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Complex chemical systems with power production driven by heat and mass transfer

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ABSTRACT

In this paper, we investigate power production in complex multireaction systems propelled by either uncoupled or coupled multicomponent mass transfer. The considered system contains two mass reservoirs, one supplying and one taking out the species, and a power-producing reactor undergoing the chemical transformations characterized by multiple (vector) efficiencies. To establish a suitable basis for these efficiencies, an approach is applied that implements balances of molar flows and reaction invariants to complex chemical systems with power production. Reaction invariants, i.e., quantities that take the same values during a reaction, follow by linear transformations of molar flows of the species. Flux balances for the reacting mixture may be written down by equating these reaction invariants before and after the reactor. Obtained efficiency formulas are applied for steady-state chemical machines working at the maximum production of power. Total output of produced power is maximized at constraints which take into account the (coupled or uncoupled) mass transport and efficiency of power generation. Special attention is given to non-isothermal power systems, stoichiometric mixtures and internal dissipation within the chemical reactor. Optimization models lead to optimal functions that describe thermokinetic limits on power production or consumption and extend reversible chemical work W_{rev} to situations in which reduction of chemical efficiencies, caused by finite rates, is essential. The classical thermostatic theory of reversible work is recovered from the present thermokinetic theory in the case of quasistatic rates and vanishing dissipation.

1. Introduction

Modeling of chemical and electrochemical power generation systems by applying thermodynamics of finite rates is a relatively unknown area. Since, by nature, these systems are strongly nonlinear, some previous work dealing with nonlinear thermal machines is helpful in defining a suitable methodology [1]. However, chemical models developed to date are only capable of treating systems of quite simple stoichiometry [2–4]. While by the introduction of internal irreversibilities these works constitute some progress in comparison with their older relatives [24,27], their limitation to the single reaction with a simple stoichiometry still remains a serious flaw. Real chemical systems contain many species participating in many reactions, and their stoichiometry is usually complex, so that the setting of consistent mole balances and recognition of system properties requires advanced mathematical methods. These methods are applied in various contexts: independence of reactions [5], reaction invariants [6–10], reference components [11], reaction control [12–14], stability analysis [15], flow invariants [16,17], and many others. Investigation of dynamical power systems requires inclusion into considerations: theory of classical exergy [18], generalized (rate containing) exergies [19,20], aspects of nonlinear kinetics [4,21–23], and, of course, knowledge of basic results obtained for heat machines producing or consuming power [25–29]. For an efficient development of the theory of thermodynamic limits, knowledge of methods of static and dynamic optimization is also of importance (e.g., [30–32], and others).

In this paper, we address basic aspects of power production in multi-component and multireaction systems propelled by fluxes of transferred reagents. Its analysis of internal imperfections is based on a new methodology in which chemical loss factors Ψ are derived from molar flow balances and associated thermodynamics rather than from purely formal settings of the earlier works [2–4]. We also identify some reaction invariants as linear transformations of the species molar fluxes as suitable bases for chemical efficiencies. The material balances for chemically reacting mixtures require to equating these reaction invariants before and after the reaction. Hence, the next new result of the present paper follows in the form of the claim that the invariants provide the suitable basis to define both partial and overall efficiencies of power production. We derive general power formulas valid for both isothermal and non-isothermal systems and, in particular, prove their applications to stoichiometric mixtures reacting with a complete conversion. Corresponding expressions for the entropy production substantiate reduction of thermal efficiencies caused by increasing

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Nomenclature

$\boldsymbol{A}$	atomic matrix
A, A^{class}	molar generalized and classical exergy ($\mathrm{J\,mol^{-1}}$)
A_j	classical affinity of reaction ($\mathrm{J\,mol^{-1}}$)
A	extended affinity of reaction ($\mathrm{J\,mol^{-1}}$)
$A_C = -\Delta G$	chemical affinity at Carnot point ($\mathrm{J\,mol^{-1}}$)
A^k	total exchange area at stage k ($\mathrm{m^2}$)
a_{v}	specific area per unit volume ($\mathrm{m^{-1}}$)
$\boldsymbol{B}$	non-square matrix of dimension (R,c)
c_{p}	molar heat capacity at the constant pressure ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
c_{m}	mass capacity of the active component of fuel ($\mathrm{mol^2\,J^{-1}}$)
e	number of elements in the reaction species
$\boldsymbol{F}^0$	column vector of inlet molar flow rates of components
F_i^0	inlet molar flow rate of component i
F_0^{lr}	inlet molar flow rate of the limiting reactant
$F_{\mathrm{T}}^{\mathrm{lr}}$	total molar flow rate of limiting reactant at the reactor inlet
$\boldsymbol{F}^{\mathrm{T}}$	column vector of total molar flow rates at the reactor inlet
$\boldsymbol{F}^0\mathrm{Ref}$	column vector of the R reference inlet molar flow rates
F	area of surface perpendicular in the flux direction ($\mathrm{m^2}$)
f_0,f_{i}	process rates (dimensionless)
g_1,g	total and overall conductance ($\mathrm{mol\,s^{-1}}$)
G	molar flow rate of a selected stream
G	Gibbs energy flux driving chemical engine ($\mathrm{J\,s^{-1}}$)
H	Hamiltonian (dimensionless)
h_σ	Hamiltonian density in entropy units ($\mathrm{J\,m^{-3}\,K^{-1}}$)
H_{TU}	height of mass transfer unit (m)
I	molar flux of inert component ($\mathrm{mol\,s^{-1}}$)
$\boldsymbol{I}$	identity matrix of dimension (R,R)
k	stage number
L	molar flow rate of the liquid purge stream
l	total number of components in the liquid purge
l	transfer area coordinate, variable of spatial extent of the system (m)
M_i	molar ratio of component i with respect to the limiting reactant
$\boldsymbol{M}$	column vector of the molar feed ratios
m	total number of reacting and inert components
N^k	cumulative flux of mole number for stages $1,2,\ldots,k$ ($\mathrm{mol\,s^{-1}}$)
$\boldsymbol{n}$	column vector of m molar flows
n	molar flux vector of chemical rates ($\mathrm{mol\,s^{-1}}$)
$\mathbf{n}_{1'}$	column vector of the m inlet molar fluxes
$\boldsymbol{n}_{\mathrm{Ref}}$	column vector of the molar fluxes for the R reference components
$\mathbf{n}_{1'\mathrm{Ref}}$	column vector of the inlet molar fluxes for R reference components
$n_{i2'}$	molar flux of component i at the outlet
$n_{i1'}$	molar flux of component i at the inlet
$N_{i2'}$	transformed outlet flux of component i
$N_{i1'}$	transform inlet flux of component i
n_j	molar flux of jth reaction equal to the product of reaction rate and volume
$\boldsymbol{O}$	zero matrix
P,p	cumulative power output and power output ($\mathrm{J\,s^{-1}}$)
Q	heat flux including effect of mass transfer ($\mathrm{J\,s^{-1}}$)
q	sensible heat flux ($\mathrm{J\,s^{-1}}$)
R	gas constant ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
$R(X,t)$	optimal work function of cost type in terms of state and time ($\mathrm{J\,mol^{-1}}$)
R	number of independent reactions
$\mathtt{R}$	rank of the atomic matrix
$R_{\max}$	largest number of independent reactions

r	chemical reaction rate ($\mathrm{mol\,m^{-3}\,s^{-1}}$)
S	entropy ($\mathrm{J\,K^{-1}}$)
S_σ	molar entropy production ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
T	temperature of controlled phase (K)
T_1,T_2	bulk temperatures of reservoirs 1 and 2 (K)
$T_{1'}T_{2'}$	temperatures of fluid circulating in thermal engine (K)
T^{e}	constant equilibrium temperature of environment (K)
T'	Carnot temperature (K)
$\dot{T} = u$	rate of temperature change in non-dimensional time (K)
t	physical time, contact time (s)
$\mathbf{u}$	control vector
u	variable controlling the fuel consumption
$V = \max(W)$	optimal work function of profit type ($\mathrm{J\,mol^{-1}}$)
V	non-square matrix of dimension (m,R) of stoichiometric coefficients for the m components in the R reactions
$\mathsf{V}_{\mathrm{Ref}}$	square matrix of dimension (R,R) of the stoichiometric coefficients for the m components in the R reactions
v	velocity ($\mathrm{m\,s^{-1}}$)
$W = P/G$	total specific work or total power per unit molar flux
W	molar work at flow, total power per unit mass flux of inert ($\mathrm{J\,mol^{-1}}$)
X	concentration of active component in fuel, moles per mole of inert ($\mathrm{mol\,mol^{-1}}$)
$\dot{X} = dX/d\tau_1$	rate change of fuel concentration in time τ_1
x	molar fraction of active component in the fuel ($\mathrm{mol\,mol^{-1}}$)
$x_{1'}$	molar fraction of reactant in chemically active part of the system ($\mathrm{mol\,mol^{-1}}$)
$x_{2'}$	molar fraction of product in chemically active part of the system ($\mathrm{mol\,mol^{-1}}$)
$\boldsymbol{x}$	column vector of m mole fractions
x_i	mole fraction of component i
$\boldsymbol{y}$	column vector of m mole fractions
y_i	mole fraction of component i
z	adjoint (Pontryagin's) variable
$\mathbf{0}$	column vector of zeros

Greeks

α_{r}	constant for linear combinations
α'	overall heat transfer coefficient ($\mathrm{J\,m^{-2}\,s^{-1}\,K^{-1}}$)
β'	overall mass transfer coefficient ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
$\boldsymbol{\varepsilon}$	column vector of the R molar extents of reaction
ε_j	molar extent of reaction j
ε	pseudoenergy as the Legendre transform of a Lagrangian
γ	cumulative conductance ($\mathrm{J\,s^{-1}\,K^{-1}}$)
$\zeta = \mu'_1 - \mu'_2$	efficiency of isomerization as a part of chemical affinity ($\mathrm{J\,mol^{-1}}$)
ζ_{mp}	efficiency of chemical engine at maximum power point ($\mathrm{J\,mol^{-1}}$)
$\eta = p/q_1$	first-law thermal efficiency (dimensionless)
θ	time interval referred to non-dimensional time τ_1 and conductance g_1 (s, dimensionless)
λ	Lagrange multiplier ($\mathrm{J\,mol^{-1}}$)
μ	chemical potential ($\mathrm{J\,mol^{-1}}$)
μ'	Carnot chemical potential for active component of fuel ($\mathrm{J\,mol^{-1}}$)
μ_1	chemical potential of active component of fuel ($\mathrm{J\,mol^{-1}}$)
$\boldsymbol{v}_i^{\mathrm{T}}$	row vector of stoichiometric coefficients for component i in each reaction
ξ	process intensity factor (dimensionless)
Π_j	one-directional part of chemical affinity for jth reaction ($\mathrm{J\,mol^{-1}}$)

σ_s	intensity of entropy production (J K^{-1} m^{-3} s^{-1})
τ	non-dimensional time, number of transfer units (x/H_{TU}) (dimensionless)
Φ	factor of internal irreversibility (dimensionless)
χ	state vector
Subscripts	
C	Carnot state (open circuit)
i	state variable (component)
j	reaction number
Ref	reference components
T	total
v	per unit volume
1,2	components 1 and 2
Superscripts	
e	environment
i	initial state
f	final state
0	inlet
$'$	Carnot quantity
-1	inverse of matrix
T	transpose matrix

rates of chemical reactions and mass transports. Our results show that the classical, reversible theory of power yield is limited to a close vicinity of the Carnot point; far from this point dissipative effects prevail and the reversible efficiencies cease to be valid. The most original features obtained here are: formulas for non-stoichiometric reactions, solutions for power yield driven by coupled heat and mass transfer and analytic extension to systems with internal dissipation. As a result, we achieve an extension of the previous results to multireaction systems with arbitrary stoichiometries which admits both external and internal losses (occurring off and within the reaction chamber). This extension shows that the efficiency of power yield in chemical flow engines is governed by an extended, space-distributed affinity which constitutes the chemical driving force for the flow engines and replaces the well-known classical affinity of lumped chemical systems [33]. The simplest space-distributed affinity manifests itself in systems with phase changes, e.g., in drying systems, where this affinity is identical with the difference of chemical potentials of moisture in solid and gas phases [34]. The reference [34] also explains how an active part of the drying-related affinity may be the source of the mechanical power.

