

# Finite-time thermodynamics: Exergy<sup>a)</sup> and optimization of time-constrained processes

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The criterion of thermodynamic ideality is introduced. It is the ratio of actual rate of entropy production to the minimal rate of entropy production. It is closely related to the exergy approach but incorporates the irreversible losses due to finite-time and nonzero rates. No explicit reference need be made to the average values of the thermodynamic potentials of the environment. The regimes with minimal entropy production for the system where chemical reaction occurs and for the set of parallel heat engines are found.

## I. INTRODUCTION

Exergy analysis and other related approaches<sup>1-6</sup> are widely used for estimation of how near a process is to "thermodynamic ideality," a term we define more precisely below. To apply this approach, one calculates the exergy loss or, in the term used more frequently in the U.S., the availability loss, as the difference between the exergy at the output of the process (or at the exit of some stage of interest) and the exergy on the input. These exergies or availabilities are calculated from the parameters of the input and output fluxes.<sup>7,8</sup> This is a simple and general method but it has some weak points and limitations which can be overcome. Here we discuss a way to extend exergy analysis using some results of finite-time thermodynamics, incorporating time or rate constraints in the conditions that define the system. Doing this makes the limiting optimal behavior of the system reflect those time or rate constraints and their consequences for the system's dissipation. The result is that evaluation of the system's performance based on finite-time limits is more realistic than is achieved by the traditional method based on reversible processes.

In the first part of our discussion, we formulate the general requirements for a criterion of "thermodynamic ideality" and discuss how the exergy loss and entropy production meet these requirements. In the second part we describe the dependence of the efficiency coefficients of the process on dissipation (entropy production). Some results of the finite-time thermodynamics concerned with the lower bounds on dissipation are given there. We suggest the introduction of a "dissipation coefficient," defined as a ratio of the actual entropy production to the minimal possible dissipation fixed by the constraints on the system—including rate or time constraints—as a new criterion of the extent of thermodynamic ideality of the process. In the third and fourth parts of this discussion, the regimes optimal according to this criterion are found for two general cases: a system in which chemical reactions occur, and a system of parallel heat en-

gines with given total power for which the optimal distribution of power among the engines is determined.

## II. REQUIREMENTS FOR A CRITERION OF THERMODYNAMIC IDEALITY

It is natural that the criterion of thermodynamic ideality meet the following requirements: (1) it depends on parameters of the process in a manner that shows how to change them in order to improve the performance of that process; (2) it does not depend on the time- or space-averaged characteristics of the environment, which can differ significantly from the actual instantaneous values; (3) It takes into account the inevitable dissipation of energy due to constrained duration included in the specification of the rate or intensity of the process.

We first illustrate this criterion and its properties with a heat engine, the classic object of thermodynamic analysis. The temperatures of the hot and cold reservoirs, the integral coefficients of heat transfer between reservoirs and the working body, and the power of the engine are the parameters of the system. In an engine generating a given power, the entropy production cannot be lower than  $\sigma^*$ .<sup>9</sup> To calculate the exergy loss in this engine one calculates the difference between the actual work done and the work done by the ideal Carnot engine (the exergy of the heat of the hot reservoir) and takes as the low temperature  $T_0$  of the cold reservoir the average temperature of the environment. This traditional definition<sup>7</sup> takes into account neither any specific characteristics of the engine, such as heat-transfer coefficients, nor the real conditions of its operation, such as the temperature of the cold reservoir which can differ significantly from the average temperature of the environment. The traditional comparison pits the real engine with its ideal, reversible counterpart which generates zero power, has infinite heat conductances, and may operate with an unrealistic temperature assigned to the cold reservoir. Such a comparison does not provide us with the most useful sort of information.

The process of heat exchange is our second example.<sup>4,5</sup> The loss of exergy for such a system is calculated as a difference of the usable energy (exergy) of the input and output

<sup>a)</sup>Exergy is, namely,  $E + T_0S - p_0V + \sum \mu_{0i}N_i$ .

fluxes; but this quantity tells us nothing about how to change the operation of the heat exchanger to decrease the energy loss for the given structural parameters, notably the geometry of the heat exchanger and the heat-transfer coefficients, and the given heat load.

Comparable examples can be found for chemical processes, mass-transfer processes, etc. To calculate the traditional exergy in such systems one uses the averaged vector of concentrations in the reservoir (environment). The components in the real vector of concentrations are apt to vary more from their averages than the temperature does.

Without denying that the exergy approach has proven itself useful for many qualitative analyses of thermodynamic systems, we will now show that some of the results of finite-time thermodynamics can be used to extend the concept of exergy analysis in ways that readily provide more detailed estimates of the performance of processes, still within the general schema in which exergy or availability loss is the fundamental objective function to be minimized.

