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# Minimal Dissipation Processes in Irreversible Thermodynamics and Their Applications

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## Abstract

It is known that the maximum efficiency of conversion of thermal energy into mechanical work or separation work is achieved in reversible processes. If the intensity of the target flux is set, the processes in the thermodynamic system are irreversible. In this case, the role of reversible processes is played by the processes of minimal dissipation. The review presents the derivation of conditions for minimum dissipation in general form and their specification for heat and mass transfer processes with arbitrary dynamics. It is shown how these conditions follow the solution of problems on the optimal organization of two-flux and multflux heat exchange. The algorithm for the synthesis of heat exchange systems with given water equivalents and the phase state of the flows is described. The form of the region of realizability of systems using thermal energy and the problem of choosing the order of separation of multicomponent mixtures with the minimum specific heat consumption are considered. It is shown that the efficiency of the rectification processes in the marginal productivity mode monotonously depends on the reversible efficiency, which makes it possible to ignore irreversible factors for choosing the order of separation in this mode.

**Keywords:** entropy production, conditions of minimal dissipation, optimal heat transfer, multithreaded heat exchange system, rectification, separation of multicomponent mixtures, boundary of the realizability of thermal machines

## 1. Problems and methodology of finite-time thermodynamics

Applied thermodynamics originates from the work of Sadi Carnot in 1824 [1]. One of the problems of thermodynamics is the study of problems on the limiting possibilities of thermodynamic systems. For a long time, these tasks boiled down to finding the maximum efficiency of heat and refrigeration machines, separation systems, and various chemical processes. The solution of these problems led to the fact that the maximum efficiency value was determined in the case when the process under study was reversible. Reversibility will include processes in which the coefficients of heat and mass transfer are arbitrarily large or the fluxes of energy and matter in the system under study are arbitrarily small. With the development of nuclear energy, a new task was set—to obtain such a cycle of a heat engine that would correspond to its maximum power with certain fixed exchange ratios with sources. This task is due to the fact that the capital expenditures for the construction

of nuclear power facilities are high with a relatively low cost of fuel spent. Variants of solving the problem of optimization thermodynamics were proposed in [2, 3].

Further development of finite-time thermodynamics was stimulated by a great deal of work of very many investigators. Here, we list names of just a few first researchers: R.S. Berry, B. Andresen, K.H. Hoffmann, P. Salamon, L.I. Rozonoer, and some others (see [1–32]).

Typical problems of optimization thermodynamics include the following: processes with minimal irreversibility; determination of the limiting possibilities of heat engines, cold cycles, and heat pumps (maximum power, maximum efficiency, many realizable modes); and analysis of the processes of separation of mixtures.

The general approach to solving problems is as follows. It is assumed that the whole system is divided into subsystems. In each subsystem, at any time moment, the deviations of the intensive variables from their average values over the volume are negligible. Consequently, the change of these variables (temperatures, pressures, etc.) occurs only at the boundaries of the subsystems, which means that the system as a whole is in a nonequilibrium state. This assumption makes it possible to use the equation of state in the description of individual subsystems, which are valid under equilibrium conditions, and ordinary differential equations can be used to describe the dynamics of the subsystems. The solution of extremal problems in this case is performed by methods of the optimal control theory for lumped parameter systems.

To study the limiting possibilities of thermodynamic systems, it is first necessary to make balance relations for matter, energy, and entropy. Moreover, the balance ratio for entropy includes dissipation  $\sigma$ , that is, the production of entropy. It characterizes the irreversibility of processes in the system. If all processes are reversible, then the dissipation is zero. If the processes are irreversible, then dissipation takes positive values. Dissipation depends on the dynamics of the processes. The set of realizability of the system in the parameter space of input and output streams is determined by the nonnegativity of dissipation. Reversible processes lie on the boundary of this set.

When a minimum possible dissipation is found as a function of flux intensities, then the inequality  $\sigma \geq \sigma_{\min}$  holds in an arbitrary real system; this contracts the region of realization. In this formulation, the set obtained incorporates the effects of process dynamics, the magnitude of fluxes, and the system's extent (due to the presence of heat and mass transfer coefficients).

In any real system, it is possible to narrow the realizability region if we find the minimum possible dissipation value as a function of the flux intensity ( $\sigma \geq \sigma_{\min}$ ). This will take into account the dynamics, the flux intensity, and even the size of the installation through the coefficients of heat and mass transfer.

Then, from the balance equations, it is necessary to derive the connection between the system performance indicators and dissipation  $\sigma$ . Performance indicators usually monotonically deteriorate with the increase of  $\sigma$ . The best values of efficiency indicators are achieved in a reversible process, which allows using them similarly to the Carnot efficiency indicators.

Next, it is necessary to solve the problem of the organization of processes in such a way that, with the given constraints, the dissipation as a function of the flux intensities is minimal. This is the most difficult step in analyzing the capabilities of thermodynamic systems.

Consider the process of studying the limiting possibilities in more detail, and begin with thermodynamic balances. Thermodynamic balances show the relationship between the fluxes (matter, energy, and entropy) that the system exchanges with the environment and the changes in these values in the system [19]. Let us summarize all the fluxes, considering incoming fluxes as positive and outgoing

fluxes as negative. Fluxes can be convective and diffusive. Convective fluxes are forced into the system and removed from it. The diffusive flux depends on the differences between the intensive variables of the system at the point where it enters and the intensive variables of the environment.

The energy balance shows the rate of change in the energy of a system, which is determined by the flux of energy that enters or is removed along with the convective fluxes of matter, the change in energy due to the diffusional exchange of matter, the currents of conductively transmitted heat, and the power of the work done. Material balance shows the change in the number of moles of substances in the system. Entropy balance shows the change in the entropy of the system, which occurs due to the influx of entropy together with the incoming substances, the influx or removal of heat, and the production of entropy due to the irreversibility of exchange processes.

If the system operates cyclically, the balances can be recorded on average for the equipment working cycle. In this case, the total change in energy, amount of matter, and entropy per cycle is zero, since the state of the system at the start and the end of the cycle is the same. Balances are transformed into a system of relations of averages over cycle-averaged components.

The equations of thermodynamic balances show the relationship between process efficiency indicators, external fluxes, and the structure of the system. The increase in entropy  $\sigma$  causes an increase in the entropy of output fluxes. At the same time, either the temperature of the fluxes at the outlet decreases, or the outlet flux of heat increases at a constant temperature. This leads to a reduction in the work of separation, the mechanical work produced by the system.

