

Finite-time thermodynamics: Conditions of minimal dissipation for thermodynamic process with given rate

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The class of thermodynamic processes with given rate and minimal entropy production is considered. The general conditions they obey are derived. It is shown how the application of those conditions to a number of particular systems produces a number of known bounds on entropy production (for heat and mass transfer processes and chemical conversion) as well as previously unknown bounds (for throttling, crystallization, and mechanical friction). [S1063-651X(98)04307-4]

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I. INTRODUCTION

The world we live in is the world of irreversible processes. The more intensive the utilization of natural resources (that is, more powerful machines, high gas and liquid flow rates, heat and mass transfer rates, etc.), the higher the driving forces of the processes and their irreversibilities. Also, the maximal possibilities of the majority of thermodynamic systems (that is, heat engine efficiency, work due to alignment of the parameters of the subsystems, energy losses in gas and liquid separation processes, etc.) [1,2] are limited by the irreversibilities of the processes in them. These possibilities reach optima in reversible regimes when durations of the processes are as long as possible and their intensities are as low as possible. Finite-time thermodynamics have been developed to provide in-principle limits of performance for processes operating within finite intervals or at a nonzero rate. It is reviewed, e.g., in [3]. Within this approach endoreversible processes are generally considered where the system consists of a number of subsystems that are internally reversible and the production of entropy is caused by the exchange between subsystems. Since in the majority of cases the performance limits correspond to the processes with minimal dissipation, a number of minimal entropy production problems in a variety of systems have been analyzed and a number of bounds on the entropy production have been obtained (in some cases the corresponding pathways were also obtained) [3–8]. As a rule, each such result was a solution of a completely new variational problem requiring significant effort to obtain. In this paper we derive general conditions of minimal dissipation that can be applied to a wide range of thermodynamic systems in a uniform way in order to obtain conditions of minimal dissipation and corresponding bound for a particular system. We demonstrate how this can be done by deriving both already known results (for heat transfer, mass transfer, and chemical conversion processes)

and previously unknown results (for throttling and crystallization processes).

As a rule the bounds are obtained here not as closed formulas but in algorithmic form as sets of nonlinear algebraic equations that can be solved easily via routine numerical methods.

These bounds and corresponding pathway conditions can be used to design the thermodynamically most efficient processes, to estimate how close is a current regime to the thermodynamic limit, to construct areas in a process state space that are thermodynamically feasible, etc.

II. THE CONDITIONS OF MINIMAL DISSIPATION

We consider the processes of minimal dissipation with given average intensity (or given average values of driving forces). Thus we try to find such a distribution of driving forces in time or space in which the irreversibility of the process is minimal and the averaged values of the driving forces over this distribution are fixed. The irreversibility of the process is estimated via the entropy production (dissipation) in the system.

A. Formulation of the problem

The thermodynamic process is characterized by two types of variables. The first one is the intensive variable. These are temperature, pressure, concentration, etc. The second type is the extensive variable. These are volume, internal energy, mole number of a substance in the system, entropy, etc. When a homogeneous system is divided into two subsystems, their intensive variables stay the same as they were in undivided system. As for extensive variables, they decrease in proportion to the ratio of the subsystem volume to the initial total volume. Let vector u_i denote the intensive variables and let x_i denote the extensive variables for the i th subsystem. When two subsystems contact with each other, the difference between u_1 and u_2 causes the flow $J(u_1, u_2)$. The function J for scalar variables u_1 and u_2 has the following features:

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$$\frac{\partial J}{\partial u_1} > 0, \quad \frac{\partial J}{\partial u_2} < 0, \quad (1)$$

$$J(u_1, u_2) = 0, \quad u_2 = u_1.$$

The argument l can describe ‘‘time’’ or ‘‘contact surface.’’ In a more general case $J = (J_1, \dots, J_j, \dots, J_m)$ is a vector of flows, $u_\nu = (u_{\nu 1}, \dots, u_{\nu j}, \dots, u_{\nu m})$ is a vector of the intensive variables of the ν th subsystem ($\nu = 1, 2$). The difference between the vectors u_1 and u_2 yields vector of the driving forces X_j . Each X_j depends on u_{1j} and u_{2j} only and satisfies Eq. (1). The entropy production, which characterizes the irreversibility of the process, is equal to the average value of the scalar product of the vectors of flows and driving forces [9,10],

$$\bar{\sigma} = \frac{1}{L} \int_0^L \sum_{j=1}^m J_j(u_1, u_2) X_j(u_{1j}, u_{2j}) dl. \quad (2)$$

We use overbars throughout the paper to denote averaging. Since functions J_j and X_j obey conditions (1) the summand of the integrand is positively defined.

Assume that we can change one of the intensive variables [$u_2(l)$ for definiteness]. Let V be the set of all feasible values of $u_2(l)$. Then the second variable $u_1(l)$ is determined by the equation

$$\frac{du_{1j}}{dl} = \varphi_j(u_1, u_2), \quad u_1(0) = u_{10}, \quad j = 1, \dots, m. \quad (3)$$

For each particular system we will define a particular form of the function $\varphi_j(u_1, u_2)$.

