systems.

2. Potential functions and dynamic limits in separation units

First we recall our assertion that bounds or limits on the energy production or consumption must be defined as purely physical quantities, independent on economical properties [1,4]. Finite-time thermodynamics (FTT) investigates effects of constraints on time and rate and bounds constructed on the basis of various optimization criteria. In particular generalized exergies are defined and calculated. The exergy bounds are both relevant and useful; both classical exergy and generalized exergies are measures of various resources and energy. These criteria are stated subject the considered assertion: when calculating energy limits, we search for (hierarchy of) diverse, *purely physical* extrema with no regard to economic optima [1,4]. It is true that a part of the methodological experience gained from the formulation of mathematical models and optimization can be preserved when passing from bound analyses to economic optimization. Yet approaches to "optimal design" that use the entropy (or exergy) as their optimization criteria make little sense from the standpoint of realistic economic design.

The exergy and heat consumed in separation units can now be treated in general terms without reference to any specific process, whether it be distillation, desorption, or drying. This leads to limits on the performance of separation processes [1,7]. For a given separation effect the lowest bound for heat consumption is determined by thermodynamics and is given by the ratio of the minimum work of separation to the related Carnot efficiency. However, this limit is unrealistically low, and, more importantly, it does not correspond to any real feed flow. An irreversible bound on the heat consumed in separation processes has been determined as a function of feed flow [7] and gives a more realistic limit. It includes the effect of entropy production σ and simplifies to the classical result in the limit of vanishing σ. These results show some resemblance to those known for the efficiency of thermal engines evaluated at the maximum power point.

For any finite-rate separation process with a given nonvanishing mass flow (average mass flow in the case of cyclic processes) the exergy consumption is larger than the corresponding reversible consumption. Since the constraint on the feed flow (and any other constraints on e.g. boundary concentrations) is operative, only a part of the entropy produced can be reduced through an optimal choice of an operational parameter.

For a given feed flow such a reduction causes a related decrease in the valuable heat; hence, the minimum of the heat consumed corresponds indeed to the minimum of σ. Thus, there exists a more realistic lower bound, greater than the classical value, on the valuable heat consumed. This bound is a function of the flow F. Any real separation process with a given feed flow will consume an amount of heat that cannot be lower than this limit. This value is still just a lower bound and is not the economically optimal heat consumption for any particular separation unit. Whatever the economical heat consumption is, for a given operational situation this consumption cannot be less than this lower bound. Knowledge of this bound is of value for design. A chemical engineer realizes however that it is not necessary to speak about entropy production at all in order to determine the lower bound on heat consumption [1,8].

3. Evaluation of work limits in sequential operations with mass transfer

In this section we first briefly expose several basic expressions which quantify limits on production or consumption of mechanical energy in sequential operations with heat exchange [1,9,10] and next pass to operations with mass exchange, initiated in [11]. The method involves generally optimization of work flux from (or to) a sequence of thermal machines thus generalizing the well-known method of evaluation of the classical exergy in reversible sequences. The problem of finite-rate limits requires sequential operations with thermal machines, such as multistage heat pumps, where total power input is minimized at constraints that describe dynamics of energy and mass exchange. The results are limiting work functions in terms of end states, duration and (in discrete processes) number of stages [1]. The notation principle for a one-stage work-consuming unit is illustrated in Fig. 1. This figure simply extends the unit in Fig. 1 of Part I. A topological scheme of a general process of multistage power production or consumption, leading to generalized exergies, is illustrated in Fig. 2.

Modelling a general work-assisted operation for the purpose of limits evaluation is a difficult task as it involves abstract (often "endoreversible") models and their extensions rather than models of real operations, yet it is consistent with general philosophy of optimization [3]. The optimization is difficult as well since it must be performed subject to constraints that take into account dynamics of heat and mass transport and rate of real work consumption. However, if the so-called Carnot intensive parameters (temperatures and chemical potentials) are used, formal analogies emerge between entropy production expressions in work-assisted and in conventional operations. These analogies are very

Temperature and chemical potentials of circulating fluid	$T_{1'}, \mu_{1'}$

q_1, n_1

r_1

T_1, μ_1

$\leftarrow P$

-- T^e, μ^e ------------------------------ q_2, n_2 ------------------- T_2, μ_2

r_2

$G_0 \rightarrow$	$T_{2'}, \mu_{2'}$
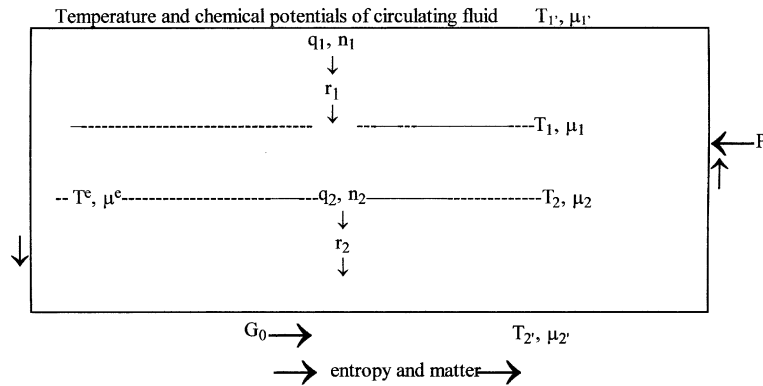
$\rightarrow$ entropy and matter $\rightarrow$

Fig. 1. Scheme of designations for an irreversible one-stage heat pump on the symbolic state chart.
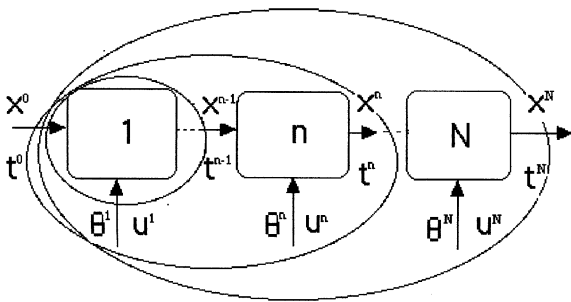
Fig. 2. A scheme of discrete process with stage size control θ^n and other controls $\mathbf{u}^n$. Bellman's principle of optimality (forward algorithm of the dynamic programming method) is applied to multistage power production or consumption. Elipse-shaped balance areas pertain to sequential subprocesses that evolve by inclusion of remaining stages.

helpful to obtain suitable models, criteria and solutions [1,10,12]. In this paper we shall exploit these analogies to obtain the energy limits for sequential work-driven operations governed by vector rather than scalar efficiencies [13]. The relevant operations involve coupled heat and mass transfer and are counterparts of well-known classical operations without work, such as conventional evaporation, extraction and drying.

To obtain physical limits for real flows with dissipation in boundary layers the Novikov–Curzon–Ahlborn (NCA) process is the appropriate benchmark [1,3,13]; the corresponding limits are those for the mechanical or electrical energy. In an endoreversible engine a resource fluid drives the Carnot engine from which the work is taken out. In an endoreversible consumer of work a fluid (e.g. drying agent) is driven in the condenser of the Carnot heat pump to which work is supplied. In both cases the control process can be schematized in Fig. 1. The fluids are of finite thermal conductivity, hence there are finite thermal resistances in the system. In a multistage operation the fluid's state $\mathbf{x}$ changes at each stage;

the set of all states (with fluid's temperatures and concentrations as state coordinates) is described by the vector sequence $\mathbf{x}^0, \mathbf{x}^1, \ldots, \mathbf{x}^N$. The set of controls (e.g. Carnot temperatures and concentrations) is represented by another vector sequence, $\mathbf{u}^0, \mathbf{u}^1, \ldots, \mathbf{u}^N$. The stage size control (e.g. the fluid's holdup time or transfer area) is usually excluded form the definition of the control vector $\mathbf{u}$; the set of the related controls is $\theta^0, \theta^1, \ldots, \theta^N$. The popular 'engine convention' used: work generated in an engine, W, is positive, and work generated in a heat pump is negative; this means that a positive work $(-W)$ is consumed in the heat pump. The sign of the optimal work function $V^N = \max W^N$ defines the working mode for an optimal sequential process as a whole. In engine modes $W > 0$ and $V > 0$. In heat-pump modes, $W < 0$ and $V < 0$, thus working with a function $R^N = -V^N = \min(-W^N)$ is more convenient. The heat-pump modes correspond with processes that start with $\mathbf{x}^0 = \mathbf{x}^e$ and terminate at a certain $\mathbf{x}^N = \mathbf{x}$ and the engine modes—with processes that start with $\mathbf{x}^0 = \mathbf{x}$ and terminate at $\mathbf{x}^e$. Their functions V^N and R^N are generalizations of the classical exergy for processes with finite durations. In the considered case of an infinite reservoir, the intensive parameters of the reservoir, i.e. its temperature T^e and chemical potentials μ_i^e, do not change along the process path, and this is why these variables reside in the formal models and potentials as constant parameters. As in the case of heat-mechanical limits [1], the range of optimizing is restricted to physical limits exclusively, regardles economic conditions of the operation. In the "endoreversible" cases perfect (second-law) efficiency of the Carnot (work-producing) engines across a finite-resource stream is essential, in more general cases, for which the NCA efficiency formula must be generalized, internal irreversibilities are included.