A novel, significant contribution of the present paper consists also in the quantitative evaluation of enhanced power limits in chemical systems and in the setting of a generalized thermokinetic theory of chemical power generation, from which the classical thermodynamic theory of chemical work is recovered in the case of vanishing rates and negligible entropy production.

To establish suitable basis for chemical analyses, we consider a multireaction system consisting of m components undergoing R independent chemical reactions (Fig. 1). Synthetically, this scheme can refer to many complex combination of unit operations; in our case, it refers to the chemical subsystem constituting a part of a larger system depicted in Fig. 2. The inlet state to the chemical subsystem is m-dimensional column vector of inlet molar flow rate of species, $\mathbf{n}_{1'}$; the outlet state of the subsystem is represented by a vector of outlet flow rates of species, $\mathbf{n}_{2'}$.

The reaction set can be written in the form

$$\nu_{1j}B_1 + \nu_{2j}B_2 + \nu_{3j}B_3 + \cdots + \nu_{mj}B_m = 0, \quad j = 1, 2, \ldots, R, \tag{1}$$

where B_i are the reacting species and $\nu_{i,r}$ is the stoichiometric coefficient of component i in reaction j. The convention used is $\nu_{i,j} > 0$ if component i is a product, $\nu_{i,j} < 0$ if it is a reactant and $\nu_{i,j} = 0$ if component i is an inert. Aris and Mah's [5] and Gadewar et al. [9] have shown that the number of mole balances for R independent reactions is $m - R$.

Apparently, one might expect that m molar balances can be written for a reaction system with m components. Yet, this is not so, because we should take into consideration the constraints imposed by R independent reactions. These constraints can be treated by using 'chemical fluxes' in relating the molar quantities of components. As we treat flow systems, we introduce into considerations, chemical flux as the product of the reaction rate and the volume. For the reaction j its chemical flux can be defined as

$$n_j = \frac{(n_{i2'} - n_{i1'})_j}{\nu_{i,j}}, \tag{2}$$

where n_j is the product of reaction j and the reaction volume, $(n_{i2'} - n_{i1'})_j$ is the molar flux of component i reacting in reaction j and $\nu_{i,j}$ is the stoichiometric coefficient of component i in reaction j.

Since a component can participate in more than one reaction, we express the overall consumption (production) of reactants (products) in terms of the 'chemical fluxes' as

$$n_{i2'} = n_{i1'} + \boldsymbol{\nu}_i^{\mathrm{T}}\mathbf{n}, \quad i = 1, \ldots, m, \tag{3}$$

where n_{i1} is the initial number of moles of component i at the cross-section $1'$, $n_{i2'}$ is the outlet number of moles of component i at the cross-section $2'$, $\boldsymbol{\nu}_i^{\mathrm{T}}$ is the row vector of dimension R of the stoichiometric coefficients of component i in each of the R reactions:

$$\boldsymbol{\nu}_i^{\mathrm{T}} = (\nu_{i,1}, \ldots, \nu_{i,R}) \tag{4}$$

and $\mathbf{n}$ is the column vector of the R chemical fluxes for each of the R reactions:

$$\mathbf{n} = (n_1, \ldots, n_R). \tag{5}$$

Eq. (3) can be written as

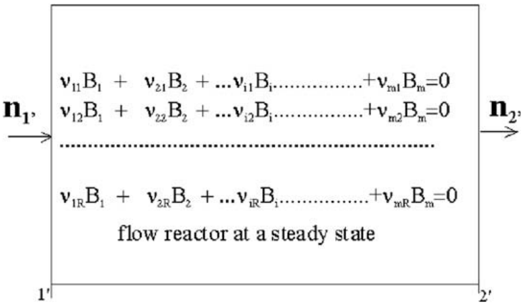

Fig. 1. A scheme of steady, multireaction system.

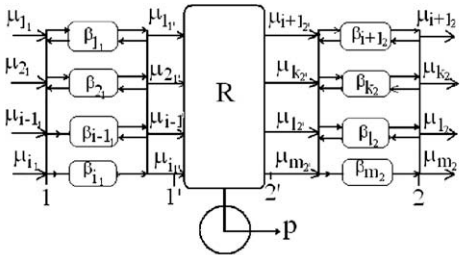

Fig. 2. A scheme of chemical power yield.

$$\mathbf{n}_{2'} = \mathbf{n}_{1'} + \mathbf{V}_{\mathbf{n}}, \tag{6}$$

where

$$\mathbf{V} = \begin{bmatrix} v_{1,1} & \dots & v_{1,R} \\ & v_{i,j} & \cdot \\ v_{m,1} & \dots & v_{m,R} \end{bmatrix} \tag{7}$$

is a non-square matrix of dimension (m,R) of the stoichiometric coefficients for the m components in the R reactions, and $\mathbf{n}_{2'} = (n_1,\dots,n_m)_{2'}^{\mathrm{T}}$ is the column vector of dimension m of outlet molar fluxes of the species and $\mathbf{n}_{1'} = (n_1,\dots,n_m)_{1'}^{\mathrm{T}}$ is the column vector of dimension m of the initial molar fluxes.

In steady-state flow systems we can eliminate the R chemical fluxes from the m equations describing the balances of molar flows, Eq. (6). This may be accomplished by choosing a subsystem of R equations from among the m Eq. (6). These are the reference components [11]. The reference equations are given as

$$\mathbf{n}_{2'\mathrm{Ref}} = \mathbf{n}_{1'\mathrm{Ref}} + \mathbf{V}_{\mathrm{Ref}}\mathbf{n} \tag{8}$$

and the reference stoichiometry matrix is

$$\mathbf{V}_{\mathrm{Ref}} = \begin{bmatrix} v_{(m-R+1),i} & \dots & v_{(m-R+1),R} \\ & v_{i,j} & \cdot \\ v_{m,1} & \dots & v_{m,R} \end{bmatrix} \tag{9}$$

and $\boldsymbol{n}_{\mathrm{Ref}} = (n_{(m-R+1)},\dots,n_m)^{\mathrm{T}}$ is the R-dimensional column vector of molar fluxes for reference components, $\boldsymbol{n}_{1'\mathrm{Ref}} = (n_{1'(m-R+1)},\dots,n_{1'm})^{\mathrm{T}}$ is the column vector of dimension R of the initial molar fluxes for the reference components. The species may be numbered such that the reference components are at the end of the column vector of molar fluxes of species. The reference components should be chosen such that the square matrix $\boldsymbol{V}_{\mathrm{Ref}}$ is invertible [11].

Applying the mole balances, Eqs. (8) and (9), the chemical fluxes can be expressed as

$$\mathbf{n} = (\mathbf{V}_{\mathrm{Ref}})^{-1}(\mathbf{n}_{2'\mathrm{Ref}} - \mathbf{n}_{1'\mathrm{Ref}}). \tag{10}$$

Substituting this expression into Eq. (3) yields

$$N_{k2'} = n_{k1'} + \mathbf{v}_k^{\mathrm{T}}(\mathbf{V}_{\mathrm{Ref}})^{-1}(\boldsymbol{n}_{2'\mathrm{Ref}} - \boldsymbol{n}_{1'\mathrm{Ref}}), \quad k = 1,\dots,m-R. \tag{11}$$

Following Gadewar et al. [9] one may now define 'transformed molar fluxes' as:

$$N_{k1'} = n_{k1'} - \mathbf{v}_k^{\mathbf{T}}(\mathbf{V}_{\mathrm{Ref}})^{-1}\mathbf{n}_{1'\mathrm{Ref}}, \quad \underline{k} = 1,\dots,m-R, \tag{12}$$

$$N_{k2'} = n_{k2'} - \mathbf{v}_k^{\mathbf{T}}(\mathbf{V}_{\mathrm{Ref}})^{-1}\mathbf{n}_{2'Ref}, \quad \underline{k} = 1,\dots,m-R, \tag{13}$$

where $n_{k1'}$ is the molar flux of component k at the inlet to the reaction chamber, $n_{k2'}$ is the molar flux of component k at the outlet, $v_k^{\mathbf{T}}$ is the row vector (of dimension m) of the stoichiometric coefficients of component i in all of the R reactions. Here $N_{k1'}$ are the reaction invariants based on the inlet molar fluxes and $N_{k2'}$ are the reaction invariants based on the outlet molar fluxes of the species. These new fluxes allow one to write the molar flow balances in Eq. (11) in the elegant, invariant form

$$N_{k2'} = N_{k1'}, \quad k = 1,\dots,m-R. \tag{14}$$

For a steady flow system with R independent reactions Eq. (14) states that "transformed molar fluxes in" = "transformed molar fluxes out", similarly to molar fluxes in non-reactive mixtures. For corresponding considerations in the context of non-flow processes that use the notions of reaction extents and may be more suitable to unsteady (e.g., batch) reactors see Gadewar [8] and Gadewar et al. [9–11]. The transformed molar fluxes numbers also constitute a basis for the suitable definitions of chemical efficiencies in complex, multireaction systems (Section 5).

2. Power yield from a general set of chemical reactions

Assume now that the reaction section shown in Fig. 1 is a part of a more complex system in which moles of reactants are transferred through various conductances β_k as illustrated in Fig. 2. The transfer mechanisms may generally be quite diverse, as discussed in Section 6. By admitting the system of such a topology we actually consider a chemical engine driven by flowing reagents for the purpose of power production. In chemical engines irreversible mass transports participate in transformations of chemical driving forces into mechanical power.

In the kinetic regime the thermodynamic driving force for reaction j is given by its standard affinity [33]

$$\begin{aligned} \mathrm{A}_j &= \Pi_j^f - \Pi_j^b = -\sum_{i=1}^m (v_{ij}\mu_i) = -\mathbf{v}^{\mathbf{T}}\boldsymbol{\mu} = \sum_{i=1}^m \left(v_{ij}(\mu_i^0 + \mathrm{R}T\ln a_i)\right) \\ &= \mathrm{R}T\ln\left(\left(k_j^f\prod_{i=1}^m a_i^{v_{ij}^f}\right)\Big/\left(k_j^b\prod_{i=1}^m a_i^{v_{ij}^b}\right)\right) = \mathrm{R}\ln\left(r_j^f/r_j^b\right). \end{aligned} \tag{15}$$

The last two lines result from the identity

$$\sum_{i=1}^m (v_{ij}\mu_i^0) = \mathrm{R}T\ln(k_j^f/k_j^b) \tag{16}$$

which follows since both the rate r_j and the affinity A_j of each reaction must vanish identically at thermodynamic equilibrium.