Consider the operation of a thermal machine that converts the heat received from a hot source with temperature  $T_+$  into work. The working fluid gives a part of the energy to a cold source with a temperature  $T_-$ . The working fluid changes its state cyclically. As an indicator of efficiency, we will consider the thermal efficiency ( $\eta = p/q_+$ )—the ratio of the work produced to the amount of heat collected from a hot source.

Let us denote the average intensity of the heat flux taken from the hot source  $q_+$  and that given to the cold source,  $q_-$ . For the generated power  $p$ , we write the equations of energy balances:

$$q_+ - q_- - p = 0, \quad (1)$$

and

$$\frac{q_+}{T_+} - \frac{q_-}{T_-} + \sigma = 0. \quad (2)$$

Since the state of the working fluid either does not change in time (for steam and gas turbines) or changes cyclically (for steam engines), then there are zeros in the right parts of the equations.

Thermal efficiency  $\eta = p/q_+$  follows from Eq. (1) in the form

$$\eta = \frac{p}{q_+} = 1 - \frac{q_-}{q_+}. \quad (3)$$

Taking into account the fact that the Eq. (2) implies

$$\frac{q_-}{q_+} = \frac{T_-}{T_+} + \sigma \frac{T_-}{q_+}. \quad (4)$$

Therefore,

$$\eta = \left(1 - \frac{T_-}{T_+}\right) - \sigma \frac{T_-}{q_+} = \frac{1 - T_-/T_+}{1 + \sigma T_-/p}. \quad (5)$$

Thermal efficiency  $\eta$  is equal to Carnot efficiency when any irreversible phenomena are absent in the system.

The growth of  $\sigma$  leads to a growth entropy of output streams; under other equal conditions, this growth reduces the flux temperature at the outlet or at a fixed temperature increases the waste heat flux. And in this and in another case, this leads to a decrease in the mechanical work produced by the system or the work of separation. Energy efficiency of thermodynamic system, characterized by the relation of useful work, produced in it, to the energy costs, reaches a maximum in the invertible processes, when  $\sigma = 0$ .

## 2. Processes with a minimal dissipation

It is known that the maximum efficiency of conversion of thermal energy into mechanical work or separation work is achieved in reversible processes. If the intensity of the target flux is set, the processes in the thermodynamic system are irreversible. In this case, the role of reversible processes is played by the processes of minimal dissipation, so it is necessary to determine conditions under which thermodynamic processes exhibit minimal dissipation for a prescribed average intensity (prescribed averaged value of driving forces).

### 2.1 The minimal dissipation's conditions

Consider two systems interacting with each other. Intensive variables for the  $i$ th system will be denoted by  $u_i$  and extensive variables by  $x_i$ . In general, these are vector variables. When systems are in contact, the difference between  $u_1$  and  $u_2$  leads to the appearance of flux  $J(u_1, u_2)$ . Function  $J$  is continuous, is differentiable, and has the following properties:

$$\begin{aligned} \frac{\partial J_j}{\partial u_{1j}} > 0, \quad \frac{\partial J_j}{\partial u_{2j}} < 0, \\ J(u_1, u_2) = 0, \quad \text{at} \quad u_2 = u_1 \end{aligned}, \quad (6)$$

for scalar  $u_1$  and  $u_2$ .

The difference between vectors  $u_1$  and  $u_2$  (of the same sign as flux  $J_j$ ) leads to appearance of driving forces  $X_j$ . Each force defines exclusively  $u_{1j}$  and  $u_{2j}$ , satisfying conditions analogous to those in Eq. (6). Entropy production  $\sigma$ , which characterizes the process irreversibility, is equal to the scalar product of the flux vector and the driving force vector, and average value of entropy is described by the formula

$$\bar{\sigma} = \frac{1}{L} \int_0^L \sum_{j=1}^m J_j(u_1, u_2) X_j(u_{1j}, u_{2j}) dl, \quad (7)$$

where the independent variable  $l$  has the interpretation of a space-time or a contacting area measure. The integrand of this functional is defined non-negatively.



We shall assume that in our algorithm (at least) one intensive variable appears, by definition  $u_2(l)$ , which may assume its values from within a certain manifold  $V$ . Yet, because of the variability of extensive variables of the first subsystem  $\left(\frac{dY_{1j}}{dl} = -J_j(u_1, u_2)\right)$ , the second variable changes in accordance with the formula

$$\frac{du_{1j}}{dl} = \varphi_j(u_1, u_2), \quad u_1(0) = u_{10}, \quad j = 1, \dots, m. \quad (8)$$

Average values of all or some selected fluxes are prescribed:

$$\frac{1}{L} \int_0^L J_j(u_1, u_2) dl = \bar{J}_j, \quad j = 1, \dots, k_1, \quad k_1 \leq m. \quad (9)$$

Further on, we consider only the case of a scalar flux. The problem for vector fluxes and its solution is considered with details in [32, 33].

The scalar flux problem involves minimizing of the integral

$$\bar{\sigma} = \frac{1}{L} \int_0^L J(u_1, u_2) X(u_1, u_2) dl \rightarrow \min_{u_2 \in V} \quad (10)$$

subject to constraining conditions:

$$\frac{du_1}{dl} = \varphi(u_1, u_2), \quad u_1(0) = u_{10}, \quad (11)$$

$$\frac{1}{L} \int_0^L J(u_1, u_2) dl = \bar{J}. \quad (12)$$

The problem (10)–(12) simplifies in an important case when the rate of change of variable  $u_1$  is proportional to the flux:

$$\varphi(u_1, u_2) = c(u_1) J(u_1, u_2). \quad (13)$$

In this case the condition of minimal dissipation assumes the form

$$J^2(u_1, u_2) = \lambda_2 \left( \frac{\partial J(u_1, u_2)}{\partial u_2} : \frac{\partial X(u_1, u_2)}{\partial u_2} \right), \quad (14)$$

whereas the condition of prescribed flux intensity can be written as

$$\int_{u_{10}}^{u_{1L}} \frac{du_1}{c(u_1)} = \bar{J} \cdot L. \quad (15)$$

The value of  $u_{1L}$  is determined regardless of the optimal solution  $u_2^*(u_1)$ .