Work limits follow in terms of the time of state change and properties of boundary layers and other dissipators. While the endoreversible modelling is of a very restricted use in predicting actual work charac-

teristics of real thermal machines, FTT models can go beyond "endoreversible limits" to treat internal dissipations as well, see [1, Eq. 59] and [26]. However, the most essential issue is that in either of two versions of FTT, of which the first gives up internal irreversibilities whereas the second one estimates these from a model, the FTT limits on energy consumption or production are stronger than those predicted by the classical exergy. In the hierarchy of limits resulting from more and more detailed models, the limits of the second and higher ranks are stronger than the limits of the first (endoreversible) rank. The weakest or the worst are limits of classical thermodynamics; they are limits of zero-th rank stemming from the classical exergy. Thus, for the purpose of enhanced bounds, any finite-time sequence of single-stream states in Fig. 2 yields limits of the higher rank in comparison with the reversible sequence leading to classical exergy [5]. This follows from the "process rate penalty" taken into account in every version of FTT.

4. Lagrange multipliers for limiting operations with mass transfer

In Part I we have shown remarkable effectiveness of the Lagrange multiplier method to find optimal temperatures T_1' and T_2', of fluid circulating in the thermal Novikov–Curzon–Ahlborn (NCA) operation. Here we shall extend that approach to all dependent controls constrained by the entropy and mass balances that govern the process of simultaneous heat and mass transfer. Notation used for a single unit and the corresponding multistage operation are respectively depicted in Figs. 1 and 2.

We consider first a generalized (mass transfer involving) single-stage operation of NCA type in which c is resource's specific heat, and r_1 and r_2 are thermal resistances, the reciprocals of respective conductances g_1 and g_2 [3]. We restrict ourselves to the case of one active component diffusing in a stagnant inert (solvent or solid). This case is sufficiently general to present basic features of the analytical method that solves the problem of energy limits. In the analysis below we use the traditional system of process variables based on temperatures and concentrations, i.e. we work without explicit introduction of chemical potentials. The energy flux ε is the sum of the pure heat flux q and the product of enthalpy h of the active component and its matter flux, n, where the latter is simply evaluated in terms of the corresponding difference of concentrations. In these coordinates the thermo-diffusional couplings appear in the energy equation that operates with combination of traditional driving forces: differences of temperature and concentration. The concentrations X are referred to the unit mass of the inert. The expression describing the

power produced in engine mode or consumed in heat-pump mode has then the form

$$P = g_1(T_1 - T_1') + h_{1'}(T_1', X_1')g_{m1}(X_1 - X_1') - g_2(T_2' - T_2) - h_{2'}(T_2', X_2')g_{m2}(X_2' - X_2). \tag{1}$$

We stress the influence of concentrations X on partial entropies of the active component, $s_{1'}$ and $s_{2'}$. Otherwise the influence of concentrations X on corresponding partial enthalpies, $h_{1'}$ and $h_{2'}$ can be ignored. This follows, in particular, from a typical equation describing partial enthalpy of active component

$$h_{1'} = \left(\frac{\partial I}{\partial X_1'}\right)_{T_1'} = c(T_1' - T_0) + r_0. \tag{2}$$

Here r_0 is the specific latent heat of phase change (evaporation heat) for the active component (moisture) in the reference temperature T_0. Equation similar to (2) holds for the partial enthalpy $h_{2'}$. The formal setting $r_0 \equiv 0$ corresponds with absence of phase changes.

The process constraint is the entropy balance in the form that takes into account the transport of entropy of active component:

$$\frac{g_1(T_1 - T_1')}{T_1'} + s_{1'}(T_1', X_1')g_{m1}(X_1 - X_1') - \frac{g_2(T_2' - T_2)}{T_2'} - s_{2'}(T_2', X_2')g_{m2}(X_2' - X_2) = 0. \tag{3}$$

Taking into account the dependence of concentrations on partial entropies is here mandatory. In fact, partial entropy $s_{1'}$ of this equation depends on both temperature T_1' and concentration X_1' in accord with the equation

$$s_{1'} = \left(\frac{\partial S}{\partial X_1'}\right)_{T_1'} = c \ln\left(\frac{T_1'}{T_0}\right) - R \ln\left(\frac{X_1'}{1 + X_1'}\right) + \frac{r_0}{T_0}. \tag{4}$$

Analogous equation (without r_0 term) holds for the partial entropy $s_{2'}$.

The modified optimization criterion adjoints constraints of entropy and mass balance

$$P' = g_1(T_1 - T_1') + h_{1'}(T_1', X_1')g_{m1}(X_1 - X_1') - g_2(T_2' - T_2)$$
$$- h_{2'}(T_2', X_2')g_{m2}(X_2' - X_2)$$
$$+ \lambda_s\left(\frac{g_1(T_1 - T_1')}{T_1'} + s_{1'}(T_1', X_1')g_{m1}(X_1 - X_1')\right.$$
$$\left. - \frac{g_2(T_2' - T_2)}{T_2'} - s_{2'}(T_2', X_2')g_{m2}(X_2' - X_2)\right)$$
$$+ \lambda_m(g_{m1}(X_1 - X_1') - g_{m2}(X_2' - X_2)). \tag{5}$$

To obtain the extremum conditions of P' with respect of controls T_1', T_2', X_1', and X_2' expressions are needed that describe partial derivatives of partial entropies and enthalpies in states $1'$ and $2'$ with respect to these controls.

Using Eqs. (2)–(4) yields the following matrix of partial derivatives for the state $1'$

$$\begin{pmatrix} \partial h_1'/\partial T_1' = c_{1'} & \partial h_1'/\partial X_1' = 0 \\ \partial s_1'/\partial T_1' = \frac{c_{1'}}{T_1'} & \partial s_1'/\partial X_1' = -\frac{R}{X_1'(1+X_1')} \end{pmatrix}. \quad (6)$$

For the state $2'$ the analogous matrix is obtained.

We can now pass to optimization of criterion P'. We first find partial derivatives of function P' with respect to control variables and multipliers λ_s and λ_m. Next we determine necessary extremum conditions of P' with respect to controls T_1', T_2', X_1', and X_2' by setting to zero corresponding partial derivatives. As the result we obtain the system of six equations containing six unknowns λ_s, λ_m, T_1', T_2', X_1' and X_2',

$$(P')_{T_1'} = -g_1 + c_{1'}g_{m1}(X_1 - X_1')$$
$$+ \lambda_s\left(-g_1 \cdot \frac{T_1}{(T_1')^2} + \frac{c_{1'}}{T_1'}g_{m1}(X_1 - X_1')\right) = 0, \quad (7)$$

$$(P')_{T_2'} = -g_2 - c_{2'}g_{m2}(X_2' - X_2)$$
$$+ \lambda_s\left(-g_2 \cdot \frac{T_2}{(T_2')^2} - \frac{c_{2'}}{T_2'}g_{m2}(X_2' - X_2)\right) = 0, \quad (8)$$

$$(P')_{X_1'} = -h_{1'}(T_1')g_{m1} + \lambda_s\left(-s_{1'}(T_1',X_2')g_{m1}\right.$$
$$\left. -\frac{R}{X_1'(1+X_1')}g_{m2}(X_1 - X_1')\right) - \lambda_m g_{m1} = 0, \quad (9)$$

$$(P')_{X_2'} = -h_{2'}(T_2')g_{m2} + \lambda_s\left(-s_{2'}(T_2',X_2')g_{m2}\right.$$
$$\left. +\frac{R}{X_2'(1+X_2')}g_{m2}(X_2' - X_2)\right) - \lambda_m g_{m2} = 0. \quad (10)$$

As in the case with pure heat transfer [1], two structurally similar equations are obtained for the multiplier of entropy balance, λ_s. Now, however, these equations are accompanied by two equations for the multiplier of mass balance, λ_m. In addition, the form of resulting equations is more complex. After transforming the systems to get the Lagrange multipliers as explicit quantities we obtain

$$\frac{-g_1 + c_{1'}g_{m1}(X_1 - X_1')}{g_1\frac{T_1}{(T_1')^2} - \frac{c_{1'}}{T_1'}g_{m1}(X_1 - X_1')} = \frac{-g_2 - c_{2'}g_{m2}(X_2' - X_2)}{g_2\frac{T_2}{(T_2')^2} + \frac{c_{2'}}{T_2'}g_{m2}(X_2' - X_2)} = \lambda_s,$$
$$(11)$$

$$-h_{1'}(T_1') + \lambda_s(g_{m1})^{-1}\left(-s_{1'}(T_1',X_1')g_{m1} - \frac{R}{X_1'(1+X_1')}\right.$$
$$\left. \times g_{m2}(X_1 - X_1')\right) = -h_{2'}(T_2') + \lambda_s(g_{m2})^{-1}\left(-s_{2'}(T_2',X_2')g_{m2}\right.$$
$$\left. +\frac{R}{X_2'(1+X_2')}g_{m2}(X_2' - X_2)\right) = \lambda_m,$$
$$(12)$$

$$\frac{g_1(T_1 - T_1')}{T_1'} + s_{1'}(T_1',X_1')g_{m1}(X_1 - X_1') - \frac{g_2(T_2' - T_2)}{T_2'}$$
$$- s_{2'}(T_2',X_2')g_{m2}(X_2' - X_2) = 0, \quad (13)$$

$$g_{m1}(X_1 - X_1') - g_{m2}(X_2' - X_2) = 0. \quad (14)$$

Note that entropy multiplier, λ_s, is defined in Eq. (11) in terms of process variables by each of two expressions of this equation. Similarly, the matter multiplier, λ_m, is defined in terms of λ_s and process variables by each of two expressions in Eq. (12). This means that the Lagrange multipliers are, in fact, eliminated, i.e. four equations obtained after rejection of Lagrange multipliers on right hand sides of the set (11)–(14) define optimal values of four control variables T_1', T_2', X_1' and X_2'. The discussed equations describe relations between temperatures and concentrations of circulating fluid at the optimal power point of the system. In case of absence of mass transfer these equations simplify to a simple set

$$-\frac{(T_1')^2}{T_1} = -\frac{(T_2')^2}{T_2} = \lambda, \quad (15)$$

$$\frac{g_1(T_1 - T_1')}{T_1'} = \frac{g_2(T_2' - T_2)}{T_2'}. \quad (16)$$

This result was obtained in Part I for heat-mechanical processes. The reader is referred to Part I for comprehensive discussion of solution of this equation system.