We also assume that the average values of all or of some of the flow vector components are given,

$$\frac{1}{L} \int_0^L J_j(u_1, u_2) dl = \bar{J}_j, \quad j = 1, \dots, k_1, \quad k_1 \leq m. \quad (4)$$

We will try to find the minimal entropy production $\bar{\sigma}$ subject to these conditions.

B. Scalar case

Let us consider the scalar case first ($m = 1$). Here the problem of minimal entropy production can be written as

$$\bar{\sigma} = \frac{1}{L} \int_0^L J(u_1, u_2) X(u_1, u_2) dl \rightarrow \min_{u_2 \in V}, \quad (5)$$

subject to

$$\frac{du_1}{dl} = \varphi(u_1, u_2), \quad u_1(0) = u_{10}, \quad (6)$$

$$\frac{1}{L} \int_0^L J(u_1, u_2) dl = \bar{J}. \quad (7)$$

The value L may be fixed or be a variable that has to be chosen optimally.

Let us assume that in the optimal process $\varphi(u_1, u_2) \neq 0$. It allows to substitute the variable l with u_1 ,

$$dl = \frac{du_1}{\varphi(u_1, u_2)}. \quad (8)$$

After this substitution the problem (5)–(7) takes the form

$$\bar{\sigma} = \frac{1}{L} \int_{u_{10}}^{u_1(L)} \frac{J(u_1, u_2) X(u_1, u_2)}{\varphi(u_1, u_2)} du_1 \rightarrow \min_{u_2 \in V, u_1(L)}, \quad (9)$$

subject to

$$\frac{1}{L} \int_{u_{10}}^{u_1(L)} \frac{J(u_1, u_2)}{\varphi(u_1, u_2)} du_1 = \bar{J}, \quad (10)$$

$$\frac{1}{L} \int_{u_{10}}^{u_1(L)} \frac{du_1}{\varphi(u_1, u_2)} = 1, \quad (11)$$

where we assume that L is fixed. The control variables in this problem are the function $u_2(u_1)$ and the value of $u_1(L)$. This problem is much simpler than the initial problem (5)–(7) since it does not contain differential constraint (6). The solution $u_2^*(u_1)$ of this problem is not a function of l but of u_1 , which is more useful in many cases.

The Lagrange function for the problem (9)–(11) is written as

$$R = \frac{1}{\varphi(u_1, u_2)} \{J(u_1, u_2)[X(u_1, u_2) + \lambda_1] + \lambda_2\}, \quad (12)$$

where λ_1 and λ_2 are Lagrange multipliers. The optimality conditions of the problem (9)–(11) are the conditions of function R minimum on u_2 for each given u_1 ,

$$u_2^*(u_1, \lambda) = \arg \min_{u_2 \in V} R(u_1, u_2, \lambda_1, \lambda_2). \quad (13)$$

When the feasible set V is unconstrained, the stationarity condition of the function R with respect to u_2 has the form

$$\frac{dR}{du_2} = (X + \lambda_1) \left(\varphi \frac{\partial J}{\partial u_2} - \frac{\partial \varphi}{\partial u_2} J \right) + \varphi J \frac{\partial X}{\partial u_2} - \lambda_2 \frac{\partial \varphi}{\partial u_2} = 0. \quad (14)$$

Conditions (14), (10), (11) and the condition of minimum of the Lagrange function’s integral with respect to $u_1(L)$,

$$\begin{aligned} \frac{d}{du_1(L)} \left(\int_{u_{10}}^{u_1(L)} R(u_1, u_2, \lambda_1, \lambda_2) du_1 \right) \\ = R(u_1(L), u_2(u_1(L)), \lambda_1, \lambda_2) = 0, \end{aligned} \quad (15)$$

determine $u_2^*(u_1), u_1(L), \lambda_1, \lambda_2$.

The problem becomes much simpler if the rate of u_1 change is proportional to the flow,

$$\varphi(u_1, u_2) = C(u_1) J(u_1, u_2). \quad (16)$$

In this case the first term in Eq. (14) is equal to zero and this equation has the following form:

$$J^2(u_1, u_2) = \lambda_2 \left(\frac{\partial J(u_1, u_2)}{\partial u_2} \right) / \left(\frac{\partial X(u_1, u_2)}{\partial u_2} \right). \quad (17)$$

The condition (10) in this case is

$$\int_{u_{10}}^{u_1(L)} \frac{du_1}{C(u_1)} = \bar{J}L. \quad (18)$$

It determines $u_1(L)$ independently from the optimal solution $u_2^*(u_1)$.