### III. EFFICIENCY COEFFICIENTS AND ENTROPY PRODUCTION

We consider a system in which heat and mass-transfer and chemical reactions may all occur and mechanical work may be done. The system may have input and output fluxes of energy and matter. We assume that the temperature and the pressure of the input and output fluxes are equal to each other and to the corresponding parameters of the environment  $T_0$  and  $P_0$ , so that, the sources of energy that create gradients of temperature and pressure are all included within the system. The reservoir of heat energy has the temperature  $T_1$ , with  $T_1 > T_0$ . It is also assumed that the heating, cooling, expansion, and compression processes comprising the overall process occur inside the system. Using the method<sup>10</sup> for the case of ideal solutions one can derive from the equations of balance for matter, energy, and entropy (per cycle for the cycle regime and per unit of time for the static regime),

$$\Delta S = \left[ Q \left( 1 - \frac{T_0}{T_1} \right) - W_{\text{sys}} + W_{\text{ext}} - W_{\text{sep}} - \Delta E_{\text{ch}} \right] (T_0)^{-1}, \quad (1)$$

where  $Q$  is the amount of transferred heat,  $W_{\text{sys}}$  and  $W_{\text{ext}}$  are the work done by the system and on the system respectively,  $\Delta S$  is the entropy produced due to irreversibility of the process,  $W_{\text{sep}} = T_0 \sum_m N_m \Delta S_m$  is the work of separation done in the system,  $\Delta S_m = -R \sum_l x_{ml} \ln x_{ml}$  is the entropy of mixing in the  $m$ th flux,  $x_{ml}$  is the molar concentration of the  $l$ th component in the  $m$ th flux,  $R$  is the universal gas constant,  $N_m$  is the number of moles per unit time in the  $m$ th flux,  $\Delta E_{\text{ch}} = \sum_j \sum_l \Delta N_{jl} \mu_l$  is the change of the energy due to chemical transformations when a stoichiometric combination of all the components is added or taken from the system in the pure form,  $\mu_l$  is the chemical potential of the  $l$ th component, and  $\Delta N_{jl}$  is the change of the number of moles of the  $l$ th component in the  $j$ th reaction. It is convenient to divide both sides of Eq. (1) by the process duration  $\tau$  and use the entropy production rate  $\sigma = \Delta S / \tau$  (dissipation) instead of produced entropy, the heat fluxes instead of the amount of heat, the power instead of work, etc., in the manner of Truesdell.<sup>8</sup>

One can see from Eq. (1) that decreasing the entropy produced in the process leads either to decreasing the energy consumption (the heat  $Q$  or the work  $W_{\text{ext}}$ ), or to increasing the work done by the system (mechanical  $W_{\text{sys}}$  or the work of separation  $W_{\text{sep}}$ ), or to increasing the energy used to produce the chemical reactions  $\Delta E_{\text{ch}}$  or to increasing the various efficiency coefficients such as  $W_{\text{sep}}/Q$  with the rest of the process parameters held fixed.

Because every one of the efficiency coefficients can be expressed in terms of the parameters of the external fluxes, specifically their compositions and rates of mass flow, one can show using Eq. (1) that the efficiency coefficients of the process depend monotonically on the amount of entropy produced.<sup>11</sup> For instance, an increase of the amount of entropy generated in the chemical process can lead to an increase in the degree of transformation, the number of moles of the component  $\Delta N_{jl}$  that participate in reaction, or to the production of a more nearly uniform output mixture, due to a decrease in the entropy of mixing. The connections between the efficiency coefficients and the entropy production for several processes are shown in Table I. Their schemes are shown in Fig. 1.

It is important to note that if the geometry of the system and the intensity of the process conducted in it are fixed, then the produced entropy cannot be reduced below some bound. Some of these bounds found in Refs. 12–17 are shown in Table II. The corresponding optimal regimes can serve as general guides for the design of the corresponding real processes, in order to attain better thermodynamic performance.

Because the model (even paradigmatic) system that gives this minimal entropy production provides a more realistic comparison than the ideal, reversible system, it is natural to define the criterion of thermodynamic ideality for the real process as the dissipation coefficient (or coefficients) which is defined as the ratio of the entropy production in the actual process to its minimum possible value,

$$k_{\text{dis}} = \frac{\sigma}{\sigma^*}. \quad (2)$$

Let us note that  $k_{\text{dis}}$  depends on the parameters of the systems only and does not depend on the average parameters of the environment. Therefore this dissipation coefficient can be used instead of exergy loss as a universal criterion of optimality for the thermodynamic ideality of the system when the energy resources are restricted.