If the flux is proportional to the driving force with constant coefficient  $\alpha$ , then the minimum entropy production equals

$$\bar{\sigma} = \frac{\bar{J}^2}{\alpha}. \quad (16)$$

## 2.2 Minimal dissipation's conditions of selected processes

Consider the conditions for the minimum dissipation of heat exchange. Let us take the temperature of the body being heated as the controlling intense variable. The driving force in the minimum dissipation problem is

$$X(T_1, T_2) = \left( \frac{1}{T_2} - \frac{1}{T_1} \right), \quad (17)$$

whereas the heat flux is  $q(T_1, T_2)$ . In the majority of cases, we may assume the energy balance in the form

$$\frac{dT_1}{dl} = -\frac{1}{c_1(T_1)} q(T_1, T_2), \quad T_1(0) = T_{10}, \quad (18)$$

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

If the process takes place in time, then the parameter  $l$  has the meaning of time, and the parameter  $L$ —the duration of the process. If a pipe heat exchanger is considered, in which the hot flux temperature changes from section to section, the value of  $c$  is the water equivalent of the flux, and  $L$  is the length of the heat exchanger.

In agreement with conditions (14), (15) describing the minimum dissipation subject a prescribed average intensity of heat flux  $\bar{q}$ , we can obtain a condition of minimum dissipation for an arbitrary law of heat transfer:

$$q^2(T_1, T_2) : \frac{\partial q}{\partial T_2} T_2^2 = -\lambda_2 = \text{const}, \quad (19)$$

$$\int_{T_{1L}}^{T_{10}} c_1(T_1) dT_1 = \bar{q} \cdot L, \quad \int_{T_{1L}}^{T_{10}} \frac{c_1(T_1) dT_1}{q(T_1, T_2)} = L. \quad (20)$$

The first of these conditions determines  $T_2^*(T_1, \lambda_2)$ , second— $T_{1L}$ , and third—constant  $\lambda_2$ .

For the Newtonian law of heat transfer

$$q = \alpha(T_1 - T_2) \quad (21)$$

with a constant heat capacity (water equivalent)  $c$ , we obtain from conditions (18)–(20)

$$\alpha^2(T_1 - T_2)^2 = -\lambda_2(-\alpha)T_2^2 \Rightarrow \alpha \left( \frac{T_1}{T_2} - 1 \right)^2 = \lambda_2. \quad (22)$$

Therefore, for an arbitrary  $l$  of an optimal process, the ratio  $\frac{T_1}{T_2}$  should be constant. This constant equals

$$\frac{T_1}{T_2} = 1 + \sqrt{\frac{\lambda_2}{\alpha}}. \quad (23)$$

As it follows from Eq. (20),  $T_{1L} = T_{10} - \bar{q}L/c$ . Finally, the condition (20) leads to the following equality:

$$\frac{\sqrt{\frac{\lambda_2}{\alpha}}}{1 + \sqrt{\frac{\lambda_2}{\alpha}}} = -\frac{c}{\alpha L} \ln \left( 1 - \frac{\bar{q}L}{cT_{10}} \right). \tag{24}$$

Substituting Eqs. (23) and (24) into the expression

$$\sigma = \frac{c}{L} \int_{T_{1L}}^{T_{10}} \left( \frac{1}{T_2(T_1)} - \frac{1}{T_1} \right) dT_1, \tag{25}$$

minimal entropy production is obtained in the form

$$\sigma_{min} = \frac{c^2 \ln^2 \left( 1 - \frac{\bar{q}L}{cT_{10}} \right)}{\left[ \alpha L + c \ln \left( 1 - \frac{\bar{q}L}{cT_{10}} \right) \right] L}. \tag{26}$$

**Table 1** presents analogous conditions of minimal dissipation for some well-known processes and corresponding expressions for minimal entropy production.

As shown in [34], the conditions of minimal dissipation make it significantly easier to estimate the limiting possibilities of thermodynamic systems. In a system with multithreaded heat exchange [35], the total heat load  $q$  and the total heat transfer coefficient  $\bar{\alpha}$  are fixed. At the input of the system,  $k$  heating fluxes with temperatures  $T_{i0}$  and water equivalents  $W_i$  come in. It is necessary to choose the parameters of heat fluxes, the structure of the system, and the distribution of heat transfer coefficients.

The conditions under which the minimum possible production of the entropy of the  $\bar{\sigma}^*$  trait is reached are also defined in [34]: (1) *At each point of contact of the heating and heated streams, the minimum dissipation conditions must be satisfied.* (2) *Temperatures of heating fluxes at the outlet of the system should be equal to each other, as well as the temperature of the heated fluxes at the outlet.* (3) *Heating fluxes, in*

Process	Conditions of minimal dissipation and entropy production
Heat transfer $q = \alpha(T_2 - T_1)$	$\frac{T_1(l)}{T_2(l)} = 1 - \frac{\beta}{\alpha L}; \sigma_{min} = \frac{\beta^2}{\alpha L - \beta}$ $\beta = W \ln \left( 1 - \frac{\bar{q}}{W T_{1(0)}} \right)$
Vector flux, linearly depending on driving forces $J = LX$	$X = \text{const. } J = \bar{J}; \sigma_{min} = \bar{J}^T L^{-1} \bar{J}$
One-sided isothermal mass transfer $g(c_1, c_2) = k(c_1(l) - c_2(l))$	$c_2(l) = c_1(l) + \frac{m}{2} - \sqrt{c_1(l)m + \frac{m^2}{4}}$ $c_1(0) \int_{c_1(l)} \frac{G d c_1}{k(1-c_1^2) \sqrt{c_1 m + \frac{m^2}{4}}} = L;$ $\sigma_{min} = \int_{c_1(l)}^{c_1(0)} \frac{RG}{(1-c_1)^2} \ln \frac{c_1 d c_1}{c_1 + \frac{m}{2} - \sqrt{c_1 m + \frac{m^2}{4}}}$
Two-sided isothermal equimolar mass transfer	$\frac{\partial g}{\partial c_1} / \frac{\partial g}{\partial c_2} = m \frac{c_2(l)(1-c_2(l))}{c_1(l)(1-c_1(l))}$ $\frac{d c_1}{d l} = -\frac{g(c_1, c_2)}{G_1}$ $c_1(0) = C_{10}, c_1(L) = c_{1L};$ $\sigma_{min} = R \int_0^L g(c_1, c_2) \ln \left[ \frac{c_1(1-c_2)}{c_2(1-c_1)} \right] d l$

**Table 1.**  
Conditions of minimal dissipation in thermodynamic processes.



which the inlet temperature is less than the calculated temperature  $\bar{T}$ , do not participate in heat exchange.