C. Vector case

In a case of vector parameters the optimality conditions for problem (2)–(4) in the form of the Pontryagin maximum principle have the following form [11]:

$$H = \sum_{j=1}^k [\psi_0 J_j(u_1, u_2) X_j(u_{1j}, u_{2j}) + \psi_j \varphi_j(u_1, u_2) + \lambda_j J_j(u_1, u_2)],$$

$$\frac{d\psi_j}{dl} = -\frac{\partial H}{\partial u_{1j}}, \quad j = 1, \dots, k, \quad \psi_j(L) = 0, \quad (19)$$

$$u_{2j}^*(l) = \arg \max_{u_{2j} \in V} H(u_1^*(l), \psi(l), \lambda), \quad j = 1, \dots, k, \quad (20)$$

where ψ_0 and λ_j are Lagrange multipliers and $\psi_j(l)$ are adjoint variables. In the nonsingular case $\psi_0 = -1$ and $\lambda_j = 0$ for $j > k_1$. The analytical solution of the set of Eqs. (19), (20), (3), and (4) is possible in very few cases only. If we assume that there are only small deviations from the thermodynamic equilibrium, then the flows J depend on the forces X via the Onsager equations

$$J = AX^T. \quad (21)$$

Here A is a positively defined matrix of phenomenological coefficients. Superscript T denotes transposition. The integrand of Eq. (2) is a positively definite square form with respect to thermodynamic forces. In this case the problem can be solved much easier. We do it in two steps.

During the first step, we break conditions (3) and find the minimum of average value of square form,

$$\bar{\sigma} = \frac{1}{L} \int_0^L (XAX^T) dl = \overline{(XAX^T)} \rightarrow \min, \quad (22)$$

subject to

$$\sum_{\nu=1}^k a_{\nu j} \overline{X_\nu} = \bar{J}_j, \quad j = 1, \dots, k_1 \quad (k_1 \leq k). \quad (23)$$

Here again the overbar denotes averaging over L . The vector of the driving forces X is the control variable in this problem. Since the problem (22) and (23) is a convex problem its solution is a constant X [12]. Hence the finding of optimal X_ν^* is reduced to the solution of a simple quadratic programming problem,

$$X^* A (X^*)^T \rightarrow \min, \quad \sum_{\nu=1}^k a_{\nu j} X_\nu^* = \bar{J}_j, \quad j = 1, \dots, k_1.$$

During the second step, we find such values of vector $u_2 \in V$ that the conditions

$$X_j(u_{1j}, u_{2j}) = X_j^*, \quad j = 1, \dots, k, \quad (24)$$

and Eqs. (3) hold. We do that by assuming that u_1 are parameters and solving the set of Eqs. (24) with respect to u_2 . This yields the dependence $u_2(u_1)$. After substituting this function into Eqs. (3) and solving those equations, we obtain $u_1^*(l)$ and $u_2^*(u_1^*(l)) = u_2^*(l)$. If it turns out that these solutions are feasible [that is, $u_2^*(l) \in V$], then problems (22) and (23) are equivalent to the initial problem (2)–(4), and (21) and we found the process with minimal dissipation. If $u_2^*(l) \notin V$, then the solution of problems (22) and (23) provides the bound on the minimal entropy production.

The second case when the problem (2)–(4) becomes significantly simpler is when the flows are independent from each other. Each flow depends on its own set of variables,

$$J_j = J_j(u_{1j}, u_{2j}), \quad j = 1, \dots, k.$$

The same is true for the forces X_j and $u_1(L)$, given by

$$\frac{du_{1j}}{dl} = \varphi_j(u_{1j}, u_{2j}), \quad u_{1j}(0) = u_{1j0}, \quad (25)$$

$$u_{1j}(L) = \bar{u}_{1j}, \quad j = 1, \dots, k.$$

Here the problem of minimal dissipation is decomposed into k scalar problems of the following form:

$$\bar{\sigma}_j = \frac{1}{L} \int_0^L J_j(u_{1j}, u_{2j}) X_j(u_{1j}, u_{2j}) dl \rightarrow \min, \quad (26)$$

subject to differential constraint (25) and

$$\frac{1}{L} \int_0^L \varphi_j(u_{1j}, u_{2j}) dl = \frac{u_{1j}(L) - u_{1j}(0)}{L}. \quad (27)$$

As it was done in the preceding section, one can write the optimality condition of this problem,

$$u_{2j}^* = \arg \min_{u_{2j} \in V_j} \left(\frac{1}{\varphi_j} (J_j X_j + \lambda_j) \right) = \arg \min_{u_{2j} \in V_j} R_j(u_{1j}, u_{2j}, \lambda_j), \quad (28)$$

which determines the optimal $u_{2j}^*(u_1, \lambda_j)$. In a weaker form of the stationarity of R_j on u_{2j} it is

$$(X_j + \lambda_j) \left(\varphi_j \frac{\partial J_j}{\partial u_{2j}} - \frac{\partial \varphi_j}{\partial u_{2j}} J_j \right) + \varphi_j J_j \frac{\partial X_j}{\partial u_{2j}} = 0. \quad (29)$$

The values of λ_j are to be found from the conditions

$$\int_{u_{1j}(0)}^{\bar{u}_{1j}} \frac{du_{1j}}{\varphi_j(u_{1j}, u_{2j}^*(\lambda_j, u_{1j}))} = L, \quad j = 1, \dots, k. \quad (30)$$

If only some of the $u_{1j}(L)$ are fixed [$u_{1j}(L) = \bar{u}_{1j}$, $j = 1, \dots, k_1$, $k_1 < k$], then λ_j and u_{1j}^* for $j = k_1 + 1, \dots, k$ are to be found jointly from the conditions

$$\left(\frac{1}{\varphi_j} (J_j X_j + \lambda_j) \right)_{u_{1j} = \bar{u}_{1j}, u_{2j} = u_2^*(\lambda_j, \bar{u}_{1j})} = 0.$$

These conditions follow from the Pontryagin maximum principle.