Assume that the reservoir with "higher" reaction potential $\prod_{1j}$ contains substrates (all system's components before the chemical transformation). Reservoir with "lower" reaction potential $\prod_{2j}$ contains products (all system components after the transformation). The reactions in the chemical chamber undergo in the purely kinetic regime, so that the classical definition of chemical affinity (15) is locally valid. The general power expression and efficiency formula for the considered system follow from the entropy conservation and energy balance in the reversible part of the system. The entropy flux continuity through the chemical chamber or the active part of the system can be stated in the form

$$\begin{aligned} &\frac{q_{1'}}{T_{1'}} + s_{1_{1'}}n_{1_{1'}} + s_{2_{1'}}n_{2_{1'}} + \dots s_{i_{1'}}n_{i_{1'}} \dots + s_{m_{1'}}n_{m_{1'}} \\ &\quad = \frac{q_{2'}}{T_{2'}} + s_{1_{2'}}n_{1_{2'}} + s_{2_{2'}}n_{2_{2'}} + \dots s_{i_{2'}}n_{i_{2'}} \dots + s_{m_{2'}}n_{m_{2'}}, \end{aligned} \tag{17}$$

where q and n_i are fluxes of heat and substances in vertical cross-sections $1'$ and $2'$ (Figs. 1 and 2). Chemically inactive substances (inerts) can also be included in this scheme.

Multiplying Eq. (17) by the common temperature $T = T_{1'} = T_{2'}$ and using the identity $h = Ts + \mu$ we obtain

$$\begin{aligned} &q_{1'} + (h_{1_{1'}} - \mu_{1_{1'}})n_{1_{1'}} + \dots + \dots (h_{i_{1'}} - \mu_{i_{1'}})n_{i_{1'}} \dots + (h_{m_{1'}} - \mu_{m_{1'}})n_{m_{1'}} \\ &\quad = q_{2'} + (h_{1_{2'}} - \mu_{1_{2'}})n_{1_{2'}} \dots + \dots (h_{i_{2'}} - \mu_{i_{2'}})n_{i_{2'}} \dots \\ &\qquad + (h_{m_{2'}} - \mu_{m_{2'}})n_{m_{2'}}. \end{aligned} \tag{18}$$

Combining Eq. (18) with the energy balance described by an equation

$$\begin{aligned} &q_{1'} + h_{1_{1'}}n_{1_{1'}} + h_{2_{1'}}n_{2_{1'}} + \dots h_{i_{1'}}n_{i_{1'}} \dots + h_{m_{1'}}n_{m_{1'}} \\ &\quad = q_{2'} + h_{1_{2'}}n_{1_{2'}} + \dots h_{i_{2'}}n_{i_{2'}} \dots + h_{m_{2'}}n_{m_{2'}} + p \end{aligned} \tag{19}$$

and defining "total heat flux" Q as the sum of the sensible heat and the mass transfer including heat flux

$$Q_1 \equiv q_1 + T_1 s_{1_1}n_{1_1} + \dots T_1 s_{i_1}n_{i_1} \dots + T_1 s_{m_1}n_{m_1} \tag{20}$$

we find in terms of total heats $Q_{1'}$ and $Q_{2'}$

$$\begin{aligned} p &= Q_{1'} + \mu_{1_{1'}}n_{1_{1'}} + \dots \mu_{i_{1'}}n_{i_{1'}} \dots + \mu_{m_{1'}}n_{m_{1'}} - Q_{2'} - \mu_{1_{2'}}n_{1_{2'}} \\ &\quad - \dots \mu_{i_{2'}}n_{i_{2'}} \dots - \mu_{m_{2'}}n_{m_{2'}}. \end{aligned} \tag{21}$$

This general result and the isothermal case of entropy balance (17) lead to the following expression for the isothermal power yield in the reversible part of the reactor

$$p = \mu_{1_{1'}} n_{1_{1'}} + \mu_{2_{1'}} n_{2_{1'}} + \ldots \mu_{i_{1'}} n_{i_{1'}} \ldots + \mu_{m_{1'}} n_{m_{1'}} - \mu_{1_{2'}} n_{1_{2'}} - \mu_{2_{2'}} n_{2_{2'}} \ldots - \mu_{i_{2'}} n_{i_{2'}} \ldots - \mu_{m_{2'}} n_{m_{2'}} \tag{22}$$

Thus, in a steady and isothermal flow process, the power yield of an endoreversible engine system is the difference between the input and output flux of the Gibb's function.

3. Power yield from chemical reactions with complete conversion

We shall yet transform Eq. (22) to a more pronouncing form specific to the case of the complete conversion. For convenience the components are numbered such that species = 1,2,…,i are substrates and species = i + 1, i + 2,…,m are products. We shall also take the advantage of the mass conservation in each chemical reaction

$$\frac{(n_{1_{1'}} - n_{1_{2'}})_j}{v_{1j}} = \frac{(n_{2_{1'}} - n_{2_{2'}})_j}{v_{2j}} \ldots = \frac{(n_{i_{1'}} - n_{i_{2'}})_j}{v_{ij}} \ldots = \frac{(n_{k_{1'}} - n_{k_{2'}})_j}{v_{kj}} = \frac{(n_{l_{1'}} - n_{l_{2'}})_j}{v_{lj}} = \frac{(n_{m_{1'}} - n_{m_{2'}})_j}{v_{mj}} \equiv -n_j. \tag{23}$$

This is an alternative form of Eq. (2). The above formula uses (common for each reaction) molar fluxes of active reagents, n_j, identical in the present case with the products of the reaction volume V and derivatives of reaction extents, ε_j, with respect to time t, (i.e., reaction rates, r_j).

In the case of complete conversion, for each j

$$(n_{1_{2'}} = n_{2_{2'}} \ldots = n_{i_{2'}})_j = 0 \tag{24}$$

(species = 1,2,…,i are substrates) and

$$(n_{i+1_{1'}} = n_{i+2_{1'}} \ldots = n_{m_{1'}})_j = 0 \tag{25}$$

(species = i + 1, i + 2,…,m are products). Thus, in this case Eq. (23) takes the form

$$-\frac{(n_{1_{1'}})_j}{v_{1j}} = -\frac{(n_{2_{1'}})_j}{v_{2j}} \ldots = -\frac{(n_{i_{1'}})_j}{v_{ij}} = \frac{(n_{i+1_{2'}})_j}{v_{i+1j}} = \frac{(n_{l_{2'}})_j}{v_{lj}} = \frac{(n_{m_{2'}})_j}{v_{mj}} \equiv n_j \tag{26}$$

(j = 1,2,…,R). Since for each i and j,

$$n_i = \sum_{j=1}^{R} (\mathrm{n}_i)_j \tag{27}$$

and Eqs. (24)–(26) are valid, total power yield of an isothermal multireaction process (22) takes the form

$$p = \sum_{j=1}^{R} \Big\{ \mu_{1_{1'}} (n_{1_{1'}})_j + \mu_{2_{1'}} (n_{2_{1'}})_j + \ldots \mu_{i_{1'}} (n_{i_{1'}})_j - \mu_{i+1_{2'}} (n_{i+1_{2'}})_j \ldots - \mu_{l_{2'}} (n_{l_{2'}})_j \ldots - \mu_{m_{2'}} (n_{m_{2'}})_j \Big\} \tag{28}$$

and, finally (keep in mind that each $n_j > 0$ and v_{ij} of substrates are negative)

$$p = \sum_{j=1}^{R} \{p_j\} = \sum_{j=1}^{R} -\{\mu_{1_{1'}} v_{1j} + \mu_{2_{1'}} v_{2j} + \ldots \mu_{i_{1'}} v_{ij} + \mu_{i+1_{2'}} v_{i+1j} \cdot + \cdot \mu_{m-1_{2'}} v_{m-1j} \ldots + \mu_{m_{2'}} v_{mj})\} n_j \tag{29}$$

n_j is the chemical flux of jth reaction equal to the product of reaction rate and volume, $n_j = r_j V$. Since $n_j = r_j V$, Eqs. (15) and (29) state that in the case of the complete chemical conversion of substrates into products, the power yield from unit volume of the reactor equals to the sum of products of the affinity-like driving forces and the rates of the reactions.

$$P = \sum_{j=1}^{R} \{\tilde{\mathrm{A}}_j n_j\} = V \sum_{j=1}^{R} \{\tilde{\mathrm{A}}_j r_j\}. \tag{30}$$

Note, however, that the affinity-like quantity $\tilde{\mathrm{A}}_j$ which appears in Eqs. (29) and (30) is not precisely identical with the classical affinity A_j of Eq. (15). The former is an extended quantity involving states in cross-section's 1′ and 2′, whereas the latter is the state function. Nonetheless, one can use the "extended affinity" $\tilde{\mathrm{A}}_j$ in calculations of reaction efficiencies and power production as shown in the further text of the present paper.

For a single reaction the chemical efficiency ζ is defined here as power yield per one mole of the invariant molar flux of active reagents; for many reactions vector of such efficiencies is defined. Such efficiency is identical with an extended affinity of the reaction in the chemically active part of the system. While it is not dimensionless, it can describe correctly the system. We shall use the affinity-based efficiency in this paper because of the suitability and popularity of affinity notion. Later, other definitions of efficiencies will be proposed.

When conversion is not complete, Eq. (22) still remains valid, yet the use of products of the reaction volume and reaction rates, n_j, is less suitable. A special case of Eq. (29), applied to the single isomerization reaction was considered by de Vos [23] and Sieniutycz [2,3]. In the classical thermodynamics of systems without power production Eq. (30) describes the product of system's temperature and its entropy production. Here, however, in agreement with Eq. (17), which assures the internal entropy conservation, power is produced from within of an ideal chemical system without any internal entropy source. This is an "internally ideal" or "endoreversible" case that admits the thermodynamic imperfections only in external parts of the chemical engine, i.e., in regions where the mass diffusion and heat transport are essential. For an isomerisation equation, a simple approach treating internal imperfections associated with entropy and mass sources has recently been presented by Sieniutycz [2]. We shall extend this approach to complex reactions in Section 11.

4. Entropy production in a system with many components and chemical reactions

Entropy production of the overall system composed of the reservoirs and the reactor can be expressed in terms of the reservoir parameters and system's fluxes

$$\sigma_s = \frac{q_2}{T_2} - \frac{q_1}{T_1} + s_{1_2} n_{1_2} + \ldots s_{i_2} n_{i_2} \ldots + s_{m_2} n_{m_2} - s_{1_1} n_{1_1} - s_{2_1} n_{2_1} - \ldots s_{i_1} n_{i_1} \ldots - s_{m_1} n_{m_1}. \tag{31}$$

To eliminate flux q_2 we apply in this equation an energy balance law (similar to Eq. (19) but written for cross-sections 1 and 2 in Fig. 2)

$$q_1 + h_{1_1} n_{1_1} + h_{2_1} n_{2_1} + \ldots h_{i_1} n_{i_1} \ldots + h_{m_1} n_{m_1} = q_2 + h_{1_2} n_{1_2} + \ldots h_{i_2} n_{i_2} \ldots + h_{m_2} n_{m_2} + p. \tag{32}$$

We obtain

$$\sigma_s = T_2^{-1} (q_1 + h_{1_1} n_{1_1} \ldots + h_{i_1} n_{i_1} \ldots + h_{m_1} n_{m_1} - h_{1_2} n_{1_2} - \ldots h_{i_2} n_{i_2} \ldots - h_{m_2} n_{m_2} - p) - T_1^{-1} q_1 + s_{1_2} n_{1_2} + \ldots s_{i_2} n_{i_2} \ldots + s_{m_2} n_{m_2} - s_{1_1} n_{1_1} - s_{2_1} n_{2_1} - \ldots s_{i_1} n_{i_1} \ldots - s_{m_1} n_{m_1}. \tag{33}$$