The concept of exergy was in fact generalized to systems operating in finite time,<sup>18</sup> however, that generalization still depends on the values of the intensive variables of the environment so it does not resolve the problem addressed by the present article. However, it does take into account explicitly the effects of time constraint on the limiting exergy or availability loss of a process. Still another generalized measure of the deviation of the process from thermodynamic ideality was defined as a ratio of irreversible to total heat exchanged.<sup>19</sup> The utility of this measure remains to be explored.

TABLE I. Relationship between efficiency coefficients and dissipation. Here  $q$  is the heat flux;  $T$  is temperature;  $P$  is power;  $\mu$  is chemical potential;  $g$  is material flux;  $\sigma$  is dissipation (entropy production);  $s$  is specific entropy,  $h$  is the specific enthalpy;  $x$  is the concentration of the key component. Subscripts and superscripts: + corresponds to the hot and - to the cold reservoirs;  $c, b$  correspond to substance;  $cb$  to the mixture;  $f$  corresponds to flegma;  $a$  to absorber,  $s$  to stripper,  $b$  to the cube.

Process	Equations of thermodynamic balances (material, energy, entropy)	Efficiency vs entropy production
Heat engine cycle	$q^+ - q^- - P = 0,$ $\frac{q^+}{T^+} - \frac{q^-}{T^-} + \sigma = 0$	$\eta = \frac{P}{q^+} = \frac{1 - T^-/T^+}{1 + T^- \sigma / P}$
Refrigerator and heat pump cycles	$q^+ + q^- - P = 0,$ $\frac{q^+}{T^+} + \frac{q^-}{T^-} + \sigma = 0$	$\eta_r = \frac{q^-}{ P } = \frac{1}{T^+/T^- - 1} \frac{T^+ \sigma}{ P }$ $\eta_{hp} = \frac{q^+}{ P } = 1 + \eta_r$
Direct and inverse	$q^+ + q^- - P = 0, \quad g^+ + g^- = 0,$	$\eta_d = \frac{P}{g^+} = \mu^+ - \mu^- - \frac{T \sigma}{g^+}$
Diffusion-mechanical cycles	$\frac{q^+ + q^- - \mu^+ g^+ - \mu^- g^-}{T} + \sigma = 0$	$\eta_r = \frac{g^-}{P} = \frac{1 - T \sigma /  P }{\mu^+ - \mu^-}$
Cycle of binary mixture separation	$q^{cb} + q^c + q^b - q^0 - P = 0, \quad g_c^{cb} - g^c = 0,$ $g_b^{cb} - g^b = 0, \quad g^{cb} = g_c^{cb} + g_b^{cb}$ $\frac{1}{T} (q^{cb} + q^c + q^b + q^0 - \mu_c^- g_c^{cb} - \mu_b^- g_b^{cb} - \mu_s^+ g^c - \mu_b^+ g^b) + \sigma = 0$	$\eta = \frac{g^{cb}}{ P } = \frac{g^{cb}}{ g^c (\mu_c^+ - \mu_c^-) +  g^b (\mu_b^+ - \mu_b^-) + T \sigma}$
Noncyclic binary mixture separation	$g_0 = g_1 + g_2, \quad g_0 x_0 - g_1 x_1 - g_2 x_2 = 0,$ $q^+ - q^- - g_0 h_0 - g_1 h_1 - g_2 h_2 = 0,$ $\frac{q^+}{T^+} - \frac{q^-}{T^-} + g_0 s_0 - g_1 s_1 - g_2 s_2 + \sigma = 0$	$\eta = \frac{g_1}{q^+} = \frac{1}{F} \left( 1 - \frac{T^-}{T^+} \right) - \sigma \frac{T^-}{F q^+}$ $F = T^- (\Delta S_{01} + a \Delta S_{02}) - \Delta h_{01} - a h_{02},$ $\Delta h_{0i} = C_p (T_0 - T_i),$ $\Delta S_{01} = \Delta S_{cm0} - \Delta S_{cmi}$ $+ C_p \ln \left( \frac{T_0}{T_i} \right) - C_p \ln \left( \frac{P_0}{P_i} \right), \quad i = 1, 2$
Absorption-stripping cycle	$q^a + q^s = 0, \quad g^a + g^s = 0,$ $\frac{q^a}{T_a} + q^s T_s - \frac{\mu_a q^a}{T_a} - \frac{\mu_s g^s}{T_a} + \sigma = 0$	$\eta = \frac{g^s}{q^a} = \frac{1/T_a - 1/T_s}{\mu_s/T_s - \mu_a/T_a}$ $- \frac{1/g^s}{\mu_s/T_s - \mu_a/T_a}$
Rectification	$g_g h_g + g_b h_b + g_f h_f + q^+ + q^- = 0,$ $g_g x_{gi} + g_b x_{bi} + g_f x_{fi} = 0, \quad i = 1, \dots, l$ $g_g s_g + g_b s_b + g_f s_f + q^+ / T_b + q^- / T_g + \sigma = 0$	$\eta = \frac{g_f}{q^+} = \frac{g_f (1/T_g - 1/T_a)}{\sum_{i=b,g,f} (g_i s_i - g_i h_i / T_g) + \sigma}$
Internal combustion engine	$g_1 b_1 + g_2 h_2 + q_0 - P = 0,$ $g_1 s_1 + g_2 s_2 + \frac{g_0}{T} + \sigma = 0$ $g_1 + g_2 = 0$	$\eta = \frac{P}{g_1} = g^1 - g^2 - \sigma \frac{T}{g_1}$ $g^i = h_i - T s_i, \quad i = 1, 2$