D. The choice of L

Introduction of the multiplier $1/L$ into criterion (2) and conditions (4) at fixed L does not change the optimal solution if L is finite, but it makes the problem meaningful if L tends to infinity. Besides, the value L itself can be a control variable, which should be chosen optimally. In this case the Lagrange functional for the corresponding extremal problem must be stationary with respect to L . For example, if L is an additional control variable in the problem (9)–(11), then its Lagrange functional has the form

$$\bar{R} = \frac{1}{L} \int_{u_{10}}^{u_1(L)} R(u_1, u_2, \lambda) du_1,$$

where the function R is determined by Eq. (12). The stationarity condition of \bar{R} with respect to L leads to the equation

$$\frac{d\bar{R}}{dL} = 0 \Rightarrow R(u_1(L), u_2(L), \lambda) = \frac{1}{L} \int_{u_{10}}^{u_1(L)} R(u_1, u_2, \lambda) du_1.$$

In the general problem (2)–(4), where L is an additional control variable, the condition

$$\begin{aligned} & \sum_{j=1}^k J_j(u_1(L), u_2(L)) [X_j(u_1(L), u_2(L)) + \lambda_j] \\ &= \frac{1}{L} \int_0^L \sum_{j=1}^k J_j(u_1, u_2) [X_j(u_1, u_2) + \lambda_j] dl \end{aligned} \quad (31)$$

is added to the set of Eqs. (19) and (20). Condition (31) is the consequence of the stationarity with respect to L of the integrated function H where the first and the third terms under the sum are multiplied by $1/L$.

III. MINIMAL DISSIPATION CONDITIONS FOR SOME THERMODYNAMIC PROCESSES

Let us show how these conditions of minimal dissipation are applied to particular processes.

A. Heat transfer

Consider a thermodynamic system that consists of two subsystems with the temperatures $T_1(l)$ and $T_2(l)$ and where heat is transferred between these subsystems. For example, this could be the counter-flux heat exchanger. The thermodynamic force X in the problem of heat transfer with minimal dissipation in this system is

$$X(T_1, T_2) = \left(\frac{1}{T_2} - \frac{1}{T_1} \right). \quad (32)$$

The flow J is the heat flow $q(T_1, T_2)$. In many cases we can assume that $\varphi = -[1/c_1(T_1)]q(T_1, T_2)$ and that the condition (6), which determines the dependence of T_1 on l , has the following form:

$$\frac{dT_1}{dl} = -\frac{1}{c_1(T_1)} q(T_1, T_2), \quad T_1(0) = T_{10}, \quad (33)$$

where $c_1(T_1)$ is the heat capacity of the heat source.

From the general conditions (17), (18), and (11) of the minimal dissipation for the given average rate of the heat flow \bar{q} for the heat transfer process, it follows that

$$q^2(T_1, T_2) = -\lambda_2 \frac{\partial q}{\partial T_2} T_2^2, \quad (34)$$

$$\int_{T_1(L)}^{T_{10}} c_1(T_1) dT_1 = \bar{q}L, \quad (35)$$

$$\int_{T_1(L)}^{T_{10}} \frac{c_1(T_1) dT_1}{q(T_1, T_2)} = L. \quad (36)$$

The first of these conditions yields $T_2^*(T_1, \lambda_2)$, the second condition determines $T_1(L)$, and the third condition determines the constant λ_2 .

For the linear law of heat exchange

$$q = \alpha(T_1 - T_2) \quad (37)$$

with the constant heat capacity c , the condition (34) yields

$$\alpha^2(T_1 - T_2)^2 = -\lambda_2(-\alpha)T_2^2 \Rightarrow \alpha \left(\frac{T_1}{T_2} - 1 \right)^2 = \lambda_2. \quad (38)$$

Thus for any l the ratio T_1/T_2 is constant and equal to

$$\frac{T_1}{T_2} = 1 + \sqrt{\frac{\lambda_2}{\alpha}}. \quad (39)$$

Because of $T_1(L) = T_{10} - \bar{q}L/c$ from Eq. (36) we have

$$\sqrt{\frac{\lambda_2}{\alpha}} = \frac{-(c/\alpha L) \ln(1 - \bar{q}L/cT_{10})}{1 + (c/\alpha L) \ln(1 - \bar{q}L/cT_{10})}. \quad (40)$$

The substitution of Eqs. (39) and (40) into the expression

$$\sigma = \frac{c}{L} \int_{T_1(L)}^{T_{10}} \left(\frac{1}{T_2(T_1)} - \frac{1}{T_1} \right) dT_1$$

yields the bound on the entropy production in a heat transfer process,

$$\sigma^* = \frac{c^2 \ln^2(1 - \bar{q}L/cT_{10})}{\alpha L + c \ln(1 - \bar{q}L/cT_{10})}.$$