The above general formula may also be written as

$$\begin{aligned}\sigma_s = q_1(T_2^{-1} - T_1^{-1}) + T_2^{-1}(\mu_{1_1}n_{1_1}\ldots + \mu_{i_1}n_{i_1}\ldots + \mu_{m_1}n_{m_1} \\ - \mu_{1_2}n_{1_2}\ldots - \mu_{i_2}n_{i_2}\ldots - \mu_{m_2}n_{m_2} - p) + (T_2^{-1} - T_1^{-1}) \\ \times (T_1s_{1_1}n_{1_1} + \ldots T_1s_{i_1}n_{i_1}\ldots + T_1s_{m_1}n_{m_1}).\end{aligned} \tag{34}$$

This result reduces to an earlier formula obtained for a special case of an isomerisation reaction [2,3]

$$\sigma_s = q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{(\mu_1 - \mu_2)n}{T_2} - \frac{p}{T_2} + \left(\frac{1}{T_2} - \frac{1}{T_1}\right)T_1s_1n. \tag{35}$$

The following form of general formula (34)

$$\begin{aligned}\sigma_s = (q_1 + T_1s_{1_1}n_{1_1}\ldots + T_1s_{m_1}n_{m_1})(T_2^{-1} - T_1^{-1}) \\ + T_2^{-1}(\mu_{1_1}n_{1_1}\ldots + \mu_{i_1}n_{i_1}\ldots + \mu_{m_1}n_{m_1} - \mu_{1_2}n_{1_2}\ldots \\ - \mu_{i_2}n_{i_2}\ldots - \mu_{m_2}n_{m_2} - p)\end{aligned} \tag{36}$$

implies a convenient redefinition of the heat flux q. Defining "total heat flux" Q as the sum of the sensible heat and the mass transfer related heat flux

$$Q_1 \equiv q_1 + T_1s_{1_1}n_{1_1} + \ldots T_1s_{i_1}n_{i_1}\ldots + T_1s_{m_1}n_{m_1} \tag{20}$$

we obtain

$$\begin{aligned}\sigma_s = Q_1(T_2^{-1} - T_1^{-1}) + T_2^{-1}(\mu_{1_1}n_{1_1}\ldots + \mu_{i_1}n_{i_1}\ldots + \mu_{m_1}n_{m_1} \\ - \mu_{1_2}n_{1_2}\ldots - \mu_{i_2}n_{i_2}\ldots - \mu_{m_2}n_{m_2} - p)\end{aligned} \tag{37}$$

and for the isomerisation reaction

$$\sigma_s = Q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{(\mu_1 - \mu_2)n - p}{T_2}. \tag{38}$$

Elimination of power p from Eq. (37) and transformed form of the energy balance (19) written in terms of Q rather than q, i.e. Eq. (21),

$$\begin{aligned}p = Q_{1'} + \mu_{1_{1'}}n_{1_{1'}} + \ldots \mu_{i_{1'}}n_{i_{1'}}\ldots + \mu_{m_{1'}}n_{m_{1'}} - Q_{2'} - \mu_{1_{2'}}n_{1_{2'}} \\ - \ldots \mu_{i_{2'}}n_{i_{2'}}\ldots - \mu_{m_{2'}}n_{m_{2'}}\end{aligned} \tag{21}$$

yields the endoreversible entropy balance

$$\begin{aligned}T_2^{-1}\sigma_s = \{Q_1(1 - T_2/T_1) - Q_{1'}(1 - T_{2'}/T_{1'})\} + (\mu_{1_1}n_{1_1}\ldots \\ + \mu_{i_1}n_{i_1}\ldots + \mu_{m_1}n_{m_1} - \mu_{1_2}n_{1_2}\ldots - \mu_{i_2}n_{i_2}\ldots \\ - \mu_{m_2}n_{m_2}) - (\mu_{1_{1'}}n_{1_{1'}}\ldots + \mu_{i_{1'}}n_{i_{1'}}\ldots + \mu_{m_{1'}}n_{m_{1'}} \\ - \mu_{1_{2'}}n_{1_{2'}} - \ldots \mu_{i_{2'}}n_{i_{2'}}\ldots - \mu_{m_{2'}}n_{m_{2'}}),\end{aligned} \tag{39}$$

whereas for the isomerisation reaction

$$\begin{aligned}\sigma_s = \frac{Q_1}{T_2}\left(1 - \frac{T_2}{T_1}\right) - \frac{Q_{1'}}{T_2}\left(1 - \frac{T_{2'}}{T_{1'}}\right) \\ + \frac{(\mu_1 - \mu_2)n - (\mu_{1'} - \mu_{2'})n}{T_2}.\end{aligned} \tag{40}$$

Thus, we arrive at the final result

$$\begin{aligned}T_2^{-1}\sigma_s = \{Q_1(1 - T_2/T_1) - Q_{1'}(1 - T_{2'}/T_{1'})\} + (\mu_{1_1}n_{1_1}\ldots \\ + \mu_{i_1}n_{i_1} - \mu_{i+1_2}n_{i+1_2}\ldots - \mu_{m_2}n_{m_2}) - (\mu_{1_{1'}}n_{1_{1'}}\ldots \\ + \mu_{i_{1'}}n_{i_{1'}} - \mu_{i+1_{2'}}n_{i+1_{2'}}\ldots - \mu_{m_{2'}}n_{m_{2'}}).\end{aligned} \tag{41}$$

This is a general form of endoreversible entropy balance in multicomponent and multireaction systems applicable to arbitrary stoichiometry.

Our purpose now is to determine how this general endoreversible formula simplifies in the case of *systems with complete conversion*. In this case, we apply the mole balance Eq. (23) for both cross-sections, 1 and 2 (primed and not), i.e., for each j

$$(n_{1_{2'}} = n_{2_{2'}}\ldots = n_{i_{2'}})_j = 0 \tag{24}$$

$$(n_{1_2} = n_{2_2}\ldots = n_{i_2})_j = 0 \tag{42}$$

(species = $1,2,\ldots,i$ are substrates) and

$$(n_{i+1_{1'}} = n_{i+2_{1'}}\ldots = n_{m_{1'}})_j = 0 \tag{25}$$

$$(n_{i+1_1} = n_{i+2_1}\ldots = n_{m_1})_j = 0 \tag{43}$$

(species = $i + 1$, $i + 2,\ldots,m$ are products).

With the mole balance, Eq. (23), we obtain equations of the type of Eq. (26)

$$-\frac{(n_{1_{1'}})_j}{\nu_{1j}} = -\frac{(n_{2_{1'}})_j}{\nu_{2j}}\ldots = -\frac{(n_{i_{1'}})_j}{\nu_{ij}} = \frac{(n_{i+1_{2'}})_j}{\nu_{i+1j}} = \frac{(n_{l_{2'}})_j}{\nu_{lj}} = \frac{(n_{m_{2'}})_j}{\nu_{mj}} \equiv n_j \tag{26}$$

for both cross-sections, 1 and 2, primed and not. We also use Eq. (27) for each i and j,

$$n_i = \sum_{j=1}^{R}(n_i)_j \tag{27}$$

The procedure is now similar to that leading to the power yield, Eqs. (28) and (29), namely, we apply the above mole flux constraints in the endoreversible entropy balance (41). The result is the entropy production of the process with a complete conversion

$$\begin{aligned}T_2^{-1}\sigma_s = \{Q_1(1 - T_2/T_1) - Q_{1'}(1 - T_{2'}/T_{1'})\} \\ + \sum_{j=1}^{R}\Big\{\Big[\mu_{1_1}(n_{1_1})_j\ldots + \mu_{i_1}(n_{i_1})_j - \mu_{i+1_2}(n_{i+1_2}) - \mu_{m_2}(n_{m_2})_j\Big] \\ - \Big[(\mu_{1_{1'}}(n_{1_{1'}})_j\ldots + \mu_{i_{1'}}(n_{i_{1'}})_j - \mu_{i+1_{2'}}(n_{i+1_{2'}})_j\ldots - \mu_{m_{2'}}(n_{m_{2'}})_j\Big]\Big\}.\end{aligned} \tag{44}$$

In this equation, we have taken into account mole balances (26) at all cross-sections of interest (primed and not). We obtain

$$\begin{aligned}T_2^{-1}\sigma_s = \{Q_1(1 - T_2/T_1) - Q_{1'}(1 - T_{2'}/T_{1'})\} \\ + \sum_{j=1}^{R}\Big\{-\Big[(\mu_{1_1}\nu_{1j}\ldots + \mu_{i_1}\nu_{ij} + \mu_{i+1_2}\nu_{i+1j}\ldots + \mu_{m_2}\nu_{mj}) \\ -(\mu_{1_{1'}}\nu_{1j}\ldots + \mu_{i_{1'}}\nu_{ij} + \mu_{i+1_{2'}}\nu_{i+1,j}\ldots + \mu_{m_{2'}}\nu_{mj})n_j\Big]\Big\}.\end{aligned} \tag{45}$$

Consequently, in terms of efficiencies

$$\begin{aligned}\zeta_j \equiv -\{\mu_1\nu_{1j} + \mu_2\nu_{2j} + \ldots \mu_i\nu_{ij} + \mu_{i+1}\nu_{i+1,j} + \ldots \mu_{m-1}\nu_{m-1,j} \\ + \mu_m\nu_{mj}\}\end{aligned} \tag{46}$$

and taking into account properties of the Carnot point (referred to the bulk states 1 and 2) we arrive at the final result

$$T_2^{-1}\sigma_s = \{(Q_1\eta)_C - Q_{1'}\eta + \sum_{j=1}^{R}\{(\zeta_{jC} - \zeta_j)n_j]\}. \tag{47}$$

We observe that, under the approximation $Q_1 = Q_{1'}$, the thermal component is the product of generalized (i.e., mass transfer including) heat flux (20) and the deviation of thermal efficiency η from the Carnot efficiency. Yet, the exact result for the thermal component involves the difference of the product of $Q_1\eta$ in the Carnot state and the actual state of the system. The mass diffusion component is the scalar product of all chemical fluxes n_j and deviations of actual chemical efficiencies from their values at the reversible (Carnot) point. The vector form of this formula is Eq. (49) below.

In the special case of isomerisation reaction $A_1 + A_2 = 0$ the above equation may be written in the form

$$\sigma_s = Q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) - Q_{1'}\left(\frac{1}{T_2} - \frac{1}{T'}\right) + T_2^{-1}[(\mu_1 - \mu_2) - (\mu_{1'} - \mu_{2'})]n, \tag{48}$$

where $T' = T_2T_{1'}/T_{2'}$ is the so-called Carnot temperature [31].

For an isothermal process with R reactions (in which $T_{1'} = T_{2'} = T_1 = T_2 = T$) and complete conversion the following vector equation follows from general Eq. (47)

$$\sigma_s = T^{-1}(\zeta_C - \zeta).\mathbf{n}, \tag{49}$$

where $\mathbf{n}$ is the chemical vector in R-dimensional reaction space. This result means that, modulo to the multiplier T^{-1}, the entropy production is the scalar product of the vector of chemical flux $\mathbf{n}$ and the deviation of chemical efficiency ζ from its reversible limit, ζ_C. The subscript C points out that the reversible efficiency refers to the Carnot point of the chemical system, also called "open circuit point" [23]. In the engine range this point is associated with vanishing reaction vector $\mathbf{n}$ and upper, reversible limit for ζ.