#### IV. CHEMICAL PROCESSES WITH MINIMAL ENTROPY PRODUCTION

As an example of application of the criterion of minimum  $k_{dis}$ , we consider the system in which the following chemical processes occur:

$$- \sum_{l \in \nu_{1j}} \alpha_{jl} K_l = \sum_{l \in \nu_{2j}} \alpha_{jl} K_l, \quad j = 1, \dots, r, \quad (3)$$

where  $K_l$  are the components which participate in reaction  $l$ ,  $l = 1, \dots, n$ ,  $n$  is the number of components,  $\nu_{1j}, \nu_{2j}$  are the subsets of components which participate in direct and re-

verse  $j$ th reactions correspondingly,  $r$  is the number of reactions,  $\alpha_{jl}$  are the stoichiometric coefficients for the components participating in direct reaction  $l \in \nu_{1j} \alpha_{jl} < 0$ , and in reverse reaction  $-l \in \nu_{2j} \alpha_{jl} > 0$ . The temperature and the pressure are constant for this system. We assume that uniform values of the intensive variables of the system are established much more quickly than the characteristic time of the chemical reaction system, i.e., faster than any bottleneck process. Hence, the system is spatially uniform at any instant of time. The problem of calculating the regime yielding the minimal entropy production for the isothermal chemical reaction system with the given intensity takes the form