Let us return to the general system, Eqs. (11)–(14). Without loss of generality, this system can be simplified by determining one of the concentrations, X_1' or X_2' from the mass balance (14) and substituting the so-obtained concentration to the remaining equations. Assume, for concreteness, that concentration X_1' was eliminated. In this way we obtain a system of three nonlinear equations with three variables T_1', T_2', and X_2' that is not susceptible for further reduction of variables. Without any further simplifications, the general equation set (11)–(14) or its equivalent system simplified as described (with variables T_1', T_2', and X_2') can be solved numerically by Newton–Raphson method ([13] of Part I). This method is efficient, and its convergence is fast.

The numerical solution constitutes the optimal data of optimal controls (T_1', T_2', X_1' and X_2') for a given state in the bulk of both fluids (T_1, T_2, X_1 and X_2). Iterating calculations for changed states of bulk (T_1, T_2, X_1 and X_2) changes numerical values of optimal controls T_1', T_2', X_1' and X_2'. In this way tables are generated that describe optimal controls as state functions of coordinates of both fluids (driving fluid of the engine and reservoir fluid). Each optimal decision not only satisfies balance equations (constraints) but also ensures the maximum power yield in engine mode of the system.

However, in number of real applications, some special simplifications are further appropriate; in these cases

yet simpler equation systems are obtained, discussed below.

At the price of a simplification, which is the replacement of temperatures T_1 and T_2 in expressions for entropy transferred with mass by the reference temperature T_0, further reduction of variables in the resulting system of equations can be made. As the result, the simplified problem may be broken down to solving only two nonlinear equations. This procedure exploits explicit formulae for partial enthalpies and entropies of active component

$$h_{1'} = \left(\frac{\partial I}{\partial X_1'} \right)_{T_1'} = c(T_1' - T_0) + r_0, \tag{17}$$

$$s_{1'} = \left(\frac{\partial S}{\partial X_1'} \right)_{T_1'} = c \ln \left(\frac{T_1'}{T_0} \right) - R \ln \left(\frac{X_1'}{1 + X_1'} \right) + \frac{r_0}{T_0}. \tag{18}$$

This equation set describing an optimal process takes then the form

$$\frac{-g_1 + c_{1'} g_{m2}(X_2' - X_2)}{g_1 \frac{T_1}{(T_1')^2} - \frac{c_{1'}}{T_0} g_{m2}(X_2' - X_2)} = \frac{-g_2 - c_{2'} g_{m2}(X_2' - X_2)}{g_2 \frac{T_2}{(T_2')^2} + \frac{c_{2'}}{T_0} g_{m2}(X_2' - X_2)}, \tag{19}$$

$$- c(T_1' - T_0) - r_0 + \lambda_s (g_{m1})^{-1} \left(-g_{m1} \left(c \ln \left(\frac{T_1'}{T_0} \right) \right. \right.$$
$$- R \ln \left(\frac{X_1'}{1 + X_1'} \right) + \frac{r_0}{T_0} \right) - \frac{R}{X_1'(1 + X_1')} g_{m2}(X_2' - X_2) \right)$$
$$= -c(T_2' - T_0) - r_0 + \lambda_s (g_{m2})^{-1} \left(-g_{m2} \left(c \ln \left(\frac{T_2'}{T_0} \right) \right. \right.$$
$$- R \ln \left(\frac{X_2'}{1 + X_2'} \right) + \frac{r_0}{T_0} \right) + \frac{R}{X_2'(1 + X_2')} g_{m2}(X_1' - X_2) \right), \tag{20}$$

$$\frac{g_1(T_1 - T_1')}{T_1'} + \left(c \ln \left(\frac{T_1'}{T_0} \right) - R \ln \left(\frac{X_1'}{1 + X_1'} \right) + \frac{r_0}{T_0} \right)$$
$$\times g_{m2}(X_2' - X_2) = \frac{g_2(T_2' - T_2)}{T_2'}$$
$$+ \left(c \ln \left(\frac{T_2'}{T_0} \right) - R \ln \left(\frac{X_2'}{1 + X_2'} \right) + \frac{r_0}{T_0} \right) g_{m2}(X_2' - X_2), \tag{21}$$

$$X_1' = X_1 - (g_{m2}/g_{m1})(X_2' - X_2). \tag{22}$$

With Eq. (19) we subsequently obtain

$$\frac{g_1 \cdot \frac{T_1}{(T_1')^2} - \frac{c_{1'}}{T_0} g_{m2}(X_2' - X_2)}{-g_1 + c_{1'} g_{m2}(X_2' - X_2)} = \frac{g_2 \cdot \frac{T_2}{(T_2')^2} + \frac{c_{2'}}{T_0} g_{m2}(X_2' - X_2)}{-g_2 - c_{2'} g_{m2}(X_2' - X_2)} \tag{23}$$

and

$$\frac{T_1}{(T_1')^2} = \frac{c_{1'}}{T_0} \frac{g_{m2}}{g_1} (X_2' - X_2) + \frac{(-g_1 + c_{1'} g_{m2}(X_2' - X_2))}{(-g_2 - c_{2'} g_{m2}(X_2' - X_2))}$$
$$\times \left(\frac{g_2}{g_1} \cdot \frac{T_2}{(T_2')^2} + \frac{c_{2'}}{T_0} \frac{g_{m2}}{g_1} (X_2' - X_2) \right). \tag{24}$$

Hence

$$T_1' = \sqrt{\frac{T_1}{T_2} \left\{ \frac{c_{1'}}{T_0 T_2} \frac{g_{m2}}{g_1} (X_2' - X_2) + \frac{(-g_1 + c_{1'} g_{m2}(X_2' - X_2))}{(-g_2 - c_{2'} g_{m2}(X_2' - X_2))} \left(\frac{g_2}{g_1} \cdot \frac{1}{(T_2')^2} + \frac{c_{2'}}{T_0 T_2} \frac{g_{m2}}{g_1} (X_2' - X_2) \right) \right\}^{-1}}. \tag{25}$$

This equation describes the connection between temperatures of circulating fluid at the optimal power point of the system. It constitutes a generalization of a result obtained in Part I, [1], for operations with pure heat transfer

$$T_1' = \sqrt{\frac{T_1}{T_2}} \cdot T_2'. \tag{26}$$

Indeed, for vanishing conductances of mass transfer g_{mi} ($i = 1, 2$) Eq. (25) simplifies to Eq. (26).

Expression in Eq. (25) describes temperature T_1' as function of (variable) state coordinates of both fluids (T_1, T_2, X_1 and X_2) and controls. This function must be substituted into two equations. The first is Eq. (20) that describes multiplier of the mass balance, whereas the second is Eq. (21) that describes the entropy balance. Thus the situation is more complicated than in the case of pure heat transfer, where only entropy balance was needed to solve the problem of this sort. The solution of the discussed problem is described by two equations of the form

$$c(T_2' - T_1') + r_0 + \lambda_s(T_2', X_1') \left\{ \left(c \ln \left(\frac{T_2'}{T_1'} \right) \right. \right.$$
$$+ R \ln \left(\frac{X_2'}{1 + X_2'} \middle/ \frac{X_1'}{1 + X_1'} \right) + \frac{r_0}{T_0} \right)$$
$$+ \left(\frac{R}{X_2'(1 + X_2')} - \frac{R}{X_1'(1 + X_1')} \frac{g_{m2}}{g_{m1}} \right) (X_2' - X_2) \right\} = 0 \tag{27}$$

and

$$\frac{g_1(T_1 - T_1')}{T_1'} + g_{m2}(X_2' - X_2)\left\{c_{1'} \ln\left(\frac{T_1'}{T_2'}\right)\right.$$

$$+ R \ln\left(\frac{X_2'}{1 + X_2'} \middle/ \frac{X_1 - (g_{m2}/g_{m1})(X_2' - X_2)}{1 + X_1 - (g_{m2}/g_{m1})(X_2' - X_2)}\right)$$

$$\left. + \frac{r_0}{T_0}\right\} - \frac{g_2(T_2' - T_2)}{T_2'} = 0. \tag{28}$$

In this set, multiplier $\lambda_s(T_2', X_2')$ and temperature $T_1'(T_2', X_2')$ are known functions defined by Eqs. (19) and (25), whereas concentration X_1' is expressed in terms of concentration X_2' as required by mass balance (22). (This is explicitly shown in the second equation of the considered system.)

Similarly as general necessary conditions, Eqs. (11)–(14), the simplified set, i.e. two Eqs. (27) and (28) must be solved numerically. The results are optimal values of controls T_2' and X_2'. Next, remaining controls, T_1' and X_1', are computed from already known equations. After getting optimal controls at maximum power conditions, numerical values of heat fluxes, q_1 and q_2, and corresponding fluxes of energy, ε_1 and ε_2, are calculated. Next, maximum power P is calculated as the difference $\varepsilon_1 - \varepsilon_2$ at the optimal point. Efficiencies of energy conversion in the system then follow. In conclusion, the elimination of Lagrange multipliers is an easy task as they are imbeded linearly in the necessary conditions of optimality. However, there are difficulties in eliminating physical variables from the system of extremum conditions, in view of (generally) nonlinear nature of optimization criterion and balance constraints.