For the following general law of heat exchange,

$$q(T_1, T_2) = \alpha(T_1^n - T_2^n), \quad (41)$$

when n is an integer, the condition (34) takes the form

$$\alpha(T_1^n - T_2^n)^2 = \lambda_2 n T_2^{n+1},$$

or

$$\frac{q(T_1, T_2)}{\alpha T_2^{n+1/2}} = \left(\frac{T_1^n}{T_2^{n+1/2}} - T_2^{n-1/2} \right) = \sqrt{\frac{\lambda_2 n}{\alpha}} = \text{const.} \quad (42)$$

At $n > -1$ then, the higher the temperature T_2 is, the higher is the heat flow, and if $n < -1$, the higher the temperature T_2 is, the lower is heat flow. If $n = -1$, then the heat flow that corresponds to the minimal dissipation is constant and equal to \bar{q} , and the minimal entropy production is

$$\sigma^* = \frac{\bar{q}^2 L}{\alpha}. \quad (43)$$

B. Isothermal mass transfer

Assume that the system consists of two subsystems with the same temperature $T(l)$ for all $l \in [0, L]$ and concentrations of the key component in the first subsystem $C_1(l)$ and in the second one $C_2(l)$. This key component is being transferred from the first subsystem into the second. C_i , $i=1,2$, are intensive variables of the problem. Both mass flow g and chemical potentials μ_i , $i=1,2$, depend on these concentrations and

$$J(u_1, u_2) \rightarrow g(C_1, C_2), \quad (44)$$

$$X(u_1, u_2) \rightarrow \frac{1}{T} [\mu_1(C_1, T) - \mu_2(C_2, T)].$$

It is assumed that the diffusion process does not change the pressure in the system. The initial concentration of the key component in the first subsystem is given. The average mass transfer rate \bar{g} is also given,

$$\frac{1}{L} \int_0^L g(C_1, C_2) dl = \bar{g}. \quad (45)$$

The entropy production due to diffusion is to be minimized:

$$\bar{\sigma} = \frac{1}{L} \int_0^L \frac{g(C_1, C_2)}{T} [\mu_1(C_1, T) - \mu_2(C_2, T)] dl \rightarrow \min. \quad (46)$$

In order to apply the general condition of minimal entropy production, one has to derive the differential equation (6) and function $\varphi(u_1, u_2) = \varphi(C_1, C_2)$. Since the flow of only the key component occurs, its concentration in the first subsystem and total quantity of substances in G_1 change according to the equation

$$\frac{d(G_1 C_1)}{dl} = \frac{dG_1}{dl} = -g(C_1, C_2). \quad (47)$$

From condition (47) it follows that

$$\frac{dC_1}{dl} = -\frac{1-C_1}{G_1} g(C_1, C_2), \quad C_1(0) = C_{10} \quad (48)$$

and

$$\frac{dG_1}{dC_1} = \frac{G_1}{1-C_1}.$$

Hence

$$G_1(C_1) = \frac{G_1(0)(1-C_{10})}{1-C_1} = \frac{\tilde{G}}{1-C_1},$$

where \tilde{G} is the amount of inert component in the first subsystem. Substitution of $G_1(C_1)$ into Eq. (48) yields

$$\frac{dC_1}{dl} = -\frac{1}{\tilde{G}} (1-C_1)^2 g(C_1, C_2), \quad C_1(0) = C_{10}. \quad (49)$$

Since the problem (46), (45), and (49) has the canonical form (5)–(7), its optimality conditions can be obtained by substituting Eqs. (17) and (18),

$$\begin{aligned} \frac{\partial T}{\partial C_2} \left(\frac{\partial \mu_1}{\partial T} - \frac{\partial \mu_2}{\partial T} - \frac{\mu_1 - \mu_2}{T} \right) - \frac{\partial \mu_2}{\partial C_2} \\ = \lambda_2 \left(\frac{\partial g}{\partial C_2} \right) \frac{T}{g^2(C_1, C_2)}, \quad \forall l \in [0, L], \end{aligned} \quad (50)$$

$$C_1(L) = \frac{C_{10} G_{10} - \bar{g} L}{G_{10} - \bar{g} L}. \quad (51)$$

For chemical potentials

$$\mu_i = \mu_0(P, T) + RT \ln C_i, \quad i=1,2, \quad (52)$$

we get $\partial \mu_2 / \partial C_2 = RT / C_2$, and conditions (50) have the form

$$-\frac{R}{C_2} = \lambda_2 \left(\frac{\partial g}{\partial C_2} \right) \frac{1}{g^2}. \quad (53)$$

The constant λ_2 is to be found from the condition

$$\int_{C_1(L)}^{C_{10}} \frac{\tilde{G}}{C_1 T(C_1, C_2) (1-C_1)^2} dC_1 = L \quad (54)$$

after substitution of $C_2^*(C_1, \lambda_2)$ in it. Backward substitution of the optimal λ_2^* into $C_2^*(C_1, \lambda_2)$ and into Eq. (49) gives optimal $C_1^*(l)$ and $C_2^*(l)$. Their substitution into the expression for σ gives the bound on the entropy production σ^* in the isothermal mass transfer process. If such a path can be found that the conditions (50) and (51) hold on it, then this bound will be realized.