5. Significance of invariant molar flux

When both reservoirs are infinite a steady state can be achieved in the system; we shall analyze this steady state. First we assume that $R = 1$, i.e., a single reaction that undergoes in the system. Then, as follows from Eq. (23) in the case of complete conversion Eqs. (24)–(26) are valid for a single reaction. Then

$$-\frac{n_{1_{1'}}}{v_1}\ldots = -\frac{n_{i_{1'}}}{v_i}\ldots = \frac{n_{i+1_{2'}}}{v_{i+1}} = \frac{n_{m_{2'}}}{v_m} \equiv n, \tag{26$'$}$$

and the isothermal power production is

$$p = -\{\mu_{1_{1'}}v_1 + \mu_{2_{1'}}v_2 + \ldots \mu_{i_{1'}}v_i + \mu_{i+1_{2'}}v_{i+1} + \ldots \mu_{m-1_{2'}}v_{m-1_{2'}} + \mu_{m_{2'}}v_{m_{2'}}\}n \tag{50}$$

so that

$$p = \tilde{A}_n = V\tilde{A}_r. \tag{51}$$

Even in this simple case the efficiency of power yield coincides with the extended affinity

$$\zeta = p/n = p/(Vr) = \tilde{A}. \tag{52}$$

To show the role of flux n and give a physical interpretation for it we begin with a special case of the isomerization reaction $A_1 + A_2 = 0$, for which the stoichiometric coefficients $v_1 = -1$ and $v_2 = 1$, and Eq. (26′) takes the form

$$n = -n_{1_{1'}}/v_1 = n_{2_{2'}}/v_2 \tag{53}$$

or, $n = n_{1_{1'}} = n_{2_{2'}}$. We note that at the reactor inlet the role of flux n is taken over by the flux of component 1 whereas at the outlet – by the flux of component 2. It is therefore reasonable to keep in mind that the efficiency basis involves flux n as an invariant property of *both* components, 1 and 2. Indeed, from Eq. (23) or by considering the trivial stoichiometry of the isomerization reaction (where $v_1 = -1$ and $v_2 = 1$), we obtain for an arbitrary cross-section y' of the reactor

$$n_{1_{2'}} - n_{1_{1'}} = v_1 n \equiv -n \tag{54}$$

$$n_{2_{2'}} - n_{2_{1'}} = v_2 n \equiv n. \tag{55}$$

Thus, after adding both these equations,

$$n_{1_{2'}} + n_{2_{2'}} = n_{1_{1'}} + n_{2_{1'}} \tag{56}$$

or, in a slightly different notation

$$(n_1 + n_2)_{2'} = (n_1 + n_2)_{1'}. \tag{56$'$}$$

Clearly, in this simple case, total flux of moles $n = n_1 + n_2$ is the same both cross-sections of the reactor, i.e., n is the reaction invariant. For the mixture with no product 2 at the reactor inlet ($n_{2_{1'}} = 0$), that leaves the reactor with the complete conversion ($n_{1_{2'}} = 0$), one has $n = n_{1_{1'}} = n_{2_{2'}}$. The last equality has been used in the form $n = n_{1'} = n_{2'}$ in a previous work dealing with the power production from an isomerization reaction, $A_1 + A_2 = 0$, [1].

Clearly, in the considered case the flux n measures an invariant molar flux; this flux appears in the power formula

$$p = \zeta n = (\mu_{1'} - \mu_{2'})n. \tag{57}$$

This formula is valid for a single-reaction, two-component-system. While formulae of this sort are known, de Vos [23] and Sieniutycz [2,3], the invariancy of the flux n they involve was not pointed out in the literature. Let us therefore keep in mind that efficiency ζ is defined as power yield per one mole of the invariant molar flux of *both* active reagents (1 and 2), that is

$$\zeta = p/n = \mu_{1'} - \mu_{2'} \tag{58}$$

i.e., not per one mole of a chosen reagent as one could, perhaps, expect. Remember also that in this theoretical scheme the efficiency is identical with the extended affinity of the reaction $\tilde{A}_j$ in the chemically active part of the system.

It is now clear that, in general multireaction flow systems, the transformed molar fluxes N_k, defined by formulae (12) and (13) for $k = 1,2,\ldots,m - R$, can constitute suitable bases for the definition of partial chemical efficiencies and a resulting overall efficiency. Thanks to the invariance property (14), the basis for each efficiency is the same for each cross-section of the flow reactor. Thus the contribution of each transformed flux to the total power (determined from some measurements or calculations) can be quantified for an arbitrary cross-section of the reactor. In the isothermal case, i.e., when thermal component of power can be ignored, the resulting power production can be obtained form the expression

$$p = \sum_{k=1}^{m-R} \zeta_k N_k \tag{59}$$

which is a generalization of the formula (57). When $m = 2$ (isomerisation or phase change of a component) Eq. (57) follows from Eq. (59).

6. Role of mass exchange equations

The mass transfer between each reservoir and the production section of the system is described by certain kinetic equations. For simplicity, we assume that these equations are linear with respect to molar fractions. The mass balances for the substances transferred, produced and consumed are contained in the equations below. For the substrates (species = $1,2,\ldots,i$ in cross-section $1'$) we can write in terms of molar concentrations x_k (corresponding with appropriate chemical potentials μ_k in Fig. 1)

$$n_{1_{1'}} = g_{1_1}(x_{1_1} - x_{1_{1'}}) \tag{60}$$

$$n_{2_{1'}} = g_{2_1}(x_{2_1} - x_{2_{1'}}) \tag{61}$$

$$\vdots$$

$$n_{i_{1'}} = g_{i_1}(x_{i_1} - x_{i_{1'}}) \tag{62}$$

whereas for the products (species = $i + 1,\ i + 2,\ldots,m$ in cross-section $2'$)

$$n_{i+1_{2'}} = g_{i+1_2}(x_{i+1_{2'}} - x_{i+1_2}) \tag{63}$$

$$n_{i+2_{2'}} = g_{i+2_2}(x_{i+2_{2'}} - x_{i+2_2}) \tag{64}$$

$$\vdots$$

$$n_{m_{2'}} = g_{m_2}(x_{m_{2'}} - x_{m_2}). \tag{65}$$

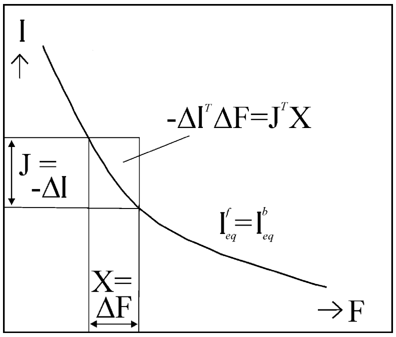

Fig. 3. Nonlinear macrokinetics of heat and mass transfer based on concomitant fluxes I^f and I^b such that the resulting flux $J = I^f - I^b$.

When the mass transfer description is in terms of chemical potentials μ_k rather than mole fractions x_k, the use of conductances of the substrates $g_{1_1}, g_{2_1}, \ldots g_{i_1}$ and those of the products $g_{i+1_2}, g_{i+2_2}, \ldots g_{m_2}$ should be replaced by the use of their suitable counterparts,

$$\beta_{1_1}, \beta_{2_1}, \ldots \beta_{i_1}, \beta_{i+1_2}, \beta_{i+2_2}, \ldots \beta_{m_2},$$

as shown in Fig. 2. In the case of nonlinear transfer processes the use of chemical potentials as the quantities which govern the complex transfer of mass may be more appropriate. Yet, these chemical potentials will necessarily have to satisfy some nonlinear equations which are exponential with respect to μ_k These equations incorporate the concept that, for each pair of states involved (i.e., 1 and 1′ or 2′ and 2), the resulting (observed) mass flux J_k is the difference of two unidirectional, "absolute" fluxes, Fig. 3, (Sieniutycz [21–23] and Lin et al. [4]).

The property of concomitant fluxes holds for all 'circulation branches' shown in Fig. 2. An example of an equation stemming from the theory of two concomitant fluxes is given below

$$n_{i_{1'}} = I_i^{eq}\left\{\exp\left(\sum_k \nu^*_{ki}\left(\mu_{k_1} - \mu_k^{eq}\right)\right) - \exp\left(\sum_k \nu^*_{ki}\left(\mu_{k_{1'}} - \mu_k^{eq}\right)\right)\right\}, \tag{66}$$

where

$$I_i^{eq} \equiv I_i^0 \sum_k \exp(\nu^*_{ki}\mu_k^{eq}) \tag{67}$$

is the common value of both absolute currents at equilibrium associated with "exchange current" I_i^0. Eq. (66) is of Marcelin-de Donder type, given here purposely in the form containing explicitly the equilibrium state. For small deviations of chemical potentials μ_k from the equilibrium the Taylor expansion yields the Onsagerian structure

$$\begin{aligned} n_{i_{1'}} &= I_i^{eq}\left\{\sum_i \nu^*_{ki}(\mu_{k_1} - \mu_k^{eq}) - \sum_k \nu^*_{ki}(\mu_{k_{1'}} - \mu_k^{eq})\right\} \\ &= I_i^{eq}\left\{\sum_k \nu^*_{ki}(\mu_{k_1} - \mu_{k_{1'}})\right\} \equiv \sum_k L^{eq}_{ki}(\mu_{k_1} - \mu_{k_{1'}}), \end{aligned} \tag{68}$$

where $L^{eq}_{ki} \equiv I^{eq}_k \nu^*_{ik}$ is the Onsager's matrix at the thermal equilibrium. An analogous formula holds for cross-sections 2′ and 2. A general equality $I^{eq}_k \nu^*_{ik} = I^{eq}_i \nu^*_{ki}$, is valid that preserves the Onsager's symmetry close to the equilibrium. For more details, the interested reader is referred to the previous work (Sieniutycz [21–23], Lin et al. [4]).

However, in the section below we restrict ourselves to the Eqs. (60)–(65) linear with respect to the molar concentrations x_k.

7. Characteristics of the chemical engine

In order to determine characteristics of the chemical engine at the steady state (unlimited stock of fuel) one searches for unknown "primed" concentrations $x_{i_{1'}}$ and $x_{k_{2'}}$ expressed in terms of a control variable. For the chemical engine the suitable control can be chemical flux n. The knowledge of the functions describing primed concentrations in terms of flux n will lead to important characteristics which link efficiency ζ with chemical flux n.

Using the usual structure of chemical potentials

$$\mu_i(x_i, T) = \mu_{i0}(T) + \mathrm{R}T \ln x_i \tag{69}$$

and the reference chemical potentials to define the normalized affinity

$$\begin{aligned} \zeta_0 \equiv -\{&\mu_{10}\nu_1 + \mu_{20}\nu_2 + \ldots \mu_{i0}\nu_i + \mu_{i+1,0}\nu_{i+1} + \ldots \mu_{m-1,0}\nu_{m-1} \\ &+ \mu_{m0}\nu_m\} \end{aligned} \tag{70}$$

we obtain an efficiency expression in the form

$$\zeta = \zeta_0 - RT \ln\left(x_{1_{1'}}^{\nu_1} x_{2_{1'}}^{\nu_2} \ldots x_{i_{1'}}^{\nu_i} x_{i+1_{2'}}^{\nu_{i+1}} \ldots x_{m_{2'}}^{\nu_m}\right). \tag{71}$$

Solving the exchange Eqs. (60)–(62) for "primed" concentrations $x_{1_{1'}}, x_{2_{1'}}, \ldots, x_{i_{1'}}$ and Eqs. (63)–(65) for analogous concentrations $x_{i+1_{2'}}, \ldots, x_{m_{2'}}$ and applying in these formulas the mole balance formula, Eq. (26′), we obtain for cross-section 1′

$$x_{1_{1'}} = x_{1_1} - n_{1_{1'}}/g_{1_1} = x_{1_1} + \nu_1 n/g_{1_1} \tag{72}$$

$$x_{2_{1'}} = x_{2_1} - n_{2_{1'}}/g_{2_1} = x_{2_1} + \nu_2 n/g_{2_1} \tag{73}$$

$$\vdots$$

$$x_{i_{1'}} = x_{i_1} - n_{i_{1'}}/g_{i_1} = x_{i_1} + \nu_i n/g_{i_1} \tag{74}$$

and, for cross-section 2′

$$x_{i+1_{2'}} = x_{i+1_2} + n_{i+1_{2'}}/g_{i+1_2} = x_{i+1_2} + \nu_{i+1} n/g_{i+1_2} \tag{75}$$

$$\vdots$$

$$x_{m_{2'}} = x_{m_2} + n_{m_{2'}}/g_{m_2} = x_{m_2} + \nu_m n/g_{m_2}. \tag{76}$$

Substituting these results into Eq. (71) we find an equation linking the reagent's flux n with the chemical efficiency ζ

$$\begin{aligned} \exp\frac{\zeta - \zeta_0}{\mathrm{R}T} = -&(x_{1_1} + \nu_1 n/g_{1_1})^{\nu_1}(x_{2_1} + \nu_2 n/g_{2_1})^{\nu_2} \\ &\ldots(x_{m_2} + \nu_m n/g_{m_2})^{\nu_m}. \end{aligned} \tag{77}$$

Thus, an explicit form exists from which ζ can be calculated as a logarithmic function of n. The qualitative picture of the relationship between n and ζ is illustrated in Fig. 4.