5. Model using Onsager symmetries for coupled heat and mass transfer

Here we consider another formulation in which Onsager theory is applied to treat work-driven operations with coupled heat and mass transfer. Equations of coupled exchange of energy and matter in the first fluid have the form

$$-\dot{H}_1 = l_1^{HH}(T_1'^{-1} - T_1^{-1}) + l_1^{HN}\left(\frac{\mu_1}{T_1} - \frac{\mu_{1'}}{T_1'}\right), \tag{29}$$

$$-\dot{X}_1 = l_1^{HN}(T_1'^{-1} - T_1^{-1}) + l_1^{NN}\left(\frac{\mu_1}{T_1} - \frac{\mu_{1'}}{T_1'}\right), \tag{30}$$

whereas those in the second fluid are

$$-\dot{H}_2 = l_2^{HH}(T_2^{-1} - T_2'^{-1}) + l_2^{HN}\left(\frac{\mu_{2'}}{T_2'} - \frac{\mu_2}{T_2}\right), \tag{31}$$

$$-\dot{X}_2 = l_2^{HN}(T_2^{-1} - T_2'^{-1}) + l_2^{NN}\left(\frac{\mu_{2'}}{T_2'} - \frac{\mu_2}{T_2}\right). \tag{32}$$

Consequently, the power produced in engine mode or consumed in heat-pump mode can be written in the form

$$P = l_1^{HH}(T_1'^{-1} - T_1^{-1}) + l_1^{HN}\left(\frac{\mu_1}{T_1} - \frac{\mu_{1'}}{T_1'}\right) - l_2^{HH}(T_2^{-1} - T_2'^{-1})$$

$$- l_2^{HN}\left(\frac{\mu_{2'}}{T_2'} - \frac{\mu_2}{T_2}\right). \tag{33}$$

The constraint of entropy balance across the perfect engine has the form

$$\frac{1}{T_2'}\dot{H}_2 - \frac{\mu_{2'}}{T_2'}\dot{X}_2 - \frac{1}{T_1'}\dot{H}_1 + \frac{\mu_{1'}}{T_1'}\dot{X}_1 = 0. \tag{34}$$

Explicitly, in view of Eqs. (29)–(32), the entropy constraint reads

$$C_S \equiv \frac{1}{T_1'}\left(l_1^{HH}(T_1'^{-1} - T_1^{-1}) + l_1^{HN}\left(\frac{\mu_1}{T_1} - \frac{\mu_{1'}}{T_1'}\right)\right)$$

$$- \frac{1}{T_2'}\left(l_2^{HH}(T_2^{-1} - T_2'^{-1}) + l_2^{HN}\left(\frac{\mu_{2'}}{T_2'} - \frac{\mu_2}{T_2}\right)\right)$$

$$- \frac{\mu_{1'}}{T_1'}\left(l_1^{HN}(T_1'^{-1} - T_1^{-1}) + l_1^{NN}\left(\frac{\mu_1}{T_1} - \frac{\mu_{1'}}{T_1'}\right)\right)$$

$$+ \frac{\mu_{2'}}{T_2'}\left(l_2^{HN}(T_2^{-1} - T_2'^{-1}) + l_2^{NN}\left(\frac{\mu_{2'}}{T_2'} - \frac{\mu_2}{T_2}\right)\right) = 0. \tag{35}$$

On the other hand the explicit form of the mass balance constraint $-\dot{X}_1 + \dot{X}_2 = 0$ is

$$C_N \equiv l_1^{HN}(T_1'^{-1} - T_1^{-1}) + l_1^{NN}\left(\frac{\mu_1}{T_1} - \frac{\mu_{1'}}{T_1'}\right) - l_2^{HN}(T_2^{-1} - T_2'^{-1})$$

$$- l_2^{NN}\left(\frac{\mu_{2'}}{T_2'} - \frac{\mu_2}{T_2}\right) = 0. \tag{36}$$

We can now pass to optimization of criterion P' that adjoints constraints by Lagrange multipliers

$$P' = P + \lambda_S C_S + \lambda_N C_N. \tag{37}$$

The control variables are $T_{1'}^{-1}$, $T_{2'}^{-1}$, $\mu_{1'}/T_1'$ and $\mu_{2'}/T_2'$. We find partial derivatives of function P' with respect to these controls and multipliers λ_S and λ_N and determine necessary extremum conditions of P' by setting to zero corresponding partial derivatives. As the result we obtain the system of six equations containing six unknowns λ_S, λ_N, $T_{1'}^{-1}$, $T_{2'}^{-1}$, $\mu_{1'}/T_1'$ and $\mu_{2'}/T_2'$. For the purpose of brevity only implicit form of these conditions is given below

$$\frac{\partial P'}{\partial T_{1'}^{-1}} = \frac{\partial P}{\partial T_{1'}^{-1}} + \lambda_S \frac{\partial C_S}{\partial T_{1'}^{-1}} + \lambda_N \frac{\partial C_N}{\partial T_{1'}^{-1}} = 0, \tag{38}$$

$$\frac{\partial P'}{\partial T_{2'}^{-1}} = \frac{\partial P}{\partial T_{2'}^{-1}} + \lambda_S \frac{\partial C_S}{\partial T_{2'}^{-1}} + \lambda_N \frac{\partial C_N}{\partial T_{2'}^{-1}} = 0, \tag{39a}$$

$$\frac{\partial P'}{\partial(\mu_{1'}/T_1')} = \frac{\partial P}{\partial(\mu_{1'}/T_1')} + \lambda_S \frac{\partial C_S}{\partial(\mu_{1'}/T_1')} + \lambda_N \frac{\partial C_N}{\partial(\mu_{1'}/T_1')} = 0, \tag{39b}$$

$$\frac{\partial P'}{\partial(\mu_{2'}/T_2')} = \frac{\partial P}{\partial(\mu_{2'}/T_2')} + \lambda_S \frac{\partial C_S}{\partial(\mu_{2'}/T_2')} + \lambda_N \frac{\partial C_N}{\partial(\mu_{2'}/T_2')} = 0,$$
(40)

$$\frac{\partial P'}{\partial \lambda_S} = C_S = 0,$$
(41)

$$\frac{\partial P'}{\partial \lambda_N} = C_N = 0.$$
(42)

As these equations are linear with respect to Lagrange multipliers, these multipliers can easily be eliminated, similarly as those in previous sections. In this way we obtain a system of four necessary optimality conditions that should be solved with respect to control variables $T_{1'}^{-1}$, $T_{2'}^{-1}$, $\mu_{1'}/T_1'$ and $\mu_{2'}/T_2'$. Numerical examples of solution are relegated to another paper, where also a discussion of the physical properties of the solution will be presented.

6. Carnot temperatures and chemical potentials in dynamical operations with mass transfer

We shall now prepare ourselves to application of Carnot temperatures and chemical potentials in operations with mass transfer. At first, we adduce suitable form of transfer equations that uses resistances, or elements of matrix inverse with respect to the conductance matrices $\mathbf{L}_1$ and $\mathbf{L}_2$ whose elements were used until now. These equations operate (primed) transfer potentials, temperatures and Planck chemical potentials of circulating fluid. For the first fluid as the (controlled) phase 1 we have

$$\frac{1}{T_1} - \frac{1}{T_1'} = r_1^{HH}\dot{H}_1 + r_1^{HX}\dot{X}_1,$$
(43)

$$\frac{\mu_{1'}}{T_1'} - \frac{\mu_1}{T_1} = r_1^{XH}\dot{H}_1 + r_1^{XX}\dot{X}_1.$$
(44)

Similarly, for the second fluid as phase 2 or thermal reservoir

$$\frac{1}{T_2'} - \frac{1}{T_2} = r_2^{HH}\dot{H}_2 + r_2^{HX}\dot{X}_2,$$
(45)

$$\frac{\mu_2}{T_2} - \frac{\mu_{2'}}{T_2'} = r_2^{XH}\dot{H}_2 + r_2^{XX}\dot{X}_2.$$
(46)

These relationships satisfy structure of matrix Ohm's law for coupled transfer processes. Their usefulness will be shown below, where dynamical processes in terms of Carnot potentials of transfer are introduced and analyzed.

Considering Stefan diffusion of active component in an inert we shall now introduce Carnot temperature T' and Carnot chemical potential of the component, μ'. For simplicity of designations we shall neglect the subscript 1 for the first (controlled) fluid. Again, medium 2 is iden-

tified with an infinite reservoir or environment (in the last case $T_2 \equiv T^e$).

From the power balance known from an analysis of the operation [11,12]

$$P = \varepsilon_1\left(1 - \frac{T_2'}{T_1'}\right) + n_1 T_2'\left(\frac{\mu_1'}{T_1'} - \frac{\mu_2'}{T_2'}\right),$$
(47)

where $\varepsilon_1 = -\dot{H}_1$ and $n_1 = -\dot{X}_1$ are interphase fluxes of energy and matter. Analyzing the first term of this equation we conclude that the definition of Carnot temperature remains the same as in the case with pure heat transfer, i.e.

$$T' \equiv T_2\frac{T_1'}{T_2'}$$
(48)

(see Part I, [1]). On the other hand, Eq. (47) and its reversible counterpart prove that the Carnot chemical potential should satisfy the equation

$$T_2'\left(\frac{\mu_1'}{T_1'} - \frac{\mu_2'}{T_2'}\right) = T_2\left(\frac{\mu'}{T'} - \frac{\mu_2}{T_2}\right).$$
(49)

This leads to following thermodynamic definition of Carnot chemical potential

$$\mu' = T'\left\{\frac{\mu_2}{T_2} + \frac{T_2'}{T_2}\left(\frac{\mu_1'}{T_1'} - \frac{\mu_2'}{T_2'}\right)\right\}.$$
(50)

We shall consider application of Carnot variables T' and μ' in dynamical processes, that means those processes in which at least one of the energy sources is finite (and thus it may exhaust). Here we assume that it is the upper reservoir that is finite, and that the lower reservoir remains infinite (it constitutes a constant environment).