If the diffusion flow is proportional to the chemical potential difference

$$g = \alpha [\mu_1(C_1) - \mu_2(C_2)]$$

and the temperature T is constant, then the solution is especially simple.

In this case from Eq. (50) it follows that

$$g^* = \text{const} = \bar{g},$$

$$\frac{dG}{dl} = \frac{\bar{g}(1-C_1)}{G_{10}-\bar{g}l} \Rightarrow C_1(l) = 1 - (1-C_{10}) \frac{G_{10}}{G_{10}-\bar{g}l}.$$

Let chemical potentials be in form (52). Then from the flow constancy condition it follows that the ratio

$$\frac{C_1}{C_2} = \exp\left(\frac{\bar{g}}{2T}\right)$$

is constant. The bound on entropy production here is

$$\bar{\sigma}^* = \bar{g}^2 / \alpha T.$$

Other laws of mass transfer are considered in [8].

C. Throttling

Let us consider gas transfer through a throttle. P_1 and P_2 denote pressure before and after the throttle. l denotes time. The flow rate of expansion is denoted as $g(P_1, P_2)$. Suppose that the process is isothermal, i.e., the temperature does not change. The entropy production is

$$\sigma = g(P_1, P_2) \frac{\mu_1(P_1, T) - \mu_2(P_2, T)}{T}. \quad (55)$$

For the ideal gas this expression takes the form

$$\sigma = g(P_1, P_2) \ln P_1 / P_2. \quad (56)$$

It is assumed that the duration of the process L and the average amount of gas transferred through the throttle during this time \bar{g} are fixed. It is also assumed that the volume from V from which gas is removed and the total amount of gas in the system are fixed. It is required to minimize the dissipation

$$\bar{\sigma} = \frac{1}{L} \int_0^L g(P_1, P_2) \frac{\mu_1(P_1, T) - \mu_2(P_2, T)}{T} dl \rightarrow \min \quad (57)$$

subject to

$$\frac{1}{L} \int_0^L g(P_1, P_2) dl = \bar{g}, \quad (58)$$

$$\frac{dP_1}{dl} = -\frac{RTg(P_1, P_2)}{V}, \quad P_1(0) = P_{10}. \quad (59)$$

Equation (59) determines the rate of pressure change when gas passes through the throttle.

The problem (57)–(59) has a canonical form (5)–(7) and (16). Equations (17) and (18) give the following optimality conditions for it:

$$Tg^2(P_1, P_2) = -\lambda_2 \left(\frac{\partial g}{\partial P_2} \Big/ \frac{\partial \mu_2}{\partial P_2} \right), \quad (60)$$

$$P_1(L) = P_{10} - \frac{RT}{V} \bar{g} L. \quad (61)$$

If it is assumed that the gas is ideal and

$$g(P_1, P_2) = \alpha(P_1 - P_2)^{1/2}$$

then the condition (60) leads to the following expression:

$$(P_1 - P_2)^3 / P_2^2 = \text{const} = \eta, \quad \forall l \in [0, L]. \quad (62)$$

In order to find the optimal dependence of $P_2^*(l)$ and the minimal entropy production $\bar{\sigma}^*$ one has to substitute the condition (62) into Eqs. (58) and (59). The optimal dependence of pressure is defined after Eqs. (59) and (62) are solved up to the constant η ,

$$P_2^*(l, \eta) = \left\{ \sqrt{\frac{4}{3} \eta^{2/3} - \frac{2}{3} \eta^{1/6} \left[\frac{\alpha RT}{V} l - f(P_{20}, \eta) \right]} - \frac{2}{3} \eta^{1/3} \right\}^3, \quad (63)$$

where

$$f(P_{20}, \eta) = \frac{3}{2} \eta^{-1/6} P_{20}^{2/3} + 2 \eta^{1/6} P_{20}^{1/3}. \quad (64)$$

The value P_{20} is to be found from Eq. (62) as the solution of the equation

$$P_{20} + \eta^{1/3} P_{20}^{2/3} = P_{10}. \quad (65)$$

The condition of the fixed duration of the process gives the equation that determines optimal η ,

$$\frac{1}{2} [P_{20}^{2/3} - P_2(L)^{2/3}] + \frac{2\eta}{3} [P_{20}^{1/3} - P_2(L)^{1/3}] = \frac{LRT\alpha\eta^{1/2}}{3V}. \quad (66)$$

The minimal entropy production is given by the following formula:

$$\bar{\sigma}^* = \frac{V}{RTL} \{ P_{10} (\ln P_{10} - 1) - P_1(L) [\ln P_1(L) - 1] - r(P_{20}) - r(P_2(L)) \}.$$

Here the function $r(P_2)$ is defined as

$$r(P_2) = P_2 (\ln P_2 - 1) + \eta^{1/3} P_2^{2/3} (\ln P_2 - 3/2).$$

The derived formulas give the bound on the minimal dissipation in the throttling process in algorithmic form. If the condition (62) does not hold in a throttling process, then its entropy production is higher than the entropy production of the process determined by Eqs. (63)–(66).