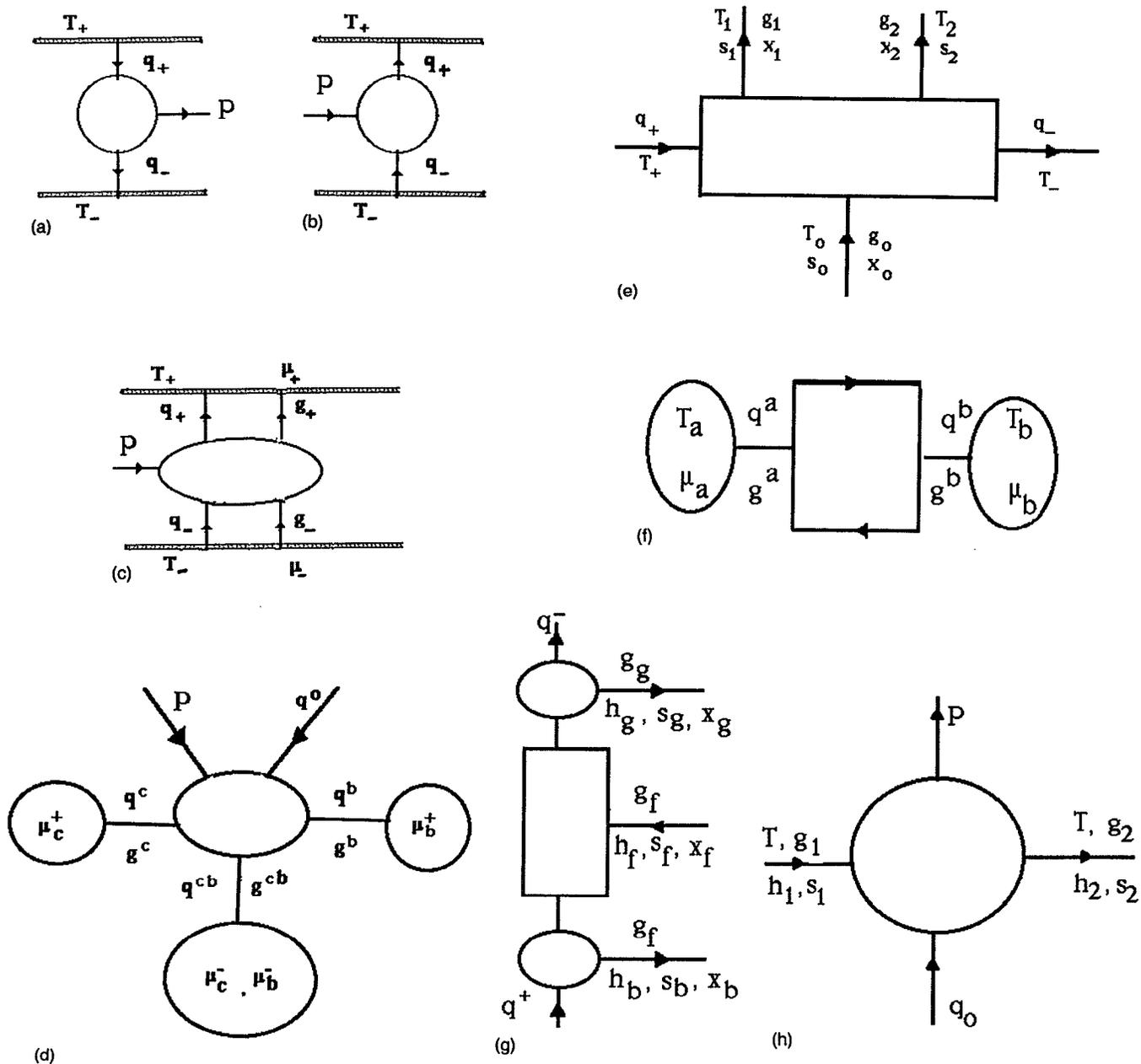


FIG. 1. Structured schemes of the standard processes: (a) the cycle of a heat engine; (b) the cycle of a refrigerator and a heat pump; (c) the diffusion-mechanical cycle; (d) the cycle of binary mixture separation; (e) noncyclic binary mixture separation; (f) the absorption-stripping cycle; (g) rectification; (h) an internal combustion engine.

$$\sigma = \frac{V}{\tau} \sum_{j=1}^r \int_0^\tau w_j(t) \frac{A_j(t)}{T} dt \rightarrow \min, \quad (4)$$

$$\frac{1}{\tau} \int_0^\tau w_j(t) dt = w_{j0}, \quad j = 1, \dots, r, \quad (5)$$

$$V \frac{dC_l}{dt} = \sum_{j=1}^r \alpha_{jl} w_j, \quad C_j(0) = C_{j0}, \quad l \in M, \quad (6)$$

here  $w_j$  is the velocity of the  $j$ th reaction,  $w_{j0}$  is the given value of the average velocity of this reaction,  $C_l$  is the molar concentration of the  $l$ th component,  $V$  is the volume of the

reaction zone,  $M$  is the subset of components whose concentrations change due to chemical process only (we assume that the concentrations of the other component are controllable externally by the operator of the system), the  $j$ th affinity  $A_j = \sum_{l=1}^n \alpha_{jl} \mu_l$ , and  $\mu_l$  is the chemical potential of the  $l$ th component.

The velocity of the chemical reaction can be described by different laws for the two cases, near equilibrium and far from equilibrium. We consider them one at a time.

### A. The system is near equilibrium

We assume that there is linear dependence of the velocities of the reactions on the thermodynamic forces

TABLE II. Dissipative characteristics of some standard systems. Here  $k$  is coefficient of heat or mass transfer;  $F, f$  are total and current contact surfaces for stationary regime and contact times for batch regime;  $q, g$  are the mass and heat fluxes;  $T_i, C_i$  ( $i=1,2$ ) are the temperatures and concentrations of the fluxes;  $W$  is the water equivalent of the heat flux;  $G_1$  is the mass rate of the first flux;  $m$  is a constant calculated from condition of minimal dissipation;  $R$  is the universal gas constant;  $J$  is the vector of fluxes;  $X$  is the vector of thermodynamic forces;  $L$  is the matrix of kinetic coefficients; and an overbar denotes the averaging over  $f$ .

Process	Conditions of the minimal dissipation	Minimal entropy production
Heat exchange of two fluxes	$\frac{T_1(f)}{T_2(f)} = 1 - \frac{\beta}{kF}$ $\beta = W \ln \left( 1 - \frac{\bar{q}}{WT_1(0)} \right)$	$\sigma^* = \frac{\beta^2}{kF - \beta}$
Linear interaction of thermodynamic systems $J = LX$	$X = \text{const}$ $J = \bar{j}$	$\sigma^* = \bar{j} L^{-1} \bar{j}$
One-way isothermal mass transfer	$c_2(f) = c_1(f) + \frac{m}{2} - \sqrt{c_1(f)m + (m/4)}$ $\int_{c_1(F)}^{c_1(0)} \frac{G}{(1-c_1^2)k\sqrt{c_1m + (m/4)} - (m/2)} = F$ $g(c_1, c_2) = k[c_1(f) - c_2(f)]$	$\sigma^* = \int_{c_1(F)}^{c_2(0)} \frac{RG}{(1-c_1)^2} \times \ln \frac{\sigma_1}{c_1 + (m/2) - \sqrt{c_1m + (m^2/4)}} dc_1$
Two-way isothermal equimolar mass transfer (binary rectification)	$\frac{\partial g}{\partial c_1} / \frac{\partial g}{\partial c_2} = m \frac{c_2(f)[1-c_2(f)]}{c_1(f)[1-c_1(f)]}$ $\frac{dc_1}{df} = -\frac{g(c_1, c_2)}{G_1}$ $c_1(0) = C_{10}, \quad c_1(F) = c_{1,F}$	$\sigma^* = R \int_0^F g(c_1, c_2) \ln \left( \frac{c_1(1-c_2)}{c_2(1-c_1)} \right) df$