Computational relations for Newtonian heat transfer are

$$\left. \begin{aligned} \bar{T} &= \frac{\sum_{i=1}^k T_{i0} W_i - \bar{q}}{\sum_{i=1}^k W_i}, \\ q^*(T_{i0}) &= W_i (T_{i0} - \bar{T}), \\ \alpha^*(T_{i0}) &= \frac{\bar{\alpha} W_i (\ln T_{i0} - \ln \bar{T})}{\sum_{i=1}^k W_i (\ln T_{i0} - \ln \bar{T})}, \\ m &= 1 - \frac{1}{\bar{\alpha}} \sum_{i=1}^k W_i (\ln T_{i0} - \ln \bar{T}), \\ \bar{\sigma}^* &= \bar{\alpha} \frac{(1-m)^2}{m}, \\ \alpha^*(T_{i0}) &= q^*(T_{i0}) = W_i = 0, \quad T_{i0} \leq \bar{T}. \end{aligned} \right\} \quad (27)$$

The system in which the entropy production calculated with parameters of all fluxes

$$\sigma = \sum_{\nu} W_{\nu} \ln \frac{T_{\nu}^{out}}{T_{\nu}^{in}} \quad (28)$$

is lower than a certain value cannot exist in reality.

Analogous relations can easily be obtained in the case when the inlet parameters of heated fluxes are prescribed.

### 3. Synthesis of heat exchange systems

In [36] the problem of the limiting possibilities of the heat exchange system (“ideal” heat exchange) was considered. The minimum possible entropy production  $\sigma^*$  was found in the system with the given values of water equivalents and input temperatures of hot or cold fluxes and given the total heat load and the total heat transfer coefficient. It is shown that for the case when the heat flux is proportional to the temperature difference (Newtonian dynamics), this irreversibility limit can be reached if at each point of contact the ratio of the absolute temperatures of the fluxes is the same, and their temperatures at the outlet of the system are the same for all fluxes whose input temperatures are fixed (hot or cold).

Conditions of ideal heat exchange impose very strict requirements on the characteristics of the system:

—Each double-flux cell must be a counter-flux heat exchanger.

—The ratio of the water equivalents of the hot and cold flux in it should be equal to the ratio in degrees Kelvin of the temperature of the cold flux at the outlet of the heat exchange cell to the temperature of the hot flux at its inlet—conditions of thermodynamic consistency.

—This ratio and its corresponding minimum possible entropy production at fixed temperatures and water equivalents of hot fluxes are related to their inlet temperatures  $T_i^0$ , the water equivalents  $W_i$ , and the total heat transfer coefficient  $K$  as:

$$\left. \begin{aligned} m &= 1 - \frac{1}{K} \sum_{i=1}^n W_i (\ln T_i^0 - \ln \bar{T}_+), \\ \sigma^* &= K \frac{(1-m)^2}{m}. \end{aligned} \right\} \quad (29)$$

—The temperature of the hot streams at the outlet should be the same and, as it follows from the conditions of the energy balance, is equal to:

$$\bar{T}_+ = \frac{\sum_{i=1}^k T_{i0} W_i - \bar{q}}{\sum_{i=1}^k W_i}, \quad (30)$$

—Hot fluxes with initial temperatures less than  $\bar{T}_+$  do not participate in the heat exchange system.

If a part of the hot fluxes condenses in the process of heat transfer, then in the expression for  $m$  (Eq. (24)), the water equivalent of the corresponding term tends to infinity. Assign the index  $k$  to the condensing fluxes and find the limit.

$W_k (\ln T_k^0 - \ln \bar{T}_+) = W_k \left( \ln T_k^0 - \ln \left( T_k^0 - \frac{q_k}{W_k} \right) \right)$  when  $W_k$  tends to infinity. Using L'Hospital's rule to disclose the uncertainties, we find that

$$\lim_{W_k \rightarrow \infty} W_k \left( \ln T_k^0 - \ln \left( T_k^0 - \frac{q_k}{W_k} \right) \right) = \frac{q_k}{T_k^0} = \frac{g_k r_k}{T_{bk}}. \quad (31)$$

Here, it is taken into account that the temperature  $T_k^0$  is equal to the condensation temperature and the thermal load is the product of the flux rate of the latent heat of vaporization.

Thus, the expression for  $m$  in the presence of condensing fluxes will be rewritten in the form:

$$m = 1 - \frac{1}{K} \left( \sum_{i \neq k} W_i (\ln T_i^0 - \ln \bar{T}_+) + \sum_k \frac{g_k r_k}{T_{bk}} \right). \quad (32)$$

In a multithreaded system integrated with the technological process, the values of water equivalents of both hot and cold fluxes are set, and often their outlet temperatures are set. Therefore, the performance of the ideal heat exchange system cannot be achieved. It is natural to set the task of synthesis of the heat exchange system of the minimum irreversibility at more rigid restrictions on characteristics of streams. The conditions of ideal heat transfer can only serve as a “guiding star” like Carnot's efficiency for thermal machines, and the value of the ratio  $\sigma^*$  to the real production of entropy in the designed system is an indicator of its thermodynamic perfection.

Next, we propose the calculated relations for the bottom estimate of the minimum dissipation in the system with the above restrictions and the synthesis of a hypothetical system in which such an estimate is implemented.

Consider a multithreaded heat exchange system containing a set of hot (index  $i$ ) and cold fluxes (index  $j$ ), with given water equivalents  $W_i, W_j$ . For each of the cold (heated) fluxes, its inlet and outlet temperatures are set to  $T_j^0$  and  $\bar{T}_j > T_j^0$ .

For hot (cooled) fluxes, except for water equivalents, their temperatures at the inlet to the heat exchanger  $T_i^0$  are set. If some flux in the system changes its phase

state, then for it except water equivalents, the flux rate  $g_i, g_j$  and heat of vaporization (condensation)  $r_i, r_j$  are fixed. The ambient temperature will be denoted as  $T_0$ .