The optimization criterion, that defines energy limit, is a curvilinear integral describing power P per unit mass flux of driving fluid. This is, in fact, the specific work generated or consumed by the system, which is the system with fluid at flow. An analysis [11,12] leads to general equation linking specific work and entropy production

$$W = P/G = -\int_{T^i}^{T^f}\left\{(1 - T_2/T')\,\mathrm{d}H + T_2(\mu'/T' - \mu_2/T_2)\,\mathrm{d}N\right\}$$
$$= -\int_{T^i}^{T^f}\left\{(1 - T_2/T)\,\mathrm{d}H + T_2(\mu/T - \mu_2/T_2)\,\mathrm{d}N\right\}$$
$$- T_2\int_{T^i}^{T^f}\left\{(1/T - 1/T')\,\mathrm{d}H + (\mu'/T' - \mu_2/T_2)\,\mathrm{d}N\right\}.$$
(51)

This equation describes the specific work produced (consumed) by the fluid controlled along its flow, and the link of that work with the entropy production. H is the enthalpy of the solution per unit mass of the inert or solvent and X is the corresponding concentration of

active component (e.g. moisture or polymer). The Gouy–Stodola law links the real work W (the first integral) with the reversible work W^{rev} (the second integral) and the negative product of T_2 and the entropy production (the third integral). The driving chemical potential, μ', appears here as an extra operational variable in the sense that it is absent in the set of variables appearing in the optimization solution. Eq. (51) refers to the "endoreversible" limit, but it may easily be generalized to processes with internal dissipation as we have shown in [1].

Eq. (51) incorporates the result of the entropy production invariance in a work-assisted operation with respect to the transformation of variables. This equation exploits the fact that an original expression for the entropy production is in terms of upper and lower thermal potentials of the fluid circulating in the thermal machine (T_1', T_2', $\mu_{1'}$ and $\mu_{2'}$). From this original expression the appropriate result for T' as function $T'(T_1', T_2', T_2)$ is the same as for the processes with pure heat transfer, and it can be written in the form (48). Likewise, in terms of upper and lower thermal potentials of the circulating fluid (T_1', T_2', $\mu_{1'}$ and $\mu_{2'}$), the driving chemical potential μ' follows as quantity described by Eq. (50). The associated model of control involves the process in which an external immiscible phase with the controlling parameters T' and μ' (or H' and X') exchanges energy and mass with the controlled solution. In particular, that model can accomodate the Onsagerian scheme of coupling in the heat and mass transfer. Here our choice of the state and control variables is caused by the fact that the most appropriate form of energy balance for a fluid at flow is in terms of the enthalpy.

Note that the theorem applies according to which the equality $T' = T_2$ at short-circuit point, where $T_1' = T_2'$, consistent with Eq. (48). Similarly, at short-circuit point, where $\mu_{1'} = \mu_{2'}$, the equality $\mu' = \mu_2$ holds which implies that the generalized theorem (including mass transfer) is valid. Again, the most essential result obtained here is the conclusion that in terms of the driving temperature T' and driving chemical potential μ' the entropy production in a work-assisted process acquires the form of the entropy production for a traditional process without any work production. Accordingly, we can implement entropy production formulas that are known for traditional processes of nonisothermal mass transfer (without work flux) into work formulae describing processes with thermal machines.

The basic conclusion here is similar as in case of processes with pure heat transfer [1]: the entropy production of an operation with a thermal machine can be expressed by certain control quantities, temperature T' and chemical potential μ', structural properties of the system. In terms of these quantities the expression for entropy production in endoreversible systems with work flux acquires form the same as in traditional process of

heat and mass exchange (without work production or consumption). This property allows for simultaneous development of thermodynamics of endoreversible thermal machines and traditional heat and mass exchangers, and also for application of well-known formulas of classical nonequilibrium thermodynamics in theory of endoreversible thermal machines.

Consequently, we should derive a suitable formula for entropy production in conventional operations that will model the entropy production in operations with thermal machines. The specific entropy produced per unit mass of the mixture is the path integral over the scalar product of the differential enthalpy–mass vector $(\mathrm{d}H, \mathrm{d}X)$ and the driving force vector $(1/T - I/T', \mu/T - \mu'/T')$. With the kinetics in the form of the functions describing rates and expressed in terms of the process intensities, the discussed integral has the form

$$S_\sigma = \int_{T^i}^{T^f} (1/T - 1/T')\mathrm{d}H - (\mu/T - \mu'/T')\,\mathrm{d}X$$
$$= \int_{t^i}^{t^f} \Big\{ (1/T - 1/T')\dot{H}(T, T', \mu, \mu') + (\mu'/T' - \mu/T)$$
$$\times \dot{X}(T, T', \mu, \mu') \Big\}\mathrm{d}t. \qquad (52)$$

In this form the entropy production equation can incorporate arbitrarily complex nonlinear relationships of thermodynamic and kinetic origin. By using Eq. (52) in work formula (51), changes of work potentials and finite-time exergies associated with minimum inevitable entropy production can be evaluated through optimization. Taking into account potential nature of first term in the two last lines of Eq. (51) we first integrate it to obtain the form

$$W = P/G$$
$$= -\int_{T^i}^{T^f} \Big\{ (1 - T_2/T')\,\mathrm{d}H + T_2(\mu'/T' - \mu_2/T_2)\,\mathrm{d}X \Big\}$$
$$= H^i - H^f - T_2(S^i - S^f) - \mu_2(X^i - X^f) - T_2$$
$$\times \int_{T^i}^{T^f} \Big\{ (1/T - 1/T')\dot{H} + (\mu'/T' - \mu/T)\dot{X} \Big\}\mathrm{d}t.$$
$$(53)$$

The result of integration is the first term of the second line that is path-independent term. This term represents a change of classical exergy whenever parameters of infinite thermal reservoir are equal to those in environment. The path dependence of work is caused by the second term of Eq. (53) containing the product of T_2 and entropy production per unit mass of inert. This proves that, for fixed end problem, the integral of entropy produced, singled out from the second line of Eq. (53), can constitute the optimization criterion alternative with respect to the work criterion. But this is just our Eq. (52). Its basic role is supported by the observation that control parameters appear only in the entropy produc-

tion integral. In fact, this integral is a curvilinear integral over the product of the differential state vector $(\mathrm{d}H, \mathrm{d}X)$ and vector of driving force $(1/T - 1/T', \mu/T - \mu'/T')$. After extremizing Eq. (53) with respect to controls T' and μ' optimal work functions R and V are found, which generalize solutions to Eq. (57) of Part I by inclusion of mass transfer.

However, our handling of kinetics is implicit up to this point. In fact, extremizing of work (or associated entropy production) must be carried out subject differential constraints describing overall kinetics of the process. These differential constraints link coordinates of controlled phase with those of controlling phase. The latter coordinates are, within the formalism accepted here, Carnot variables that are optimized. The simplest (linear) form of differential constraints satisfying Onsagerian symmetries and having incorporated Carnot controls is derived below. The closing aim of the procedure is to build these constraints in the entropy optimization criterion.

To formulate and handle kinetic constraints in an explicit way, we use the theorem of Part I [1] in its generalized form including mass transfer processes. It tells us that in the special case without any work production (i.e. at short-circuit point) expressions for the driving thermal parameters $(T', \mu', H', X',$ etc.) in terms of the state variables $(T, \mu, H, X,$ etc.) and their time derivatives $(\dot{T}, \dot{\mu}, \dot{H}, \dot{X},$ etc.) describe the environment (or reservoir) parameters. Thus by exploiting a given *classical* kinetics (the one which governs the process without work production) we determine intensive parameters of driving states. We thus obtain constraints that describe an overall classical kinetics under action of overall driving forces.

Here we apply the kinetic model of the coupled linear kinetics that satisfies Onsager's reciprocity relations. For the first fluid as controlled phase Eqs. (43) and (44) of previous section are valid

$$\frac{1}{T_1} - \frac{1}{T_1'} = r_1^{HH}\dot{H}_1 + r_1^{HN}\dot{X}_1, \tag{43}$$

$$\frac{\mu_{1'}}{T_1'} - \frac{\mu_1}{T_1} = r_1^{NH}\dot{H}_1 + r_1^{XX}\dot{X}_1. \tag{44}$$

Similarly, for the second fluid as phase 2 or thermal reservoir, Eqs. (45) and (46) hold

$$\frac{1}{T_2'} - \frac{1}{T_2} = r_2^{HH}\dot{H}_2 + r_2^{HX}\dot{X}_2, \tag{45}$$

$$\frac{\mu_2}{T_2} - \frac{\mu_{2'}}{T_2'} = r_2^{XH}\dot{H}_2 + r_2^{XX}\dot{X}_2. \tag{46}$$

In particular, these kinetic equations hold at the purely dissipative state (short circuit point) of the system where there is no work production $(T_1' = T_2'$ and $\mu_{1'} = \mu_{2'})$, the energy and mass fluxes are continuous through the interface (i.e. $\dot{H}_1 = \dot{H}_2 = \dot{H}$ and $\dot{X}_1 = \dot{X}_2 = \dot{X}$), and the iden-

tities $T_2 = T'$ and $\mu_2 = \mu'$ hold. Applying these identities in Eqs. (43)–(46) we find

$$\frac{1}{T_1'} = \frac{1}{T_1} - r_1^{HH}\dot{H}_1 - r_1^{HN}\dot{X}_1, \tag{54}$$

$$\frac{\mu_{1'}}{T_1'} = \frac{\mu_1}{T_1} + r_1^{NH}\dot{H}_1 + r_1^{XX}\dot{X}_1 \tag{55}$$

and

$$\frac{1}{T_2'} = \frac{1}{T'} + r_2^{HH}\dot{H}_2 + r_2^{HX}\dot{X}_2 \tag{56}$$

$$\frac{\mu_{2'}}{T_2'} = \frac{\mu'}{T'} - r_2^{XH}\dot{H}_2 - r_2^{XX}\dot{X}_2. \tag{57}$$