$$w_j = \sum_{k=1}^r L_{jk} \frac{A_k}{T}, \quad (7)$$

in which case the problem (4)–(6) is reduced to the average problem<sup>20</sup>

$$(\bar{w}^T L^{-1} \bar{w}) \rightarrow \min, \quad \bar{w} = w_0, \quad (8)$$

where  $w = \{w_j\}$  is the vector of reactions velocities,  $L^{-1}$  is the inverse of the matrix  $L = \|L_{ij}\|$ , and the overbar denotes the operation of averaging over time  $\bar{f} = (1/\tau) \int_0^\tau f(t) dt$ .

The solutions of this problem are the constant velocities of reactions

$$w_j^*(t) = w_{j0} \quad (9)$$

and the minimal entropy production is

$$\sigma^* = w_0^T L^{-1} w_0.$$

This solution can be realized if we can control concentrations of at least  $r$  components. The optimal dependencies of their concentrations on time are to be found from conditions (6), (8), and (9). If the components are ideal gases, the velocities take the form

$$w_{j0} = - \sum_{k=1}^r \frac{L_{jk}}{T} \left( \sum_{l=1}^n \alpha_{kl} [\mu_l(T) + RT \ln C_l(T)] \right), \quad j = 1, \dots, r. \quad (10)$$

The concentrations of the other components are

$$C_l(t) = C_{l0} + \left( \sum_{j=1}^r \alpha_{jl} w_{j0} \right) t. \quad (11)$$

If only one reaction occurs ( $r=1$ ) and  $L$  is a scalar, then the single control concentration (call it  $C_c$ ) is defined by the expression

$$C_c(t) = \left( \frac{1}{d} \prod_{l=1, l \neq c}^n (C_{l0} + \alpha_l w_0 t)^{\alpha_l} \right)^{1/\alpha_c}, \quad (12)$$

where

$$d = \exp \left[ \left( \sum_{l=1}^n \alpha_l \mu_l(T) \right) [(RT) - w_0/(LR)]^{-1} \right].$$

If several reactions occur in the system then the optimal concentrations should be found by solving the set of Eqs. (10) and (11) which are linear with respect to the logarithms of the unknown concentrations.

## B. System is far from equilibrium

We do not treat the general case of the system far from equilibrium. Rather, we assume that only one reaction occurs in the gas phase in the system and that it is described by the law of mass action

$$w = w_1 - w_2, \quad (13)$$

where  $w_1 = k_1 \prod_{i=1}^{\nu} (C_i)^{-\alpha_i}$  and  $w_2 = k_2 \prod_{i=\nu+1}^n (C_i)^{\alpha_i}$  are the velocities of the direct and reverse reactions,  $l=1, \dots, \nu$

stand for the components which participate in the direct reaction, and  $l = \nu + 1, n$  for the components in the reverse reaction.

Taking into account that

$$A = RT \ln \left( \frac{k_l}{\prod_{i=1}^n C_i^{\alpha_i}} \right) = RT (\ln w_1 - \ln w_2),$$

where  $k_l = k_1/k_2$  is the equilibrium constant of the reaction, we reduce the problem (4)–(6) to the following form:

$$\begin{aligned} \sigma &= \frac{V}{\tau} \int_0^{\tau} w(t) \frac{A(t)}{T} dt \\ &= \frac{VR}{\tau} \int_0^{\tau} [w_1(t) - w_2(t)] \ln \left( \frac{w_1(t)}{w_2(t)} \right) dt \rightarrow \min, \end{aligned} \quad (14)$$

subject to

$$\frac{1}{\tau} \int_0^{\tau} w(t) dt = w_0. \quad (15)$$

If we assume that  $w_1 > w_2$  and that the velocity of the direct reaction is restricted

$$w_1 < w^{\max}, \quad (16)$$

the problem (14), (15), (16) becomes the problem of the average. This has a solution

$$w_1^*(t) = w^{\max}, \quad w_2^*(t) = w^{\max} - w_0,$$

$$\sigma^* = VR w_0 \ln \left( \frac{w^{\max}}{w^{\max} - w_0} \right).$$

The optimal dependencies of concentrations on time are to be found from conditions