Under these conditions, the thermal load of the system is equal to the total energy required for heating all cold fluxes and is determined by the equality:

$$\bar{q} = \sum_j q_j = \sum_j W_j (\bar{T}_j - T_j^0). \quad (33)$$

The difference in the conditions imposed on the hot and cold fluxes is due to the fact that for cold fluxes leaving the system with a temperature less than a predetermined one, heating is required, i.e., additional energy costs, and for hot ones, if their outlet temperature is greater than a predetermined one, cooling is required, which is much easier.

Entropy production is the difference between the total entropy of outgoing fluxes and the total entropy of incoming fluxes. Initially, we assume that all fluxes enter and leave the system in the same phase state, the pressure change in the system is small, and the heat capacity is constant. Then, the change in the entropy of each flux is the product of its water equivalent by the logarithm of the ratio of its inlet and outlet temperatures in degrees Kelvin [37]. So, it follows from the conditions of the thermodynamic entropy balance that:

$$\sigma = \sigma_+ + \sigma_- = \sum_i W_i (\ln \bar{T}_i - \ln T_i^0) + \sum_j W_j (\ln \bar{T}_j - \ln T_j^0). \quad (34)$$

The first of these terms is negative, the second is positive, and their sum is always greater than  $\sigma^* > 0$ .

Note that all variables determining the value of the entropy growth of cold fluxes are given by the conditions of the problem, so that the minimum entropy production corresponds to the minimum at a given thermal load of the first summand by temperatures  $\bar{T}_i$ .

The formal statement will take the form:

$$\sigma_+ = \sum_i W_i (\ln \bar{T}_i - \ln T_i^0) \rightarrow \min / \sum_i W_i (T_i^0 - \bar{T}_i) = \bar{q} = \sum_j W_j (\bar{T}_j - T_j^0). \quad (35)$$

The Lagrangian of this problem

$$L = \sum_i W_i (\ln \bar{T}_i - \ln T_i^0) - \lambda \sum_i W_i (\bar{T}_i - T_i^0). \quad (36)$$

The conditions of its stationarity in  $\bar{T}_i$  lead to equality:

$$\bar{T}_i = \frac{1}{\lambda}. \quad (37)$$

Thus, in any water equivalents and input temperatures of hot streams, minimum dissipation corresponds to such an organization of heat transfer for which the temperatures of hot streams at the exit are the same.

In general, coolant fluxes at the system inlet can have different phase states: vapor, liquid, or vapor-liquid mixture. The same states can be at the output of the stream.

—If the flux does not change its phase state, but changes only the temperature, then we assume that its temperature at the input to the cell  $T_k^0$ , the water equivalent

$W_k$ , and for cold fluxes the temperature at the output  $\bar{T}_k$  are known. The temperature of the hot streams at the output of the  $\bar{T}_+$  system is selectable (see Eq. (30)).

—If the cold flux changes its phase state so that at the inlet it is a liquid at boiling point and at the outlet it is saturated with steam (let us define it as “evaporating”), the weight flux rate  $g_j$ , the boiling point  $T_{bj}$ , and the heat of vaporization  $r_j$  are given. The same is true for hot “condensing” streams. They have a saturated steam state at the inlet and a liquid state at the boiling point at the outlet.

Thus, the first step in the synthesis algorithm of heat exchange systems is the preparation of initial data, in which actual fluxes and their characteristics are converted into calculated fluxes. They can be of two types: those that do not change their phase state (heated and cooled) and those that change it at the boiling point (evaporating and condensing). End-to-end fluxes are not included in the calculation. To calculate the total heat load production, use the following expression:

$$\sum_{jh} W_{jh} (\bar{T}_{jh} - T_{jh}^0) + \sum_{bj} g_{bj} r_{be} = \bar{q}. \quad (38)$$

Minimum dissipation implies fulfillment of the “counterflow principle”: the cold streams with higher temperatures must be in contact with the hot flux with a higher temperature. The latter requirement, as well as the equality of temperatures of hot streams at the outlet, corresponds to the conditions of the ideal heat transfer [36].

As the hot fluxes move from one contact cell to the next, their temperature changes due to the recoil of the heat flux. At the output of the system, the heat flux given by them is  $\bar{q}$ , and the temperature is  $\bar{T}_+$ . Let us denote by  $q$  the given heat load in some intermediate state of hot fluxes. As the hot streams cool down, it changes from zero to  $\bar{q}$ .

In this case, we assume that when the hot flux with the highest input temperature (first) is cooled to a temperature of  $T_2^0$ , the first and second fluxes are combined, so that their water equivalents are summed. A similar union occurs with the third flux, etc., until the temperature of the equivalent hot flux drops to the previously calculated formula (30)  $\bar{T}_+$ . If a condensing flux is at a certain temperature  $T_{bi}$  in the number of hot fluxes, the temperature of the equivalent flux is constant and equal to  $T_{bi}$  until the equivalent flux transfers the heat of condensation  $q_{bi} = g_{bi} r_i$ . The dependence of the temperature of the hot flux equivalent on the given heat load  $T_+(q)$ , we will call the contact temperature of the hot fluxes.

Cold fluxes are ordered by their outlet temperature, so that  $j = 1$  corresponds to the flux with the highest output temperature. For cold fluxes, the value of  $q$  is equal to the current required heat load, i.e., the heat they need to obtain to satisfy the conditions imposed on their temperature and output state. The greater the  $q$ , the lower the cold flux temperature corresponding to this value. In this case, we assume that when the temperature of the first flux decreases, two events are possible:

1. Its temperature will drop to the set temperature at the output of the second stream.
2. Its temperature will drop to its initial temperature.

In the first case, the first cold flux is calculated combined with the second. In the second case, it is excluded from the system and transferred to the heating of the second stream. This procedure continues until an equivalent cold flux reaches the lowest cold flux temperature at the system inlet. The number of threads included in the equivalent cold flux is changed by adding fluxes with lower temperatures at the

outlet and due to the exclusion from streams with the highest temperatures at the entrance. But each value of  $q$  corresponds to the value of  $T_-(q)$  of the contact temperature of cold fluxes.

The dependencies of the current contact temperatures can be calculated from energy balance conditions similar to the expression (25). For equivalent hot flux:

$$T_+(q) = \frac{\sum_{i=1}^{S_+(T_+)} W_i T_i^0 - q}{\sum_{i=1}^{S_+(T_+)} W_i}, \quad (39)$$

where  $S_+(T_+)$  is the set of indices of hot fluxes for which the inlet temperature is greater than the current contact temperature ( $T_i^0 > T_+(q)$ ).