As an example of application of the above general equation consider the isomerization reaction $A_1 + A_2 = 0$ for which the stoichi-

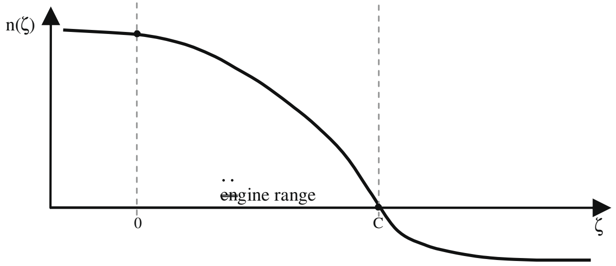

Fig. 4. Invariant flux of active components in terms of efficiency ζ.

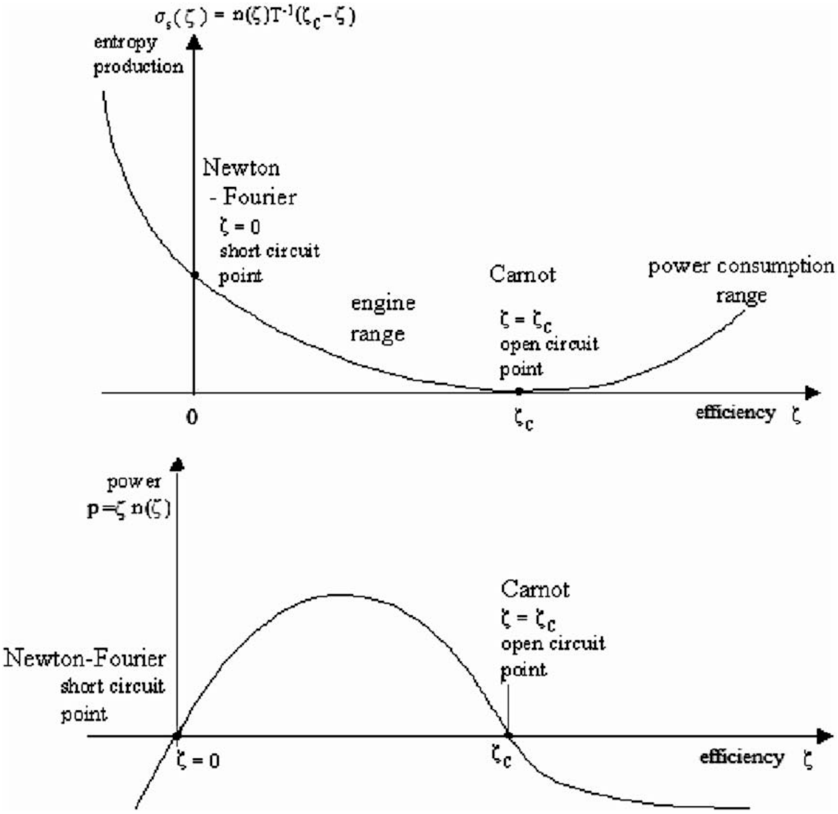

Fig. 5. Entropy production and power versus chemical efficiency ζ in one-dimensional system. Classical theory of power yield is limited to a close vicinity of the Carnot point.

ometric coefficients $\nu_1 = -1$ and $\nu_2 = 1$. The general formula (77) then leads to the following equation describing ζ in terms of n

$$\zeta = \zeta_0 - RT\ln\{(x_{1_1} - n/g_{1_1})^{-1}(x_{2_2} + n/g_{2_2})\}$$
$$= \zeta_0 + RT\ln\left(\frac{x_{1_1} - n/g_{1_1}}{x_{2_2} - n/g_{2_2}}\right). \tag{78}$$

This special result was obtained in our earlier work [2,3]. Eq. (77) can be considered as the generalization of Eq. (78) for an arbitrary chemical reaction with the complete conversion.

For the function $\zeta(n)$ defined by Eq. (77) the one-dimensional case of multireaction entropy production (49) and power yield (29) is illustrated graphically in Fig. 5.

Eqs. (77) and (78) prove that the effective concentrations of the reactants in the upper reservoir, $x_{i\text{eff}} = x_i - g_i{}^{-1}n$, are decreased, whereas the effective concentrations of the products in the lower reservoir, $x_{k\text{eff}} = x_k + g_k{}^{-1}n$, are increased due to the finite chemical flux, n. This causes that efficiency ζ decreases nonlinearly with n. When the effect of resistances g_i^{-1} and g_k^{-1} is ignorable or flux n is very small, reversible efficiency, ζ_C, is attained.

Since the system's power function is described by the product $\zeta(n)$ n, this power is equal to zero in the points where $n = 0$ and $\zeta = 0$. The first is associated with the so-called Carnot point, the second with the vanishing driving force of the reaction within the chemical reactor. Consistently with the mathematical theorem of Rolle, power function $p(n) = \zeta(n)$ n exhibits a maximum for a finite value of fuel flux, n.

Variables n and ζ are examples of two controls with respect to which maximum power may be sought. For instant, as shown in Fig. 5, power function exhibits a maximum for some efficiency, a chemical analogue of the well known Chambadal–Novikov–Curzon–Ahlborn efficiency (*CNCA* efficiency: [27–29]).

8. Generalization for multiple reactions

It is easy to generalize the above treatment for the situation when R independent reactions occur in the system. Using the chemical potentials in actual and reference states we define R partial efficiencies (for each reaction)

$$\zeta_j \equiv -\{\mu_1\nu_{1j} + \mu_2\nu_{2j} + \ldots \mu_i\nu_{ij} + \mu_{i+1}\nu_{i+1,j} + \ldots \mu_{m-1}\nu_{m-1,j} + \mu_m\nu_{mj}\} \tag{46}$$

and R normalized affinities (70)

$$\zeta_{0j} \equiv -\{\mu_{10}\nu_{1j} + \mu_{20}\nu_{2j} + \ldots \mu_{i0}\nu_{ij} + \mu_{i+1,0}\nu_{i+1,j}$$
$$+ \ldots \mu_{m-1,0}\nu_{m-1,j} + \mu_{m0}\nu_{mj}\}. \tag{79}$$

We thus obtain R efficiency expressions

$$\zeta_j = \zeta_{0j} - \mathrm{RT}\ln\left(x_{1_{1'}}^{\nu_{1j}} x_{2_{1'}}^{\nu_{2j}} \cdot x_{i_{1'}}^{\nu_{ij}} x_{i+1_{2'}}^{\nu_{i+1,j}} \cdot x_{m_{2'}}^{\nu_{mj}}\right). \tag{80}$$

($j = 1,2,\ldots,R$). Using exchange Eqs. (72)–(76) for "primed" concentrations and applying mole balances of the multireaction system, Eqs. (26) and (27), we obtain generalized expressions linking the boundary concentrations of the reactor with chemical fluxes n_j. For the cross-section 1′

$$x_{1_{1'}} = x_{1_1} + \sum_{j=1}^{R} \nu_{1j}n_j/g_{1_1} \tag{81}$$

$$x_{2_{1'}} = x_{2_1} + \sum_{j=1}^{R} \nu_{2j}n_j/g_{2_1} \tag{82}$$

$$\vdots$$

$$x_{i_{1'}} = x_{i_1} + \sum_{j=1}^{R} \nu_{ij}n_j/g_{i_1} \tag{83}$$

and, for cross-section 2′

$$x_{i+1_{2'}} = x_{i+1_2} + \sum_{j=1}^{R} v_{i+1j} n_j / g_{i+1_2} \tag{84}$$

$$\vdots$$

$$x_{m_{2'}} = x_{m_2} + \sum_{j=1}^{R} v_{mj} n_j / g_{m_2}. \tag{85}$$

Substituting these results into Eq. (80) we find a set of R equations each having the structure of the single-reaction equation (77). This set may be given a vector–matrix form explicit with respect to all efficiencies. In such a form the multireaction result constitutes a single vector equation

$$\zeta = \zeta_0 - \mathrm{R}T \ln \left\{ \prod_{s=1}^{i} (x_{s_1} + (\boldsymbol{v}\mathbf{n})_s / g_{k_1})^{v_s} \times \prod_{p=i+1}^{m} (x_{p_2} + (\boldsymbol{v}\mathbf{n})_p / g_{p2})^{v_p} \right\}, \tag{86}$$

where v_s and v_p are vectors composed of stoichiometric coefficients of species s and p in all R independent chemical reactions. Vector Eq. (86) links R chemical fluxes n_j (flux vector $\mathbf{n}$) with R chemical efficiencies ζ_j (efficiency vector ζ). In fact, this vector equation describes the relation between R-dimensional efficiency vector, ζ and R-dimensional vector of chemical fluxes, $\mathbf{n}$. Qualitatively, each of R relations is of the type presented in Fig. 4.

9. Propelling the engine by coupled mass transfer

Exchange Eqs. (60)–(65) can be generalized (for both reactants s and products p) to treat the coupled transfer phenomena. This is associated with the use of non-diagonal conductance matrices for substrates and products contained in common matrix $\mathbf{g}$. In general the matrix $\mathbf{g}$ is a square matrix that involves the mass transfer conductances of all species (reactants and products).

Allowing non-diagonal entries in $\mathbf{g}$ we abandon the uncoupled description (neglect of crossing effects) that was used up to now. A coupled-process generalization uses the matrix–vector notation and leads to the diffusion–reaction equations (81) and (82) in the form

$$\mathbf{x}_{1'} = \mathbf{x}_1 + \mathbf{g}_1^{-1} v_1 \mathbf{n}, \tag{87}$$

$$\mathbf{x}_{2'} = \mathbf{x}_2 + \mathbf{g}_2^{-1} v_2 \mathbf{n}. \tag{88}$$

In these equations the distinction between reactants and products is assured respectively by lower indices 1 and 2. Thus vector $\mathbf{x}_1$ refers to reactants and vector $\mathbf{x}_2$ to products, both sets being disjoint. Disjoint are also sets of coordinates of resistance matrices $\mathbf{g}_1^{-1}$ and $\mathbf{g}_2^{-1}$ .Yet, both considered equations are coupled due to the presence of (R dimensional) chemical flux vector $\mathbf{n}$ whose components are equal to the product of reaction rates and reactor volume. A vector equation describing the coupled-transfer characteristics that link the vectors of efficiencies and chemical fluxes is the coupled-transfer generalization of Eq. (86)

$$\zeta = \zeta_0 - \mathrm{R}T \times \ln \left\{ \prod_{s=1}^{i} (x_{s_1} + (\mathbf{g}_1^{-1} v_1 \mathbf{n})_s)^{v_s} \times \prod_{p=i+1}^{m} (x_{p_2} + (\mathbf{g}_2^{-1} v_2 \mathbf{n}) p)^{v_p} \right\}. \tag{89}$$

The compact notation used here uses a vector of logarithm functions that emerge because v_s and v_p are vectors composed of stoichiometric coefficients of species s and p in all R independent chemical reactions.