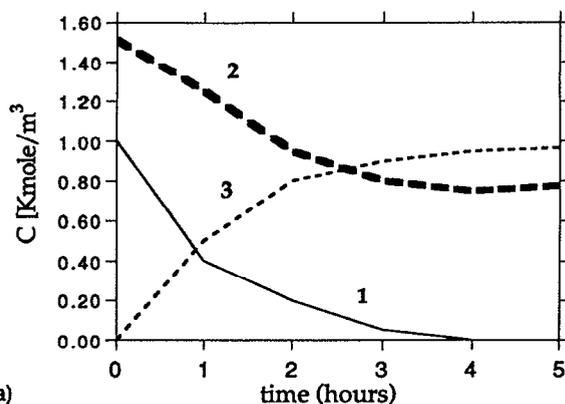
$$k_1 \prod_{l=1}^{\nu} [C_l(t)]^{-\alpha_l} = w^{\max}, \quad k_2 \prod_{l=\nu+1}^n [C_l(t)]^{\alpha_l} = w^{\max} - w_0,$$

$$C_l^*(t) = C_{l0} + \left( \frac{\alpha_l w_0}{V} \right) t, \quad l \in D.$$

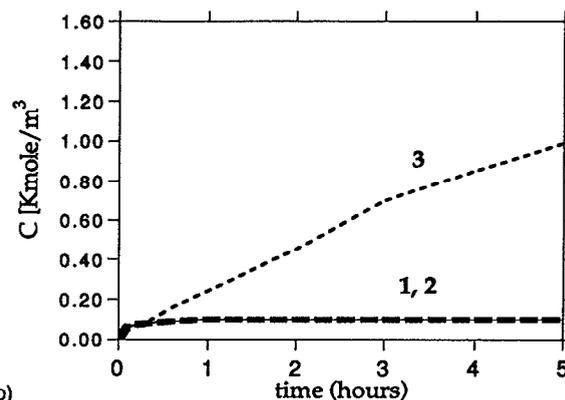
Thus, to control the process optimally it is necessary to increase the concentrations of the components which participate in the direct reaction, for example, to add them periodically to the system, and to decrease concentrations of the components which participate in the reverse reaction, for example, to withdraw them periodically.

The control of the irreversible chemical reaction far from equilibrium is simpler than the near-equilibrium system because one only needs to adjust the concentrations in the system to keep the velocity of reaction constant. As an example we consider the process  $K_1 + K_2 \xrightleftharpoons[k_2]{k_1} K_3$ ,  $k_1 \gg k_2$ . Here  $K_1$  is

the styrene-divinylbenzene copolymer,  $K_2$  is trimethylamine, and  $K_3$  is the anion-exchanger AB-17-8. The optimal dependence of the concentrations on time have been found from Eqs. (11) and (12) and the corresponding rates of the concentration changes have been found from equations of material balance. It turned out that the optimal dependencies of rates on time are approximated by straight lines parallel to



(a)



(b)

FIG. 2. Dependencies on time for (1) the concentrations of styrene-divinylbenzene copolymer, (2) the concentration of trimethylamine, and (3) the concentration of anion-exchanger. (a) The regime when all components are placed into reactor before the start of the process; (b) the optimal regime.

the abscissa. Figure 2(a) illustrates the case in which components are placed in the reactor before the process is allowed to start. Figure 2(b) shows the optimal regime. The dependencies of concentrations on time for the styrene-divinylbenzene copolymer are shown by curves 1, for trimethylamine by curves 2, and for anion-exchanger AB-17-8 by curve 3. The results of modeling showed that the approximation to the optimal regime allows us to reduce the waste of raw material, specifically the surplus of introduced trimethylamine, about 26%.

Similar problems can be formulated for the steady state of a chemical process that occurs in the regime of ideal displacement in a piped flow reactor. The only difference is that instead of clock time, one should use the time that the reagents spend in the reactor.

## V. DISTRIBUTION OF POWER AND CALCULATION OF THE MINIMAL ENTROPY PRODUCTION IN A SET OF PARALLEL HEAT ENGINES

As a second example we consider the use of the dissipation coefficient for estimating the thermodynamic ideality of a system of  $n$  parallel heat engines. It is assumed that the total power  $\dot{P}$  of this system and all the coefficients of heat transfer between the hot and cold reservoirs and each of the working engines are given. The actual entropy production  $\dot{\sigma}$  in this system should be compared with the possible minimal

$\bar{\sigma}^*$ . The entropy production in each one of the heat engines in the system must be minimized subject to the given total power and this power has to be distributed among the engines in such a way that

$$\bar{\sigma} = \sum_{i=1}^n \sigma_i^*(P_i) \rightarrow \min, \quad \sum_{i=1}^n P_i = \bar{P}. \quad (17)$$

The solution of this problem gives  $\bar{\sigma}^*$  which characterizes the thermodynamically ideal regime, and thus allows us to calculate the dissipation coefficient  $k_{\text{dis}} = \bar{\sigma}/\bar{\sigma}^*$  and to find out how the power load has to be distributed among the engines.