(As in Eqs. (52) and (53), subscript 1 of the resource fluid may be omitted.) After substituting $T_1' = T_2'$ and $\mu_{1'} = \mu_{2'}$ and taking respective differences of above equations we obtain the driving intensities T' and μ' in the form

$$\frac{1}{T'} = \frac{1}{T_1} - (r_1^{HH} + r_2^{HH})\dot{H}_1 - (r_1^{HX} + r_2^{HX})\dot{X}_1 \tag{58}$$

and

$$\frac{\mu'}{T'} = \frac{\mu_1}{T_1} + (r_1^{XH} + r_2^{XH})\dot{H}_1 + (r_1^{XX} + r_2^{XX})\dot{X}_1. \tag{59}$$

Consequently, the overall kinetics in terms of driving and controlled intensities, i.e. in the form that applies in Eqs. (52) and (53), is represented by the equations

$$\frac{1}{T_1} - \frac{1}{T'} = r^{HH}\dot{H}_1 + r^{HX}\dot{X}_1, \tag{60}$$

$$\frac{\mu'}{T'} - \frac{\mu_1}{T_1} = r^{XH}\dot{H}_1 + r^{XX}\dot{X}_1. \tag{61}$$

(See next section for equivalent equations in terms of conductances.) With these equations and Onsager's reciprocity relations, entropy production (52) assumes the classical form

$$S_\sigma = \int_{T^i}^{T^f} (1/T_1 - 1/T')\,\mathrm{d}H_1 + (\mu'/T' - \mu_1/T_1)\,\mathrm{d}X_1$$
$$= \int_{t^i}^{t^f} \{r^{HH}\dot{H}^2 + 2r^{HX}\dot{H}\dot{X} + r^{XX}\dot{X}^2\}\,\mathrm{d}t \tag{62}$$

or

$$S_\sigma = \int_{T^i}^{T^f} (1/T_1 - 1/T')\,\mathrm{d}H_1 + (\mu'/T' - \mu_1/T_1)\,\mathrm{d}X_1$$
$$= \int_{t^i}^{t^f} \{g^{HH}(1/T_1 - 1/T')^2 + 2g^{HX}(1/T_1 - 1/T')$$
$$\times (\mu'/T' - \mu_1/T_1) + g^{XX}(\mu'/T' - \mu_1/T_1)^2\}\,\mathrm{d}t. \tag{63}$$

The second integral contains kinetic constraints, Eqs. (43)–(46), built in the integral (52). The positiveness of conductance matrix **g** proves that the second law of thermodynamics is satisfied identically by model based on Onsager's theory.

For a related multistage process, i.e. the cascade in Fig. 2, the entropy production is

$$S_\sigma^N = \sum_1^N \left\{ g^{HH}(1/T_1^n - 1/T'^n)^2 + 2g^{HX}(1/T_1^n - 1/T'^n) \right.$$
$$\left. \times (\mu'^n/T'^n - \mu_1^n/T_1^n) + g^{XX}(\mu'^n/T'^n - \mu_1^n/T_1^n)^2 \right\} \theta^n. \tag{64}$$

For constant (state independent) resistances, the trajectory optimizing integral criteria (62) and (63) is characterized by the constancy of rate vector along the path. This is a generalization of a result that is well known for heat-mechanical processes without mass transfer [1,3]. (See also Refs. [53,54] and [56–58] in [1].)

In conclusion, in spite of work flux in the system, we have obtained functionals of entropy production that preserve formal structures the same as those in traditional processes (without work). Use of Carnot variables was crucial to achieve that formalism. Optimization of entropy production in typical processes under assumption of constancy of coefficients leads quite generally to constancy of the entropy production intensity along an optimal path. For quadratic entropy production, optimization of both functionals (those of work and those of entropy production, Eqs. (53) and (62)), imply constancy of driving forces along an optimal path. These properties are sometimes imbeded in the so-called principle of equipartition of the entropy production or principle of equipartition of thermodynamic forces [1,3]. However, the 'principle' is valid only when there is no constraints imposed on parameters of the controlling phase. In the case of operative constraints, the principle is violated. Postquadratic terms in the optimization criterion and nonlinearities in kinetic equations may also cause violation of the principle.

7. Unification of energy limits in operations with and without work

Let us now focus on limiting properties of the optimal models. Consider, for example, Eq. (53) in the optimal case. In terms of the Carnot temperatures and chemical potentials, T' and μ', the limiting minimum work in engine mode can be described by the optimal performance function

$$R(T^i, T^f, X^i, X^f, \tau^f - \tau^i)$$
$$\equiv \max(P/G_f) = -\int_{T^i}^{T^f} \{(1 - T_2/T')\,dH$$
$$+ T_2(\mu'/T' - \mu_2/T_2)\,dX\}$$
$$= H^i - H^f - T_2(S^i - S^f) - \mu_2(X^i - X^f) - T_2$$
$$\times \min \int_{t^i}^{t^f} \{g^{HH}(1/T_1 - 1/T')^2 + 2g^{HX}(1/T_1 - 1/T')$$
$$\times (\mu'/T' - \mu_1/T_1) + g^{XX}(\mu'/T' - \mu_1/T_1)^2\}\,dt. \tag{65}$$

Likewise, for heat-pump mode, where work is consumed

$$R(T^i, T^f, X^i, X^f, \tau^f - \tau^i)$$
$$\equiv \min(-P/G_f) = -\int_{T^i}^{T^f} \{(1 - T_2/T')\,dH$$
$$+ T_2(\mu'/T' - \mu_2/T_2)\,dX\}$$
$$= H^f - H^i - T_2(S^f - S^i) - \mu_2(X^f - X^i) + T_2$$
$$\times \min \int_{t^i}^{t^f} \{g^{HH}(1/T_1 - 1/T')^2 + 2g^{HX}(1/T_1 - 1/T')$$
$$\times (\mu'/T' - \mu_1/T_1) + g^{XX}(\mu'/T' - \mu_1/T_1)^2\}\,dt. \tag{66}$$

This equation generalizes exergy cost of production of a definite resource in finite time, Eq. (57) of Part I [1], to the case of operations with coupled heat and mass transfer. It also describes the "endoreversible" limit for minimum mechanical energy supplied to achieve a prescribed separation of the fluid mixture. These formulae may easily be generalized to processes with internal dissipation as we have shown in [1]. Note that in reversible case, the maximum work in the engine mode is described by the optimal function $V^{rev} = -R^{rev}$. Eq. (66) serves in the realm of thermal machines as a representation of their limiting work. The minimization in Eq. (66) automatically eliminates the controlling (primed) parameters from S_σ, thus generating the potential R_σ that depends only on the initial and final states and the process duration.

In both modes described by Eqs. (65) and (66) state and control variables are linked by overall differential constraints (60) and (61). These constraints can also be written in a more common form using overall conductances

$$\dot{H}_1 = g^{HH}\left(\frac{1}{T_1} - \frac{1}{T'}\right) + g^{HX}\left(\frac{\mu'}{T'} - \frac{\mu_1}{T_1}\right) \tag{67}$$

and

$$\dot{X}_1 = g^{XH}\left(\frac{1}{T_1} - \frac{1}{T'}\right) + g^{XX}\left(\frac{\mu'}{T'} - \frac{\mu_1}{T_1}\right). \tag{68}$$

In these equations $(g^{HX})^{-1} = (g_1^{HX})^{-1} + (g_2^{HX})^{-1}$ are overall conductances that constitute the symmetric matrix **g**.

For multistage processes with heat pumps or engines a fully analogous discrete picture exists with sums replacing integrals and differential ratios instead of derivatives. The discrete counterparts of optimal cost functions (65) and (66) are then associated with minimum of the entropy production (64). For example, in heat-pump mode the same entropy production appears in work expression for the limiting sequential operation

$$R^N(T^0, T^N, X^0, X^N, \tau^N - \tau^0)$$
$$\equiv \min(-P^N/G_f) = H^N - H^0 - T_2(S^N - S^0)$$
$$- \mu_2(X^N - X^0) + T_2 \min \sum_1^N \{g^{HH}(1/T_1^n - 1/T'^n)^2$$
$$+ 2g^{HX}(1/T_1^n - 1/T'^n)(\mu'^n/T'^n - \mu_1^n/T_1^n)$$
$$+ g^{XX}(\mu'^n/T'^n - \mu_1^n/T_1^n)^2\}\theta^n. \tag{69}$$

This is "exergy cost of production" of a definite resource in finite time and in sequential operation with finite number of stages, the physical energy limit as counterpart of cumulative exergy cost known in thermal engineering and ecology [2]. Optimization in this criterion is subject to the following difference constraints

$$\frac{H_1^n - H_1^{n-1}}{\theta^n} = g^{HH^n}\left(\frac{1}{T_1^n} - \frac{1}{T'^n}\right) + g^{HX^n}\left(\frac{\mu'^n}{T'^n} - \frac{\mu_1^n}{T_1^n}\right) \tag{70}$$

and

$$\frac{X_1^n - X_1^{n-1}}{\theta^n} = g^{XH^n}\left(\frac{1}{T_1^n} - \frac{1}{T'^n}\right) + g^{XX^n}\left(\frac{\mu'^n}{T'^n} - \frac{\mu_1^n}{T_1^n}\right). \tag{71}$$

$$\frac{t_1^n - t_1^{n-1}}{\theta^n} = 1. \tag{72}$$

The last constraint represents definition of the time interval, which is a measure of the stage size. Extra local constraints can be added to the set (72) including size limitations. For details of optimization procedure based on a discrete algorithm of Pontryagin's type the reader is referred to literature [3,4].