Since the R-dimensional vectors $\mathbf{n}$ and ζ are related, at least in theory, power produced in the reactor might be determined as a function of ζ or in terms of $\mathbf{n}$. Yet, the only explicit function is the one from which ζ can be expressed as a logarithmic function of $\mathbf{n}$ (the inverse function describing $\mathbf{n}$ in terms of ζ is implicit). Here is a unique working formula for power production in terms of $\mathbf{n}$

$$P = \zeta \cdot \mathbf{n} = \zeta_0 \cdot \mathbf{n} - \mathrm{R}T\mathbf{n} \ln \left\{ \prod_{s=1}^{i} (x_{s_1} + (\mathbf{g}_1^{-1} v_1 \mathbf{n})_s)^{v_s} \times \prod_{p=i+1}^{m} (x_{p_2} + (\mathbf{g}_2^{-1} v_2 \mathbf{n}) p)^{v_p} \right\}. \tag{90}$$

The power function is now spanned in the R-dimensional space of reaction fluxes $\mathbf{n}$. Again, similarly as in a single reaction, this power is equal to zero in points where $\mathbf{n} = 0$ and $\zeta = 0$. The first is associated with the so-called Carnot point, the second with “short circuit point”, the point of vanishing driving force of the reaction within the chemical reactor. Consequently, the power function $p(\mathbf{n}) = \zeta \cdot \mathbf{n}$ exhibits a maximum for a finite value of flux vector, $\mathbf{n}$.

The maximum power point is the result of maximizing of power expression (90) with respect to chemical vector $\mathbf{n}$ as a free control. Analytical methods are seldom effective. Sometimes one uses diagrams of function $p(\mathbf{n})$ to determine the maximum point graphically. In general, the information regarding the maximum point can be obtained by applying the methods of numerical search. A large number of numerical procedures, known from the static optimization, is available (e.g., [30–32]). An iterative procedure starts at an arbitrary point $\mathbf{n}^0$ and proceeds along a certain direction, say $\mathbf{k}^1$, to assure an increase (maximization) of the objective, power p, until its extremum in the direction $\mathbf{k}^1$ is reached. To find this “directional extremum” a single variable search for a peak is applied [30]. A single variable, l, measures distances covered in various directions. In the first search, the magnitude of the step is selected so as to extremize power p_{L} along the direction $\mathbf{k}^1$. Assuming that the magnitude of the step extremizing p_{L} is equal to l^1, the corresponding decision is $\mathbf{n}^1 = \mathbf{n}^0 + \mathbf{k}^1\, l^1$. The so-obtained $\mathbf{n}^1$ is simultaneously the starting value of $\mathbf{n}$ for the second step, etc. Each numerical method (steepest ascent, gradient, Gauss-Seidel, Powell, etc.) generates directions $\mathbf{k}^q$ at the step q in a different way, yet each one converges to the extremum of power. For comparison of various search methods see [31].

Only in the case of a simple isomerization reaction $A_1 + A_2 = 0$ an explicit analytical formula expressing n in terms of ζ does exist. In this special case power p may be described in terms of ζ by the following equation

$$p = \zeta n = \zeta \frac{x_1 - x_2 \exp\left(\frac{\zeta - \zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1} \exp\left(\frac{\zeta - \zeta_0}{RT}\right)} \tag{91}$$

de Vos [27]. Function $n(\zeta)$ contained in Eq. (91) is the inverse of function $\zeta\ (n)$ in Eq. (78). The graphical illustration of power p in terms of ζ is consistent with Fig. 5.

The line of produced power represented by Eq. (91), has two zero points. The first is the “short circuit point” (point of vanishing efficiency), and, the second is the “open circuit point” or Carnot point at which the feeding of the system by the fuel is infinitely slow. The function $n(\zeta)$ contained in Eq. (91) describes for $\zeta = 0$ a feed rate of the active reagent at the short circuit point.

Power expression (91) exhibits a maximum power attained for a certain efficiency ζ_{mp} that may be obtained either graphically or by one of the numerical search methods discussed above. One may also solve numerically an equation

$$\frac{dp}{d\zeta} = 0 \tag{92}$$

by Newton–Raphson method. The numerical solution generates a function of the optimal efficiency

$$\zeta_{mp} = f(\zeta_0, T, x_1, x_2, g_1, g_2). \tag{93}$$

This is the chemical counterpart of the Chambadal–Novikov–Curzon–Ahlborn efficiency (CNCA efficiency). Substituting Eq. (93) into the n expression of Eq. (91), leads to the corresponding flux n at the maximum power point.

$$n_{mp} = f(\zeta_0, T, x_1, x_2, g_1, g_2). \tag{94}$$

10. Generalized entropy production

For the intensity of the entropy generation in multireaction systems a vector generalization of the previous findings established in a single-reaction system is valid. Entropy is not produced only at the Carnot point, where the components of the efficiency vector are ζ_{jC}. Therefore, modulo to the temperature factor T^{-1}, the generalized entropy production is the scalar product of two R dimensional vectors, the vector of efficiency deviation $\zeta_C - \zeta$ and the vector of chemical flux, $\mathbf{n}$

$$\sigma_s = \frac{(\boldsymbol{\zeta}_{\mathbf{C}} - \boldsymbol{\zeta}).\mathbf{n}}{T} \tag{49}$$

Refs. [2,3]. Since both ζ and $\mathbf{n}$ are linked, σ_s can be presented in terms of each vector ζ or $\mathbf{n}$. When the control is the chemical flux of the fuel, $\mathbf{n}$, then, from Eqs. (86) and (89)

$$\zeta_c - \zeta_0 = -\mathrm{R}T \ln\left(\prod_{s=1}^{i}(x_{s_1})^{\nu_s} \prod_{p=i+1}^{m}(x_{p_2})^{\nu_p}\right) \tag{95}$$

and

$$\sigma_s/\mathrm{R} = -\mathbf{n}.\ln\left\{\prod_{s=1}^{i}(x_{s_1})^{\nu_s} \prod_{p=i+1}^{m}(x_{p_2})^{\nu_p} \times \prod_{s=1}^{i}(x_{s_1} + (\mathbf{g}_1^{-1}\nu\mathbf{n})_s)^{-\nu_s} \right.$$
$$\left. \times \prod_{p=i+1}^{m}(x_{p_2} + (\mathbf{g}_2^{-1}\nu\mathbf{n})_p)^{-\nu_p}\right\}. \tag{96}$$

In the special case of reaction $A_1 + A_2 = 0$, for which the stoichiometric coefficients $\nu_1 = -1$ and $\nu_2 = 1$, Eq. (96) yields.

$$\sigma_s = Rn\ln\left(\left(\frac{x_{1_1}}{x_{2_2}}\right)\left(\frac{x_{2_2} + ng_{2_2}^{-1}}{x_{1_1} - ng_{1_1}^{-1}}\right)\right) \tag{97}$$

which corrects the omission of multiplier n in our previous work (Sieniutycz [2,3]).

In the "short circuit" point of the system, there is no power production for any value of vector ζ_0, despite the potential for chemical reactions. Only entropy is produced. This case may be regarded as "classical", occurring in a purely dissipative system, where lossy elements predominate so significantly that the chemical reaction does not produces any power, despite of its non-vanishing rate and an existing finite potential of ζ_0 (but not ζ) for the power production.

From Eqs. (49) and (95) we find

$$(\sigma_s)_{\zeta=0} = \frac{\boldsymbol{\zeta}_{\mathbf{C}}.\mathbf{n}}{T} = \mathbf{n}.\left(\frac{\zeta_0}{T} - \mathrm{R}\ln\prod_{s=1}^{i}(x_{s_1})^{\nu_s}\prod_{p=i+1}^{m}(x_{p_2})^{\nu_p}\right). \tag{98}$$

This result agrees with a classical formula where the entropy production per unit volume equals the product of reaction rate and chemical affinity in the entropy representation. Yet, this classical result does not hold when the system produces power, i.e., it is an "active system". For power-producing systems generalized result, Eq. (96), should be applied.

If both $\zeta_0 = 0$ and $\zeta = \mathbf{0}$ the "short circuit" state is the one without chemical reactions. This, does not mean, however, that the flux $\mathbf{n}$ in Eq. (49) and (95) vanishes because the mass diffusion can still proceed making the system a diffusion engine in which i reactants in reservoir 1 are chemically identical with i products in reservoir 2 (i.e., $s = p$, $A_1 = A_{i+1}$, $A_i = A_m$ and $-\nu_s = \nu_p = \nu = 1$ for each component i), yet the concentrations in 1 and 2 are different. The entropy is then produced only by the multicomponent mass transport

$$(\sigma_s)_{\zeta=0,\zeta_C=0} = \frac{\zeta_C.\mathbf{n}_0}{T} = \sum_{k=1}^{i}\frac{\zeta_{C_k}}{T}\left(\frac{x_{k_1} - x_{k_2}}{(g_{k_1})^{-1} + (g_{k_2})^{-1}}\right)$$
$$= \mathbf{R}\sum_{k=1}^{i}\ln(x_{k_1}/x_{k_2})\left(\frac{x_{k_1} - x_{k_2}}{(g_{k_1})^{-1} + (g_{k_2})^{-1}}\right). \tag{99}$$

In the case of binary mixture this formula can be written as [2,3]

$$(\sigma_s)_{\zeta=0,\zeta_C=0} = T^{-1}\frac{(\mu_1 - \mu_2).(x_1 - x_2)}{(g_1)^{-1} + (g_2)^{-1}}. \tag{100}$$

The discussed equation describes the situation in which the reactor does not exist, the fuel stream flows by two sequentially connected conductors, and the constant molar flux of the binary mixture, n, is determined by the specification of the overall conductance g.

11. Extension to systems with internal dissipation

Here, for simplicity, we restrict ourselves to a single-reaction system, yet with an arbitrary chemical reaction. Power optimization in practical generators calls for the relaxation of the assumption about the reversibility of chemical reaction and taking into account the (internal) entropy production associated with this process. Moreover chemical efficiency ζ defined as power yield per one mole of the invariant molar flux n is insufficient to characterize a non-isothermal generator in which an extra component of power appears associated with the temperature difference between the reservoirs. Therefore, we shall also comment a possible extension of the theory to the more general case of the dissipative chemical reaction in a non-isothermal system.