To solve this problem we use the heat and entropy balance equations for this system,

$$\sum_{i=1}^n q_i^+ - \sum_{i=1}^n q_i^- - \bar{P} = 0, \quad (18)$$

$$\frac{\sum_{i=1}^n q_i^+}{T^+} - \frac{\sum_{i=1}^n q_i^-}{T^-} + \sum_{i=1}^n \sigma_i = 0. \quad (19)$$

Here  $q_i^+$  and  $q_i^-$  are the heat fluxes between the working

body of the  $i$ th engine and the hot and cold reservoirs, respectively. All hot reservoirs have approximately the same temperature  $T^+$  and likewise the temperatures of all cold reservoirs are close to the common value  $T^-$ . Denoting the result of summation on  $i$  from 1 to  $n$  as overbar we obtain

$$\bar{\sigma} = \frac{1}{T^-} (\bar{q}^+ \eta_r - \bar{P}), \quad (20)$$

where  $\eta_r$  stands for the efficiency of the reversible Carnot cycle. Thus, decreases of  $\bar{\sigma}$  corresponds to decreases of energy consumption.

The problem of optimal distribution of the power load takes the form

$$\bar{q}^+ = \sum_{i=1}^n \frac{P_i}{\eta_i(P_i, \alpha_i^+, \alpha_i^-, T^+, T^-)} \rightarrow \min, \quad \sum_{i=1}^n P_i = \bar{P}. \quad (21)$$

Here  $\eta_i$  is the maximal efficiency coefficient for the irreversible heat engine with heat-transfer coefficients  $\alpha_i^+$  and  $\alpha_i^-$  between the hot and cold reservoirs and the working body, respectively and power of the  $i$ th system is  $P_i$ . The analytical expressions for these were obtained in Ref. 9,

$$\eta_i = \frac{2P_i}{P_i + [\alpha_i(T^+ - T^-)/4] - [P_i^2 - (\alpha_i P_i/2)(T^+ + T^-) + (\alpha_i^2/16)(T^+ - T^-)^2]^{1/2}}. \quad (22)$$

Here  $\alpha_i$  is the equivalent coefficient of heat transfer,

$$\alpha_i = \frac{\alpha_i^+ \alpha_i^-}{(\sqrt{\alpha_i^+} + \sqrt{\alpha_i^-})^2}. \quad (23)$$

After substitution of  $\eta_i$  into Eq. (22) and solution of this problem using the method of Lagrange multipliers, we get the following as the conditions of minimal total dissipation:

$$\frac{2P_i - \alpha_i s}{\sqrt{P_i^2 - \alpha_i P_i s + \alpha_i^2 \delta^2}} = \text{const}, \quad i = 1, \dots, n. \quad (24)$$

Here

$$s = \frac{T^+ + T^-}{2}, \quad \delta = \frac{T^+ - T^-}{4}.$$

Condition (24) together with given value of the total power allows us to calculate  $P_i^*$  and then  $q_i^+$  from expression (21) for the given values of  $s$ ,  $\delta$ , and  $\alpha_i$ . Then the value of  $\sigma^*$  is to be found from Eq. (20).

## VI. CONCLUSIONS

Every process operating with given intensity inevitably produces some entropy. The minimal value of this entropy and the corresponding regime of operation can now be calculated. It is reasonable to take this regime as a thermodynamically ideal one and to compare the real processes with it in order to determine how close they are to their limit. To characterize this closeness numerically we suggest using the ratio of the actual and minimal entropy production (2), instead of the ratio of the actual to the (reversible) Carnot efficiency. During analysis of the process or of its stages, it is more relevant to calculate not the exergy losses but the dissipation coefficients  $\eta_{\text{dis}}$  or increments  $\Delta S - \Delta S^*$  and then try to improve the process on the basis of these. The thermodynamically optimal dependencies of the fluxes on time should be taken into account during the design of the real control parameters: rates of flow of materials, temperatures and concentrations of the input fluxes. Note that in some cases, for example, the counter flow heat exchange with a linear law of heat transfer, the thermodynamically optimal regime can be realized and the value of  $\eta_{\text{dis}}$  set to 1.<sup>13</sup>

The dissipation coefficient (or entropy production) is also preferable to use because it depends on the parameters of the system itself only, in contrast to the exergy, which depends on the parameters of the environment, which can be (and often are in practice) unknown or far from the average values. This is especially a problem with concentrations.

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