Similarly, for the contact temperature of the equivalent cold flux, we have:

$$T_-(q) = \frac{\sum_{j \in S_-(T_-)} W_j \bar{T}_j - q}{\sum_{j \in S_-(T_-)} W_j}, \quad (40)$$

where  $S_-(T_-)$  is the set of indices of cold fluxes for which the contact temperature  $T_-$  satisfies the inequality  $\bar{T}_j > T_-(q) > T_j^0$ .

The curves of the current contact temperatures decrease monotonically with the growth of  $q$ , with  $T_+(q) > T_-(q)$ . On each of these curves, the points (nodes) are selected, in which either the composition of the fluxes entering the equivalent flux changes or the condensation/evaporation process takes place. In the latter case, horizontal sections appear on the curves. On the curve  $T_-(q)$ , there can be vertical jumps if the flux temperature  $T_j^0 > \bar{T}_{j-1}$ .

The interval  $\delta q_\nu$  from one of the nodes on any of the contact curves to the nearest node on the same or another curve is characterized by the same composition and phase state of the contacting fluxes. We will call it *the homogeneity interval*.

For each such interval of  $\delta q_\nu$ , three combinations of contacting fluxes are possible:

1. Both equivalent fluxes change their phase states.
2. The hot equivalent flux is cooled and the cold is heated.
3. One of the fluxes changes its phase state, and the other is cooled or heated.

Contact temperature curves provide all the data necessary to calculate the heat transfer coefficient of the cell in which the contact is made:

—Water equivalents of  $W_+$ ,  $W_-$  is equal to the sum of the equivalents of water fluxes which are part of the equivalent contacting fluxes.

—Temperatures of equivalent fluxes at the inlet and outlet of the interval of homogeneity is known.

—The thermal load of such a computational cell is  $\delta q_\nu$ .

Depending on which of these contact combinations is implemented, it is possible to select the type of cell hydrodynamics and find  $K_\nu$ . Finding the heat transfer coefficient  $K_\nu$  for each  $\nu$  interval of homogeneity and summing these coefficients over all intervals, we obtain the total coefficient  $K$ , which can be achieved by organizing the countercurrent heat exchange of equivalent fluxes. In turn, knowledge of the heat load  $\bar{q}$  and the total heat transfer coefficient allows us to calculate the minimum possible entropy production  $\sigma^*$  by the formula (29) and estimate the degree of thermodynamic perfection of the constructed system as  $\eta = \frac{\sigma^*}{\sigma^0}$ , where  $\sigma^0$  is total entropy production in the system.



#### 4. The region of realizability of systems

An irreversible factor affecting machine power or pump performance is finite heat transfer coefficients  $\alpha_i$  between heat sources and the working fluid. We substitute the minimum possible entropy production into Eq. (5) and obtain the condition determining the maximum power:

$$p = \eta_k q_+ - \sigma_{\min}(q_+) T_- . \quad (41)$$

As  $\sigma_{\min}(q_+)$  increases faster than  $q_+$ , there exist a maximum of power in the region of realizability.

To minimize the production of entropy, it is necessary that with each contact of the working medium with the sources the conditions of minimum dissipation, which depend on the dynamics of heat transfer, are met. For a source of infinite capacity and the temperature of the working fluid in contact with, it should be constant. For Newtonian dynamics, the ratio of working fluid temperature and sources should have been constant. So, if the temperature of the source changes due to the final capacity, then the temperature of the working fluid should change, remaining proportional to the temperature of the source.

For sources of infinite capacity, the optimal cycle of a heat machine with maximum power for any heat transfer dynamics should consist of two isotherms and two adiabats, and it turned out that the efficiency corresponding to the maximum power (it is called the Novikov-Curzon-Ahlborn,  $\eta_{nca}$ ) is only a function of the Carnot efficiency:

$$\eta_{nca} = 1 - \sqrt{1 - \eta_C} . \quad (42)$$

The maximum difference between  $\eta_C$  and  $\eta_{nca}$  is achieved when the ratio of absolute temperature of the hot and cold sources is 0.25, when  $\eta_C=0.75$ .

For power that is less than the maximum possible, the maximum efficiency of the heat machine is equal to

$$\eta_{\max}(p) = 1 - \frac{1}{2T_+} \left[ T_+ + T_- - \frac{p}{\alpha} - \sqrt{(T_+ - T_-)^2 + \left(\frac{p}{\alpha}\right)^2 - 2\frac{p}{\alpha}(T_+ + T_-)} \right] . \quad (43)$$

In this case,  $\alpha$  is expressed as

$$\alpha = \frac{\alpha_+ \alpha_-}{\alpha_+ + \alpha_-} . \quad (44)$$

As  $p \rightarrow 0$ , the efficiency  $\eta_{\max}$  tends to Carnot efficiency and as

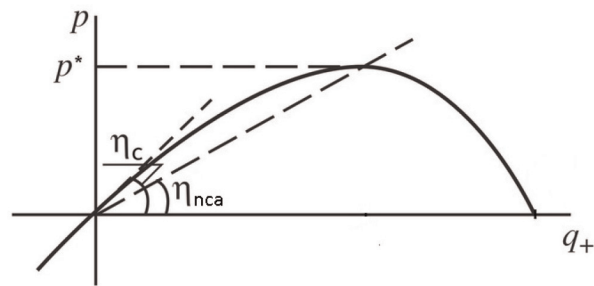
$$p \rightarrow p_{\max} = \alpha \left( \sqrt{T_+} - \sqrt{T_-} \right)^2 . \quad (45)$$

Corresponding thermal efficiency approaches the efficiency value obtained by Novikov, Curzon, and Ahlborn (42).

The nature of the set of realization modes is shown in **Figure 1**.

Similar results can be obtained for the heat pumps. Since the flux of costs is mechanical energy, the set of realizable modes has the form of a convex upward and unbounded parabola.





**Figure 1.**  
Power of thermal machine as a function of driving heat flux.

## 5. Rectification processes

In the separation process, energy is spending on getting the work of separation. The work of separation can be obtained as an increase in the free energy of the streams leaving the system compared to the energy of the mixture flux at the system inlet. The energy expended can be thermal or mechanical. In systems of separation with thermal energy, the set of realizable modes coincides in the form with heat engines. In this case, the rectification processes will be the most important and energy-intensive. In the section below, the process of thermal separation of a two-component mixture is considered, and considerations which allow one to proceed to the determination of the order of separation of multicomponent mixtures are obtained.