Consequently, internal entropy production σ_s^{int} and a set of positive internal coefficients for products, ψ_p, each satisfying the inequality $\psi_p > 1$, are introduced to describe the internal imperfections within the chemical chamber. With these quantities one may set suitable balance equations of the internal part of engine. In terms of total energy flux (20) power yield, resulting from the energy balance the internal (reacting) chamber, is given by Eq. (21)

$$p = Q_{1'} - Q_{2'} + \mu_{1_{1'}}n_{1_{1'}} + \ldots\mu_{i_{1'}}n_{i_{1'}}\ldots + \mu_{m_{1'}}n_{m_{1'}} - \mu_{1_{2'}}n_{1_{2'}}$$
$$-\ldots\mu_{i_{2'}}n_{i_{2'}}\ldots - \mu_{m_{2'}}n_{m_{2'}}, \tag{21$'$}$$

where we have introduced "total heat flux" defined by an Eq. (20). In the case of complete conversion this equation simplifies to an expression describing the apparent non-isothermal power yield

$$p = Q_{1'} - Q_{2'} + \mu_{1_{1'}}n_{1_{1'}} + \ldots\mu_{i_{1'}}n_{i_{1'}} - \ldots\mu_{i+1_{2'}}n_{i+1_{2'}}\ldots - \mu_{m_{2'}}n_{m_{2'}}. \tag{101}$$

In the special case of an isomerisation equation $A_1 + A_2 = 0$ this yields

$$p = Q_{1'} - Q_{2'} + \mu_{1'}n_{1'} - \mu_{2'}n_{2'}. \tag{102}$$

The virtue of using total heat $Q_{1'}$ is the additive contribution of the total heat flux to power yield in the power formula containing chemical efficiency in the form of the driving force or affinity $\mu_{1'} - \mu_{2'}$. Since the identification of the chemical driving force or affinity with the chemical efficiency is possible only in the thermodynamically reversible reaction, we shall show here how the internal entropy production and incomplete conversion affect the form of the efficiency expressions.

The entropy and mass balances of the internal or chemical part of the engine are

$$\frac{Q_{2'}}{T_{2'}}-\frac{Q_{1'}}{T_{1'}}=\sigma_s^{\rm int}, \tag{103}$$

$$n_{p2'}-n_{p1'}=\sigma_p^{\rm int}. \tag{104}$$

This set contains the positive source $\sigma_p^{\rm int}$ characterizing incomplete conversion of product p between sections 1′ and 2′ of the chemical chamber. From these equations we find, respectively, in terms of internal productions of entropy and product p

$$\frac{Q_{2'}}{Q_{1'}}=\frac{T_{2'}}{T_{1'}}+\frac{T_{2'}\sigma_s^{\rm int}}{Q_{1'}}=\left(1+\frac{T_{1'}\sigma_s^{\rm int}}{Q_{1'}}\right)\frac{T_{2'}}{T_{1'}}\equiv\Phi\frac{T_{2'}}{T_{1'}} \tag{105}$$

and

$$\frac{n_{p_{2'}}}{n_{p_{1'}}}=1+\frac{\sigma_p^{\rm int}}{n_{p_{1'}}}\equiv 1+\frac{1}{\Psi_p-1}, \tag{106}$$

where p refers to arbitrary product. In the power equations written down below internal imperfection functions Φ and ψ_p are defined in terms of internal sources and system's operational parameters in accordance with the definitions

$$\Phi\equiv 1+\frac{T'_1\sigma_s^{\rm int}}{Q_{1'}} \tag{107}$$

$$\Psi_p\equiv 1+\frac{n_{p1'}}{\sigma_p^{\rm int}}=\frac{n_{p2'}}{n_{p2'}-n_{p1'}}. \tag{108}$$

For an engine, $\Phi > 1$ and $\psi_p > 1$.

Let us now take into account the balance of mole numbers in the general case of a system with arbitrary inlet and outlet molar flows

$$\frac{(n_{1_{1'}}-n_{1_{2'}})_j}{\nu_{1j}}=\frac{(n_{2_{1'}}-n_{2_{2'}})_j}{\nu_{2j}}\ldots=\frac{(n_{i_{1'}}-n_{i_{2'}})_j}{\nu_{ij}}\ldots=\frac{(n_{k_{1'}}-n_{k_{2'}})_j}{\nu_{kj}}$$
$$=\frac{(n_{l'_1}-n_{l_{2'}})_j}{\nu_{lj}}=\frac{(n_{m_{1'}}-n_{m_{2'}})_j}{\nu_{mj}}\equiv -n_j. \tag{23}$$

With these general formulas one can propose the multi-component extension of the previous approach postulated in an earlier work [2]. The approach in fact assumes that the basic equality of the complete conversion model

$$n_{1_{2'}}=n_{2_{2'}}\ldots=n_{i_{2'}}=0 \tag{24′}$$

is still valid (i.e., substrates $1,2,\ldots,i$ do not appear in cross-section 2′), but that

$$n_{i+1_{1'}}=n_{i+2_{1'}}\ldots=n_{m_{1'}}\neq 0 \tag{109}$$

which means that there must be some input fluxes of products $= i+1,\ i+2,\ldots,m$ at the inlet cross-section 1′ in order to achieve required final products. Then instead of "perfect equality" (26) applied for $R = 1$ we have

$$-\frac{n_{1_{1'}}}{\nu_1}\ldots=-\frac{n_{i_{1'}}}{\nu_i}\ldots=\frac{n_{i+1_{2'}}-n_{i+1_{1'}}}{\nu_{i+1}}=\frac{n_{m_{2'}}-n_{m_{1'}}}{\nu_m}\equiv n. \tag{110}$$

This can be written in the form

$$-\frac{n_{1_{1'}}}{\nu_1}\ldots=-\frac{n_{i_{1'}}}{\nu_i}\ldots=\frac{n_{i+1_{2,}}}{\nu_{i+1}n_{i+1_{2'}}/(n_{i+1_{2'}}-n_{i+1_{1'}})}$$
$$=\ldots\ldots\frac{n_{m_{2'}}}{\nu_m n_{m_{2'}}/(n_{m_{2'}}-n_{m_{1'}})}\equiv n. \tag{111}$$

An equivalent form of this equation contains factors ψ_p defined above as the values of ratios $\psi_p = n_{p2}/\Delta n_p$ for products ($i+1,\ldots,$m), each satisfying the property $\psi_p > 1$

$$-\frac{n_{1_{1'}}}{\nu_1}\ldots=-\frac{n_{i_{1'}}}{\nu_i}=\frac{n_{i+1_{2'}}}{\nu_{i+1}\Psi}\ldots=\ldots\frac{n_{m_{2'}}}{\nu_m\Psi}\equiv n. \tag{112}$$

The non-isothermal power yield (101) is now, in fact, an apparent formula. After using Eq. (112) the power assumes the form

$$p=Q_{1'}(1-\Phi T_{2'}/T_{1'})-\{\mu_{1_{1'}}\nu_1+\ldots\mu_{i_{1'}}\nu_i+\Psi\mu_{i+1_{2'}}\nu_{i+1}$$
$$+\ldots\Psi\mu_{m-1_{2'}}\nu_{m-1_{2'}}+\Psi\mu_{m_{2'}}\nu_{m_{2'}}\}n. \tag{113}$$

A formal interpretation of this power formula is based on effective increase of chemical potentials of products and outlet Gibbs flux, which causes the reduction of chemical efficiency. Considering a physical viewpoint, however, the explanation of the efficiency decrease uses the observation that there are now products (species of lower μ_k) in the inlet stream to the system, which decrease the inlet Gibbs fluxes of the reagents and hence reduce the apparent efficiency. Whichever of these two interpretations is accepted a decrease of power production is predicted.

The approach presented here is similar to that known in the theory of imperfect heat machines which operates with the factor of internal irreversibilities Φ (satisfying the inequality $\Phi > 1$ and acting multiplicatively on the temperature of circulating fluid contacting with the second reservoir, $T_{2'}$. The effective temperature of this fluid $T_{2'}^{\rm eff}$ equals then $\Phi T_{2'}$, as shown in the thermal efficiency formula (105). Of course, this effect causes the decrease of the thermal efficiency. In the chemical case the role similar to Φ is played by coefficient ψ (or the family of such coefficients, ψ_p, when each member pertains to a different product). The effective chemical potential of product p becomes $\psi_p\mu_p$ at 2′; since each $\psi_p > 1$ the effective chemical potentials of products that reside in the chemical efficiency are higher than actual ones. This effect decreases chemical efficiencies (driving forces and affinities).

Power formula, Eq. (113), generalizes the idealized power of Eq. (101). Vector nature of efficiency manifests itself in non-isothermal chemical systems. The first or thermal component of the power yield describes power generated by the total heat flux with the decreased (non-Carnot) thermal efficiency $\eta = 1 - \Phi T_{2'}/T_{1'}$. Whereas the second or chemical component describes the power yield caused by the chemical reaction. The chemical power is generated with the lowered (non-ideal) chemical efficiency

$$\zeta_\Psi\equiv-\{\mu_{1_{1'}}\nu_1+\ldots\mu_{i_{1'}}\nu_i+\Psi\mu_{i+1_{2'}}\nu_{i+1}+\ldots\Psi\mu_{m-1_{2'}}\nu_{m-1_{2'}}$$
$$+\Psi\mu_{m_{2'}}\nu_{m_{2'}}\}. \tag{114}$$

The chemical term in the power formula predominates in systems that work closely to isothermal conditions. Effectively, in the engine mode where $\Phi > 1$ and $\psi > 1$, an imperfect chemical system (with internal irreversibilities), behalves as it would work with the higher temperature of circulating fluid in its lower branch ($\Phi T_{2'}$ instead $T_{2'}$) and with a decreased affinity of an effective value

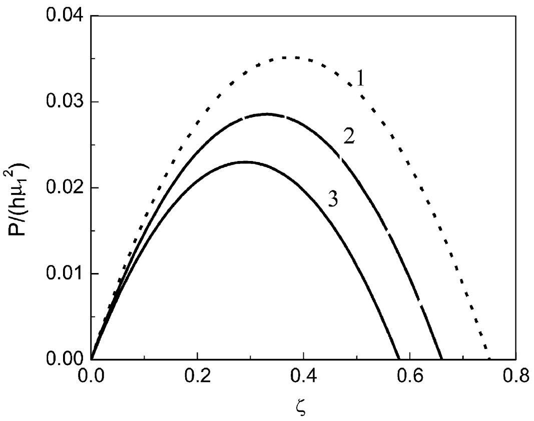

Fig. 6. Change of power output P in the irreversible chemical engine in terms of chemical efficiency ζ. Lines 1, 2 and 3 pertain to imperfection factor ψ = 1, 1.1, and 1.2, respectively.

(114). Of course, power production is decreased by these imperfections. An example of the engine power reduction caused by the irreversibility factor $\psi > 1$ is shown in Fig. 6; the results are consistent with those of Lin et al. [4].

12. Concluding remarks

In their recent paper Bergman, Faghri, and Viskanta [35] attributed the frontiers in transport phenomena research and education to: energy systems, biological systems, security, information technology, and nanotechnology. This fact stresses, in particular, the role of chemical power systems in the contemporary researches. In the present paper, an approach has been applied that implements balances of molar fluxes and reaction invariants to complex chemical systems with the power production. This approach predicts reduction of chemical efficiencies caused by finite rates and leads to the evaluation of power limits in complex multicomponent and multireaction systems driven by the mass transport of reactants. Conditions for the maximum production of power have been given for complex chemical systems. The reduction of power yield caused by the system's imperfections is different than that evaluated from the classical expression for the entropy production. In fact, we have shown that the classical result for the entropy production, Eq. (98), does not hold when the system produces power, i.e., it is an "active system". For power-producing systems a novel generalized result, Eq. (96), has been obtained. The solution for limits of power produced or consumed in a irreversible chemical system is a fundamental result whose scientific rank is comparable to the solution for the work limit in static reversible system. While the latter solution (in terms of Gibbs function) is classical and quasistatic, the former one involves rate or irreversible effects. For given transfer conductances (products of transfer coefficients and area) the irreversible solution can be applied to problem of arbitrary complex chemistry.

Special results have been presented for non-isothermal power systems, stoichiometric mixtures, isomerization reactions and internal dissipation within the chemical reactor. In this last case we shall abandoned "endoreversibility", i.e., presented a proposal for the extension of the basic theory to the more general case when a dissipative chemical reaction undergoes within the non-isothermal chemical system.

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