D. Crystallization

During crystallization process, the key component crystallizes out of solution onto the surface of the crystals already present, where its concentration is higher than the equilibrium concentration in the solution. The initial dimensions

(masses) of the crystals are disperse. At any instant, the set of crystals can be described by a distribution of their masses. We denote the concentration of the crystallizing substance in the liquid as C_1 and its equilibrium concentration under the given pressure P and temperature T as C_2 . The flux of mass is denoted as $g(C_1, C_2)$ and l denotes time. The entropy production in a crystallization process as in any mass transfer process is expressed by the following formula:

$$\sigma = g(C_1, C_2) \frac{\mu_1(C_1) - \mu_2(C_2)}{T}. \quad (67)$$

The chemical potentials are

$$\mu_1 = \mu^0(T, P) + RT \ln C_1$$

and

$$\mu_2 = \mu^0(T, P) + RT \ln C_2,$$

so that

$$\sigma = g(C_1, C_2) R \ln \frac{C_1}{C_2}. \quad (68)$$

First, we consider this process for a single crystal. The flow g depends on the net surface of the crystal F , which, in turn, depends on the mass of the crystal M . The net mass of the crystal changes according to the equation

$$\frac{dM}{dl} = \alpha F (C_1 - C_2), \quad M(0) = M_0, \quad M(L) = \bar{M}.$$

For the crystal with the mass M , the net surface is proportional to the $2/3$ power of its mass. Hence,

$$\frac{dM}{dl} = KM^{2/3} (C_1 - C_2). \quad (69)$$

The ratio K depends on the mass transfer ratio and the crystal shape and can be determined experimentally. We assume here that there is no nucleation and recrystallization.

The problem of minimal dissipation in crystallization process takes the form

$$\bar{\sigma} = \frac{1}{L} \int_0^L KM^{2/3} (C_1 - C_2) R \ln \frac{C_1}{C_2} dl \rightarrow \min_{C_1} \quad (70)$$

subject to constraint

$$\int_0^L KM^{2/3} (C_1 - C_2) dl = (\bar{M} - M_0). \quad (71)$$

The optimality condition for this problem,

$$\frac{M^{2/3} (C_1 - C_2)^2}{C_1} = \frac{\lambda_2}{KR} = \text{const} = \eta, \quad \forall l \in [0, L], \quad (72)$$

follows from the general conditions (17) and (18). Conditions (72) and Eq. (69) give the differential equation that determines $C^*(t)$ up to the constant η . In order to do that, we replace \dot{M} and M by \dot{C}_1 and C_1 :

$$\dot{C}_1^* = -\frac{\sqrt{\eta} \sqrt{C_1^*} (C_1^* - C_2)^3}{C_1^* + C_2}, \quad C_1(0) = C_{10}. \quad (73)$$

The constant η is to be found from Eq. (71) and c_{10} is determined by M_0 [Eq. (72)]. Their backward substitution into the expression for σ gives the bound on the entropy production in crystallization process σ^* .

If we do not assume that all crystals are the same, then the net surface F_Σ in the expression of the entropy production σ_Σ should be the result of averaging of $F_i(M_i)$ over all M_i . Since $F_i(M_i)$ is convex, the F_Σ is less than the value of the net surface calculated by assuming that the masses of all the crystals are the same and equal the average crystal mass at $t=0$. Since entropy production depends monotonically on the mass transfer coefficient, it increases if the surface of the crystal increases. Therefore the use of the dependence $\bar{F}_\Sigma = KM^{2/3}$ and the corresponding bound determined by Eqs. (71)–(73) give a lower bound on the entropy production in crystallization process.

E. Mechanical friction

Let us consider a system that consists of two subsystems separated by a piston. The pressures in these subsystems are denoted as P_1 and P_2 correspondingly. The temperature of the system T is constant during the process. The pressure difference causes the piston to move. The rate of the volume's change for each of the subsystems due to this pressure difference is denoted as $v(P_1, P_2)$. Since in most cases this velocity depends only on the difference $P_1 - P_2$, the rate of the entropy production may be written as

$$\sigma(\Delta P) = \sigma(P_1 - P_2) = \frac{v(P_1 - P_2)}{T} (P_1 - P_2) \rightarrow \min. \quad (74)$$

This value can be minimized if the average velocity value \bar{v} is given,

$$\frac{1}{L} \int_0^L v[P_1(l) - P_2(l)] dl = \bar{v}. \quad (75)$$

When $\Delta P = P_1 - P_2$ is written as $\Delta P(v)$, the problem of finding the regime of minimal dissipation takes the form

$$\frac{1}{T} \bar{\sigma}(v) = \frac{1}{T} \frac{1}{L} \int_0^L v \Delta P(v) dl \rightarrow \min, \quad \bar{v} = v_0. \quad (76)$$

This is a standard averaged problem of nonlinear programming. From the general theory of this problem [12], it follows that if $\sigma(v)$ is concave, then the optimal velocity must be constant and equal to \bar{v} . Otherwise the solution of the averaged problem of nonlinear programming Eq. (76) corresponds to the ordinate of the convex hull of the function $\sigma(v)$ at the point $v = \bar{v}$. The velocity takes no more than two values v^1 and v^2 . These values are defined by the following conditions:

$$R(\lambda^*, v^j) = \max_{\lambda} \min_v [\sigma(v) + \lambda(v - \bar{v})]. \quad (77)$$

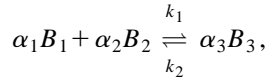
The function R has the same value at points v^i ($i=1,2$). The fraction γ of the interval L during which $v^*(l)=v^1$ is to be found from the condition

$$\gamma v^1 + v^2(1-\gamma) = \bar{v}, \quad 1 \geq \gamma \geq 0.$$

The bound is reached in every process where $v=v^1$ during γ_1 fraction of the interval L and $v=v^2$ all the other time.