Let the following parameters be defined for a mixture of two components:  $q_i$ ,  $T_i$ ,  $s_i$ ,  $p_i$ ,  $h_i$ ,  $x_i$ ,  $\mu_i$ —molar consumption, temperature, molar entropy, pressure, enthalpy, concentration of key component, and its chemical potential in  $i$ th stream. Assume the index  $i = 0$  for the separated stream, index  $i = 1$  for the stream of the enriched key component (for which  $x_1 > x_0$ ), and index  $i = 2$  for the stream cleared of the key component ( $x_2 < x_0$ ). Heat flux  $q_+$ , brought (coming) from a source of temperature  $T_+$ , is supplied to the separation system, whereas heat flux  $q_-$  is rejected to a source of temperature  $T_-$ . Equations of thermodynamic balances are of the form:

$$\begin{aligned} g_0 &= g_1 + g_2, \quad g_0 x_0 - g_1 x_1 - g_2 x_2 = 0, \\ q_+ - q_- + g_0 h_0 - g_1 h_1 - g_2 h_2 &= 0, \\ \frac{q_+}{T_+} - \frac{q_-}{T_-} + g_0 s_0 - g_1 s_1 - g_2 s_2 + \sigma &= 0. \end{aligned} \quad (46)$$

The ratio of target mass flux  $g_1$  and heat flux  $q_+$  may be accepted as the thermal efficiency of the separation process:

$$\eta = \frac{g_1}{q_+}. \quad (47)$$

Using material balances of Eq. (46), we shall express  $g_2$  in terms of  $g_1$  and introduce coefficient  $a = (x_1 - x_0)/(x_0 - x_2)$ . Then, the second flux satisfies  $g_2 = a g_1$ . Eq. (46) assumes the forms

$$q_+ - q_- + g_1 (\Delta h_{01} + a \Delta h_{02}) = 0, \quad (48)$$

$$\frac{q_+}{T_+} - \frac{q_-}{T_-} + g_1 (\Delta s_{01} + a \Delta s_{02}) + \sigma = 0. \quad (49)$$

Here,  $\Delta s_{01} = s_0 - s_1$ ,  $\Delta s_{02} = s_0 - s_2$  are the entropy increases, whereas  $\Delta h_{01} = h_0 - h_1$ ,  $\Delta h_{02} = h_0 - h_2$  are enthalpy increases in corresponding streams. It is mandatory that the concentrations of the key component in streams are prescribed.

We transform Eq. (48) to the form  $q_- = q_+ + g_1(\Delta h_{01} + a\Delta h_{02})$  and substitute the expression obtained into Eq. (49). The frontier of the realization set is characterized by the following equation:

$$g_1 = \frac{1}{F} \left( 1 - \frac{T_-}{T_+} \right) q_+ - \sigma \frac{T_-}{F}. \quad (50)$$

Here,  $F = T_-(\Delta s_{01} + a\Delta s_{02}) - \Delta h_{01} - a\Delta h_{02}$ . The increases of enthalpy and entropy contained in  $F$  have the forms

$$\Delta h_{0i} = C_p(T_0 - T_i), \quad i = 1, 2, \quad (51)$$

$$\Delta s_{0i} = C_{p0} \ln T_0 - C_{pi} \ln T_i - R \ln \frac{P_0}{P_i} + \Delta s_{\text{mix}0} - \Delta s_{\text{mix}i}, \quad i = 1, 2.$$

The entropy of mixing per one mole of mixture is:

$$\Delta s_{\text{mix}i} = R[(1 - x_i) \ln (1 - x_i) + x_i \ln x_i], \quad i = \overline{0, 2}. \quad (52)$$

Note that the ratio  $T_-/F$  depends on reversible factors only. In the reversible process, the entropy production  $\sigma$  is zero, and the thermal efficiency reaches a maximum equal to the multiplier at the heat flux in Eq. (42).

As a productivity you can take any of the streams, even the stream of a separated mixture, because with given compositions of the streams they are proportional.

A reversible estimate of the thermal efficiency of the separation process and the shape of the border of the realizability region can be clarified by finding the minimum possible for a given productivity and dynamics of heat and mass transfer value  $\sigma$  and its dependence on the coefficients of dynamics and heat flux.

If the dynamics of heat transfer can be approximated by the Fourier law and the mass transfer flux is proportional to the difference of chemical potentials, then the minimum dissipation is proportional to the square of the cost of heat. The boundary of the set of realizable modes in this case has a parabolic form

$$g = bq - aq^2. \quad (53)$$

Then, the efficiency of a separation column in the maximum productivity mode is equal to one half of the reversible efficiency:

$$\eta^* = 0, 5\eta^0 = 0, 5b. \quad (54)$$

Qualitative expressions linking characteristic coefficients  $a$  and  $b$  with parameters of the separation column were obtained [38]:

$$b = \frac{T_B - T_D}{T_B A_G} = \frac{\eta_k}{A_G}, \quad a = \left[ \frac{1}{\beta_B T_B T_+} + \frac{1}{\beta_D T_D T_-} + \frac{2(x_D - x_B)}{kr^2} \right] \frac{T_D}{A_G}. \quad (55)$$

Here,  $A_G$  is the molar reversible work of mixture separation, equal to the difference between molar free energy of streams leaving the column and the free energy of raw stream,  $T_D$ ,  $T_B$  are the temperatures in the condenser and the kettle of the column,  $r$  is the molar evaporation heat,  $\beta_D$ ,  $\beta_B$  are the coefficients of heat exchange

in the condenser and the kettle, and  $k$  is the effective coefficient of mass transfer for column height.

The coefficients  $a$  and  $b$  can be found not only by Eq. (55) but also by the results of measurements on the current column. This allows us to solve many problems associated with finding a set of realizability, including the problem of choosing the order of separation. It is important that the efficiency in maximum performance mode depends only on the reversible efficiency. The following condition, sufficient for to be independent of  $a$ , is valid.