Eqs. (65), (66) and (69) describe endoreversible limits for mechanical energy consumption between two given states and for a given number of transfer units associated with finite holdup time. Even these limits are stronger than that those predicted by the classical exergy. What can be said about yet stronger limits which involve internal dissipation in the participating thermal machines? For limits of higher rank Eqs. (65), (66) and (69) are replaced by their generalizations including internal entropy generation within engines as additive components of the entropy generation, S_σ. Here we need to recall the hierarchy of limits and role of Gouy–Stodola law, stressed in Part I [1].

For a still stronger limit, other components of total entropy source are included at the expense of a more detailed input of information, but with the advantage that the limit is closer to reality. For a sufficiently high rank of the limit, it approaches the real work closely, but also the cost of the related information becomes very large. What is important then, is a proper compromise associated with the accepted limit of a finite rank.

8. Generalized exergies as measures of energy limits

However, up to now a precise set of conditions under which Eqs. (65), (66) and (69) could serve as a suffi-

ciently exact model for economics of work-assisted systems is unknown. While our models are sufficient to generate physical energy limits, modelling for the purpose of economics is an essentially different issue that requires complex network modelling and taking into account many technical aspects. For these different purposes, extended studies in finite-time thermodynamics of complex real engines and heat pumps with heat and mass transfer are also necessary [11]. In systems of this sort humid gases and hygroscopic solids are utilized by endoreversible heat pumps while exchanging mass and heat. Should economic optimization be the case, a thermal system could be optimized by the customary approach which would require: a detailed network modelling, inclusion of economic accounting, and occasional imbedding of the optimized system into a broader environment to include interacting chains. On the other hand, in the scheme of physical energy limits, described here, consideration of relation between irreversibility and costs is unnecessary [9].

Minimization of total work consumed over a finite duration leads to a finite-time exergies of gas and solid, A_g and A_S. Formulae for such exergies follow from optimal work expressions, Eqs. (65), (66) and (69), when the final states are identified with the states of equilibrium with the environment [11,12]. With the knowledge of classical exergy, A^{rev}, a numerical procedure can generate data for both A and $\min S_\sigma$. Enhanced bounds on work production and consumption are basic applications of finite-time exergies.

A finite-time exergy of humid gas, A, was defined [12] which contains the classical exergy of this gas [5,6] increased in the case of heat-pump mode by the product of the environment temperature T^e and the minimum entropy production, S_σ. For the engine mode, the classical exergy decreases by the product of the environment temperature T^e and the minimum of the entropy production. For continuous changes of the gas state $A = A^{rev} \pm T^e \min S_\sigma$. The plus sign refers to processes departing from the equilibrium and the minus sign to processes approaching the equilibrium. The reversible component in A agrees with a general formula for the classical thermal exergy of a non-reacting mixture [5]. For a multistage process, a discrete counterpart of A can be generated numerically; the computations should refer to a sufficiently large N in order to accurately approximate the continuous exergy. The function A contains the minimum entropy production $\min S_\sigma$ in terms of end thermodynamic states and nondimensional duration (the number of mass transfer units). This is a nonclassical term, vanishing for infinite durations. With the knowledge of the classical exergy, A^{rev}, the numerical procedure can generate data for both A and $\min S_\sigma$. In the notion of finite-time exergy enhanced bounds are incorporated on the work production and consumption. Yet, since effective analytical formulae for

finding finite-time potentials of humid gas and moist solid are unknown and difficulties of finding them persist, numerical methods are crucial. For example, by using a formula for the classical exergy of solid [5,6] and Eq. (53) we can numerically generate the finite-time work potential for the solid phase in the hygroscopic regime.

By exploiting heat and mass transfer analogies [11], we apply Eqs. (63) and (64) as proper formulas serving to evaluate minimum $S_\sigma = R_\sigma$, in operations with thermal machines. A related condition is that the non-dimensional time $\tau = g/G$ is based on the overall mass transfer conductance $g_g = k_g A$, whereas Carnot controls are suitable variables with respect to which the minimization of S_σ is made. That procedure suffices to model well enough specific entropy production in generalized thermal machines in which a fluid mixture or polymer solution interacts with the environment through generalized endoreversible engine or heat pump. Similar approach is used to model generalized thermal machines in which the moist solid interacts with the environment through an endoreversible engine or heat pump. In the case of solid approximation caused by this procedure can be rough if the model ignores phase changes and related entropy production, and, moreover, concepts of transfer coefficients and of related conductances are not as much correct as those for fluids.

9. Remark on peculiarities of solar-assisted operations

It is an optimization procedure that automatically eliminates the controlling (Carnot) parameters from S_σ thus leading finally to optimum work potential R, which depends only on the initial and final states and the process duration. In multistage processes the potential depends also on total number of stages. However, the main idea of the method using Carnot intensity variables as controls is based on the identity of *thermodynamic* equations describing the entropy production in processes with and without work in terms of the control variables T' and μ'. This is, in fact, caused by abstract nature of thermodynamic equations that are free from the time variable and materials characteristics. On the other hand, the complete identity of *kinetic* expressions, that describe the entropy production and fluxes in processes with and without work, holds only for linear kinetic models. In general nonlinear cases the identity is not satisfied; thus the use of the method based on the control variables T' and μ' requires a modification. This is briefly described in [9] for solar assisted operations that involve nonlinear models due to the radiative energy transfer. In nonlinear cases, equations that describe overall kinetics are different in processes with and without work, even if they both are expressed in terms of Carnot controls T' and μ'. While the full coincidence is still attained at the "short circuit point" of the system, beyond that point coefficients of overall kinetics become dependent on controls (T' and μ') and form divergence is observed between structures of both equations. Our process description must take this divergence into account. For details, see [9,13].

10. Energy limits in living systems

Considerations and analyses on energy limits can be extended to optimization in systems with living organisms. In this work we only briefly focus on energy limits associated with the idea of the extremum development governed by the entropy-related criteria of evolution, e.g. the so-called complexity [14]; this is where the thermodynamic method developed here should find a natural use. The idea of extremum development refers to some recent information-theoretic models of multistage living systems that are characterized by sequentially evolving states [15]. The information concept is not only appropriate to complex systems but is also well-quantitatively defined [16]. Diverse models can serve to evaluate energy limits quantitatively, for this issue the reader is referred to literature [17]. In this section we consider only some basic, qualitative issues.

In living systems a nonequilibrium entropy has to be applied, as, in any sufficiently general description of a complex living system, we deal with an inherently nonequilibrium system. Sometimes, for special paths, they can achieve the equilibrium and derive equilibrium conditions, but it is generally transition between two nonequilibrium states that is of interest. This state of affair implies an analogy with nonequilibrium statistical physics. There, even if the process terminates at isoenergetic equilibrium, the equilibrium conditions along with Boltzmann distribution are derived from the entropy maximum condition in a closed system, and extremizing method uses entropy in an arbitrary macroscopic state, not in the equilibrium state; see, e.g. [18]. Generally, however, the idea of maximum of a potential function, which may even be more general than complexity or nonequilibrium entropy, subject to given side conditions or constraints is used [15].

Complex living systems have developed various strategies to manipulate their self-organization in order to satisfy the principle of minimum complexity increase. Ultimately, however, the physical laws set limits to their size, functioning and rate of development. For example, the physical law of thermal conduction sets the size of warmblooded aquatic animals which require a minimum diameter (of ca. 15 cm) in order to survive in cold oceans [19]. Species that survive in ecosystems are those that funnel energy into their own production and reproduction and contribute to autocatalytic processes in the ecosystem. Also, there are data that show that poorly

developed ecosystems degrade the incoming solar energy less effectively than more mature ecosystems [20]. The cornerstone there is to view living systems as stable structures increasing the degradation of the incoming solar energy, while surviving in a changing and sometimes impredictable environment. All these structures have one feature in common: they increase the systems ability to dissipate the applied gradient in accordance with the so-reformulated second law of thermodynamics [20]. In all these situations the second law imposes constraints that are necessary but not sufficient cause for life itself. In fact, reexamination of thermodynamics proves that the second law underlines and determines the direction of many processes observed in the development of living systems. As an ecosystem develops, it becomes more effective in removing the exergy part in the energy it captures, and this exergy is utilized to build and support organization and structure. Time and its derivative cycling play a key role in evolution of these complex systems. Evolution itself is a time dependent process and the understanding of cycling is of great methodological and cognitive importance [20].

In particular, optimization theory of pulsating physiological processes can shed some light on the basic understanding of development and evolution [21]. Optimal strategies of streets tree networks and urban growth can mimic development of living systems [22]. A related paper displays thermodynamic behavior of living systems during their development and evolution [23]. Living organisms are treated therein as multistage systems by a complexity criterion based on information-theoretic entropy. Classical thermodynamic quantities do not appear in these approaches, yet the statistical model is governed by an extremum principle, which, as in thermodynamics, implies extremal properties for a potential. Discrete and nonlinear models describe dynamics in metric spaces that may be curvilinear. Some features of living organisms can be predicted when describing their complex evolution in terms of variational principles for shortest paths along with suitable transversality conditions. In the related models quantities similar to entropy production are extremized, and Onsager-like symmetries are discovered in the discrete models of development [15].