F. Chemical conversion

Consider an isothermal chemical reactor of ideal mixing with periodic action. In this reactor the following reactions takes place:



where B_i are the initial and final components and α_i are stoichiometric coefficients. We assume that $\alpha_1 < 0$, $\alpha_2 < 0$, and $\alpha_3 > 0$. The reaction velocity is determined by the law of active masses

$$W(X) = k_1 X_1^{-\alpha_1} X_2^{-\alpha_2} - k_2 X_3^{\alpha_3} = W_1 - W_2. \quad (78)$$

Here $X_i = N_i(l)/N_{\Sigma}(l)$ is the mole concentration of the i th component, $N_i(l)$ is the number of moles of the i th component in the system, and $N_{\Sigma}(l) = \sum_i N_i(l)$.

The entropy production

$$\sigma = -\frac{W}{T} A, \quad (79)$$

where $A = -\sum_{i=1}^3 \alpha_i \mu_i$ is the affinity of chemical reaction. For the ideal solutions

$$\mu_i = \mu_i^0(T, P) + RT \ln X_i.$$

Hence

$$A = -\sum_{i=1}^3 \alpha_i \mu_i^0(T, P) - RT \sum_{i=1}^3 \alpha_i \ln X_i.$$

According to [13] the first term in this expression is equal to

$$-\sum_{i=1}^3 \alpha_i \mu_i^0 = RT \ln k_e(T, P).$$

The equilibrium constant k_e is the ratio of velocities of direct and reverse reactions,

$$k_e(T, P) = \frac{k_1(T, P)}{k_2(T, P)}.$$

So we have

$$A = RT \left(\ln \frac{k_1}{k_2} - \sum_i \ln X_i^{\alpha_i} \right)$$

or

$$A = RT \ln \frac{k_1 X_1^{-\alpha_1} X_2^{-\alpha_2}}{k_2 X_3^{\alpha_3}} = RT \ln \frac{W_1}{W_2}.$$

Let the average velocity of reaction

$$\frac{1}{L} \int_0^L W(X) dl = \bar{W} \quad (80)$$

be given. The reaction velocity $W(t)$ is a control. This velocity determines how the conversion degree changes,

$$\frac{d\xi}{dl} = W, \quad (81)$$

and how the amount of moles changes,

$$\frac{dN_i}{dl} = \alpha_i W, \quad i=1,2,3.$$

Thus, we have

$$N_3(l) = N_{30} + \alpha_3 \xi(l),$$

and the total number of moles can be calculated as

$$N_{\Sigma}(l) = N_{\Sigma 0} + \xi(l) \sum_{i=1}^3 \alpha_i.$$

The velocity of the reverse reaction has the form

$$W_2 = k_2 \frac{N_3(l)}{\sum_i N_i(l)} = k_2 \frac{N_{30} + \alpha_3 \xi(l)}{N_{\Sigma 0} + \xi(l) \sum_i \alpha_i}.$$

Finally, we reduce the problem of minimizing the dissipation in the system to the following form:

$$\bar{\sigma} = \frac{1}{L} \int_0^L R W \ln \frac{W + W_2(\xi)}{W_2(\xi)} dl \rightarrow \min_w, \quad (82)$$

subject to the constraints

$$\frac{1}{L} \int_0^L W(t) dl = \bar{W} \quad (83)$$

and

$$\frac{d\xi}{dl} = W, \quad \xi(0) = 0, \quad (84)$$

where

$$W_2(\xi) = k_2 \frac{N_{30} + \alpha_3 \xi}{N_{\Sigma 0} + \xi \sum_i \alpha_i}. \quad (85)$$

Since this problem has a canonical form (4)–(7), its optimality condition is

$$\frac{W^2}{W + W_2(\xi)} = \frac{\lambda L}{R} = \text{const}, \quad \forall l \in [0, L], \quad (86)$$

and Eqs. (81) and (83) allow us to find the optimal values $W^*(I)$, $\xi^*(I)$, and the corresponding bound on the entropy production.

IV. CONCLUSION

We examined the class of the minimal dissipation processes, which is as important physically as a class of the reversible processes. It reduces the limits of our potentialities such that in some cases these limits turn out to be realizable and may be widened only by extra embedding (contact surface increasing) or by reducing the process intensity. We

derive the general conditions that hold for any minimal dissipation process as well as the corresponding bounds. We demonstrate how these results can be used for particular systems. The new optimality conditions and corresponding bounds for throttling and crystallization processes have been obtained.

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