**The sufficiency condition for independence of  $\eta^*$  of  $a$  [34]:**

*If the partial derivative  $\frac{\partial \sigma(a,b,q)}{\partial q}$  depends continuously on some scalar function  $z(a,q)$  and the ratio  $\frac{\sigma(a,b,q)}{q}$  is a function of  $z$ , then the thermal efficiency in the maximum productivity mode is defined exclusively in terms of variables  $b$ , characterizing the reversible process. The condition is satisfied for thermal machines and for binary rectification.*

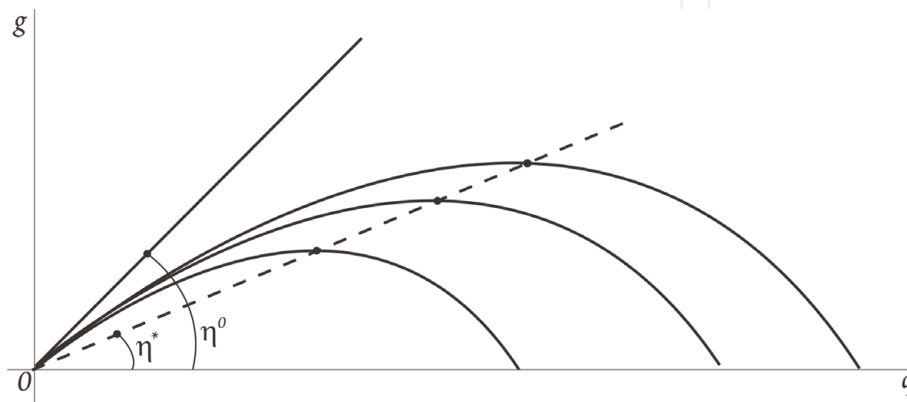
In **Figure 2** shows an example of the boundaries of realizable sets in cases where  $\sigma((a,b,q))$  does not depend on  $a$ .

With decreasing dynamic coefficients, the entropy production increases. The set of realizable modes is compressed, while the maximum performance points with a corresponding heat flux remain on a straight line with a slope of  $\eta^*$ .

### 5.1 Order of separation: rule of temperature multipliers

We arrange the substances according to the property  $\gamma$  used for separation (boiling point in the rectification processes). We normalize  $\gamma$  so that it is in the range from 0 to 1. The order of separation of substances may be direct or reverse. In the case of a direct order, the stream with the components  $\gamma < \gamma_1$  is first separated, and then, the stream with large values of  $\gamma$  is divided into two sub-streams so that the first one has  $\gamma_1 \leq \gamma < \gamma_2$  and the second one  $\gamma \geq \gamma_2$ . In the case of reverse order, the stream with the components  $\gamma > \gamma_2$  is first separated, and then, the stream with lower values of  $\gamma$  is divided into two sub-streams so that the first one has  $\gamma_1 \leq \gamma < \gamma_2$  and the second one  $\gamma \leq \gamma_1$ .

Let  $A$  denote the work of separation of the mixture. The  $A$  includes the factor  $RT_0$ , where  $R$  is the universal gas constant and  $T_0$  is the ambient temperature. Then, the entropy of the separated fluxes will decrease in proportion to the work of separation  $A$ . In a reversible case, a decrease in the entropy of the material flux should be compensated by an increase in the entropy of the heat flux. If  $T_+$  and  $T_-$



**Figure 2.**  
Nature of change of the realization frontier with the irreversibility increase.

are the temperatures of heat supply and removal, then the increase in entropy of the heat flux can be expressed as  $\delta s_q = q(1/T_- - 1/T_+)$ . The total cost of heat depends on the order of separation, while the total work does not depend on the order of separation. At each separation stage, the heat flux is proportional to the separation work at this stage, with the proportionality multiplier  $K_T = \frac{T_+T_-}{T_+ - T_-}$ . Temperature factors are determined by the choice of the separation boundary. Denote by  $K_{T1}$  and  $K_{T2}$  the temperature factors corresponding to the separation boundary  $\gamma_1$  and  $\gamma_2$ , respectively, and by  $A_{21}$  and  $A_{22}$  the work of separation of the mixture in the second stage in the direct and inverse order of separation. The total cost of heat per mole of the input mixture in the direct and reverse order of separation can be written as:

$$q_1 = K_{T1}(A_0 - A_{21}) + K_{T2}A_{21}, \quad q_2 = K_{T2}(A_0 - A_{22}) + K_{T1}A_{22}. \quad (56)$$

To determine the separation order, it is necessary to calculate the difference:

$$\Delta q = (K_{T1} - K_{T2})[A_0 - A_{21} - A_{22}]. \quad (57)$$

If the result of the calculation Eq. (57) is negative, then it is reasonable to choose a direct separation order. If the result is positive—a reverse order.

In the case of a multistage system, this rule applies to each of two successive stages. It is easy to see that the expression in square brackets in Eq. (57) is non-negative. From here follows the rule of temperature multipliers (see [39]): The separation boundaries must be chosen so that the temperature multipliers do not decrease from stage to stage. In the case when the separation efficiency in the maximum performance mode depends only on the reversible efficiency, the rule of temperature multipliers is also valid. It is important that the information that is needed to calculate temperature factors is much more accessible and accurate than the information on the dynamics of the processes in the column.

## 6. Conclusions

This chapter discusses the problems of optimization of thermodynamics and methods of analysis of systems and describes the types of thermodynamic balances, the relationship between the performance of the process, and the production of entropy. Also, it is shown that in the absence of irreversibility, the thermal efficiency is equal to the Carnot efficiency.

The conditions are found under which the thermodynamic processes at a given average intensity have minimal dissipation, expressions for determining the minimum dissipation and entropy with the Newtonian heat transfer law are obtained, and expressions for the cases of vector flux, one-sided isothermal, and two-sided equimolar mass transfer are given.

The synthesis algorithm makes it possible to build heat exchange systems with minimal irreversibility, in which restrictions on water equivalents, temperatures, and phase states of the flows are fulfilled, which imply combining the fluxes into two equivalent ones. The nature of the set of realizable modes of heat engines and pumps is described. It is shown that the efficiency corresponding to the maximum power mode does not depend on heat transfer coefficients, but is only a function of the Carnot efficiency.

Separation processes are considered, and estimates of the thermal efficiency of the separation process and the shape of the realizable area boundary are obtained

for them. It is shown that the efficiency in the mode of maximum performance depends only on the reversible efficiency. The rule of temperature multipliers is described, which allows to determine the separation order in multistage systems.

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