11. Final considerations

First of all we stress the observation that even the nonNewtonian nature of heat and/or mass transfer (when described in terms of Carnot intensities or primed quantities) does not change the general thermodynamic formalism. On the other hand, the nonNewtonian nature influences the formal structure of the heat and mass exchange kinetics only beyond their linear approximation. Since various industrial bodies may exhibit com-

plex nonNewtonian properties, the method is capable of evaluating energy limits in arbitrarily complex mass transfer and heating systems (with, e.g., drying bodies, radiation fluids, polymers, etc.). This is a fundamental point, which is also the feature that makes our results essential. In fact, it is just complexity of rheological properties of substances used in industry and practical devices which makes our general results valuable in practice.

Sometimes a scepticism is expressed whether the principles based on finite-time thermodynamics can be useful to optimize thermal systems with nonequilibrium processes, especially systems of complex topology such as thermal networks [24,25]. While a large portion of these objections can be overcome [26], we shall not enter here into this debate, as it is enough to recall the assertion made in the introduction of Part I of this paper [1]. This assertion states that an economic problem of the system optimization and the physical problem of work limits for a resource (considered here) are two different problems. The real work supplied to a compressor at economically optimal conditions may sometimes be dozen times larger than the mechanical energy (exergy) limit associated with the production of a key substance; this is a well-known fact from the theory of Linde operation, for example [8,27]. In the realm of energy limits, the trade-off between the exploitation and investment costs and the problem of investment reduction by admission of exergy losses are most often irrelevant issues. Yet, at the interface of thermodynamics with economics all issues related to the trade-off are essential [28,29]. Moreover, the entropy source minimization, restricted to interior of the physical system considered, may have no relevance to an economic optimum of a product yield, where some cumulative generation criteria may be attributed to a valuable final product [2]. On the other hand, these cumulative criteria have little in common with physical limits on energy consumption.

Our method does yield endoreversible and higher-order generalizations of standard exergy. At the limits of zeroth rank all processes are reversible, and only then the method yields the standard exergy function. In general, the method serves to evaluate enhanced energy limits in highly nonequilibrium, kinetically driven processes of mass and energy transfer. We stress hierarchical nature of the finite-time thermodynamic limits (FTT limits), where endoreversible limits are one step better than those derived from the classical exergy.

Of the two basic fields compared, exergy analysis [2,5] and FTT [3], only the latter can systematically include various concepts of contemporary irreversible thermodynamics. (This inclusion is also possible in Bejan's method of entropy generation minimization [33], but it is not in the second law analyses). To evaluate energy limits of the first rank, FTT acts in a seemingly oversimplified manner: it cuts hierarhy of the limits at

the level of endoreversibility (endoreversible exergies), and often works with kinetic models based on ordinary differential equations. The simplicity of these models and an aggregated information on which FTT rests are frequently the source of misunderstanding. Adversaries of FTT commonly ignore the fact that the highly useful notion of the classical exergy is associated with even simpler models than endoreversible: the reversible ones. In fact, however, limits of higher ranks correspond with quite realistic models, and the potential of FTT for incorporating results from dissipative fluid mechanics or nonequilibrium field thermodynamics has been shown [30]. The role of FTT should become more pronounced in the future because of its flexibility in generating irreversible limits of any order through the use of information contained in the entropy generation. Its potential is enhanced by the explicit use of the concept of the process state and state control in the generalized sense of process dynamics.

Actually most approaches based on second law analyses are global; they frequently rely on the input and output streams of a definite system. By elementary examples and calculations David [31] has shown that the globality is a dangerous feature, which may lead to basic errors in design. The positiveness of the global entropy produced, σV, (corresponding to given inputs and outputs) does not prove that the process is physically possible. For example, for some global values of σV the temperature profiles in a countercurrent condenser may show a temperature cross and the required heat transfer will actually not occur [31]. Similar effects are also known for highly nonisothermal sorption, drying processes and for chemical reactors [8]. Therefore, only local approaches that link the differential balances with kinetics are fully reliable. But such approaches are rare in most second law analyses; consider [2,5,24]. Because of this limitation such global analyses are more useful for identifying improper processes than for proving that an actual design will work. Yet second law analyses have proven their usefulness by discovering inefficiencies in existing large plants composed of simple subsystems (objects) and in these subsystems themselves. Along with FTT, Bejan's method of the entropy generation minimization (EGM) [32,33] has contributed significantly to the development of analyses including the simultaneous (local) treatment of balance and kinetics.

It is FTT that has introduced a well-defined concept of state into the thermodynamic modelling of processes. Moreover, this field introduced the rate penalty concept and uses it in a systematic way for arbitrary processes, not only for electrochemical cells, where it has been known for a long time. Of the few novel theoretical concepts of FTT, such as finite-time exergies and extended potentials [3,4], the former is now being exploited to stress its value. The latter have actually been used earlier in a number of engineering applications of exergy

to the optimization of thermal and separation processes [3,8]. These approaches have produced some results that help avoid basic errors in design; they show e.g. the requirement of concentration of the transfer area into regions of high process intensity [3].

It is FTT that contributed to the development of new processes and/or operations [3]. In the case of simple kinetics or when equilibrium stage concepts can be applied, second law analyses are capable of providing several valuable results for new operations [27,34]. However, in spite of a very large number of works and a few spectacular applications, little theoretical progress has been achieved to date in classical second law analyses [2,5]. Design based on classical exergy analyses is mainly justified when properties of equipment and systems configurations do not vary significantly. The globality property of classical exergy analyses forces them to use models that are not far from black box models. For example, the vast area of heat pumps frequently uses these analyses based on assumed rough values for the performance coefficients of the various component objects and carries information that is basically restricted to a variety of pictorial schemes [35]. The treatment of storage units and energy avoidance systems involving classical second law analyses are too often out of date, and none of them has even approached the rigour of the exact analysis of such systems which extends the classical mathematical theory of regenerators originated by Hausen [36]. While sufficient in thermal engine theory, the use of constant, diagonal resistances (linear theory without couplings) is insufficient for complex energy converters in which strong nonlinearities and/or coupling effects are essential. The lost work is decreased in a natural way in systems with coupling; the magnitude of the effect depends on the relative magnitude of the kinetic cross coefficients (as compared to diagonal ones). Sometimes the effect can be negligible, as is the case for, e.g., Soret mass transfer. However, it becomes substantial for transport problems with phase transitions, e.g. frost heave [37], and for many processes of electrochemical and biochemical energy conversion [38]. The maximum efficiency depends then on the degree of coupling; only "completely coupled" systems can approach the second law efficiency of unity as a limit. Coupling can sometimes be enhanced by an optimization, change in the type of contacting, etc. Until now these problems have only rarely been approached using second law analyses [5,24]. Incorporating nonlinear kinetics may also improve frequent quantitative flaws of these analyses and make the efficiencies computed more reliable. All this discussion proves that the systematic use of kinetic information, required in EGM and FTT methods, [33,3] will play an essential role in any future progress.

In order to utilize in full the power of thermodynamic analyses in engineering, one must often go beyond

conventional second law analyses [31,39]. In chemical process design the real limits on the reactor yield derive from sources other and more restrictive than the second law. Often they appear as constraints and inefficiencies of available technology; these, however, may have consequences that can be treated by thermodynamic analyses. For example, low overall thermal efficiencies can be a thermodynamic consequence of the lack of a suitable catalyst. The limits related to usual catalysts can, however, be overcome by the use of highly selective catalysts (e.g. shape selective zeolite catalysts). They integrate selective transport with catalysis in a way that is not only energy efficient but also cheap [39]. Second law analyses placed in the context of such problems can play both a more subtle and a more useful role in chemical engineering than they do now.

As approaches to complex system design based on second law analyses have been developed the emphasis has changed from exergy (energy) minimal to cost optimal units and networks [40]. While this reorientation does not constitute a real problem in FTT, second law analyses (restricted to the availability and exergy criteria) have a limited chance of proving their real usefulness in such extended schemes. For example, contemporary design of heat exchanger networks involves real-life objectives that contain both a quantitative part (cost of equipment, energy and resources) and a qualitative part (safety, operability, controllability, flexibility, etc.). The industrial problem is very complex and involves a combinatorial approach to the match between hot and cold streams, flow configuration choice, equality and inequality constraints on the temperature dependent properties, materials, pressure drop limitations, etc. All this leads to the trend towards complex thermoeconomies and requires abandonment of purely thermodynamic concepts.

The mission and essence of chemical engineering is "to come up with processes to make materials wanted by man—new or improved processes to replace older less efficient ones, and processes to make completely new materials" [41]. This is now being accomplished by innovations in new catalysts, new reaction pathways or new contacting patterns. In a hydrogenation example [41] the packed bed with the so-called supported liquid catalyst replaces more conventional units (bubble columns, spray columns, tubular reactors, etc.). The packed bed contains ingeniously prepared porous catalyst pellets with an extremely large internal surface. This idea allows one to replace the tons of hot, expensive liquid catalyst in the conventional units (which would cost millions of dollars) with just a few grams of catalytic liquid for the whole operation. This is just one of many examples that illustrate the role of surfaces and thin layers in contemporary chemical engineering. However, the applications of second law analyses to such processes are still in an embryonic state. In general, the irreversible

thermodynamics of surfaces and phase changes have little been used within second law analyses. Their realm is now limited to processes where the role of surface effects is negligible or where these effects are purely reversible. Surface dissipation is, however, substantial in many catalytic systems, surfactant layers and electrochemical systems. This situation must change if second law thermodynamics is to play a significant role in contemporary engineering and technology.

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