GENERAL PROBLEMS OF TRANSPORT THEORY

THERMODYNAMIC ANALYSIS OF MULTISTAGE MECHANICAL SEPARATION PROCESSES

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From the viewpoint of thermodynamics at a finite time, the limiting possibilities of mechanical separation systems are considered. Lower limits of energy expenditure are obtained for separation systems with a given performance. It is shown that these expenditures do not tend to zero, when one of the components of the mixture being separated tends to a unit concentration. The estimates obtained are used to analyze multistage separation systems with recycles and, in particular, isotope separation systems. For each systems, relationships between the flows, contact surfaces, and the stage number are found, which follow from the conditions of minimum dissipation under the assumption of the constancy of the enrichment factor. A condition of the optimality of the order of separation of multicomponent mixtures in mechanical systems has been obtained.

Keywords: *multicomponent mixtures, multistage mechanical separation systems, realizability region, contact surface, entropy production, isotope separation.*

Introduction. Despite of the fact that the first works on optimization thermodynamics (thermodynamics at a finite time) were published in the early 1960s, and since then this branch of irreversible thermodynamics has been actively developed [1], the possibilities of optimization thermodynamics and its applications to technological systems are far from being exhausted.

A work on the form of the cycle of a heat engine, for which the power of the engine is maximum, was published in France as early as at the end of the nineteenth century. But only with the development of nuclear power engineering this problem acquired practical importance, and, starting with the well-known article by I. I. Novikov published in the Journal of Nuclear Energy [2], a huge number of studies were devoted to the limiting capabilities and optimal cycles of heat engines and later of refrigerating machines. Later, largely due to the efforts of the schools of S. Berry in the USA and L. Rozonoer in Russia, the problems on the limiting possibilities of thermodynamic systems of different nature with nonzero flows were recognized as a separate area of thermodynamics.

A significant part of energy is spent by humanity on separation processes. These processes differ greatly by the nature of the energy used and by the design. Absorption and adsorption–desorption cycles, rectification, vaporization, drying, and zone melting are used to separate thermal energy and are therefore classified as thermal processes. Centrifugation and membrane separation use mechanical energy; therefore, these processes are called mechanical. Boshnyakovich [3] pointed out that the largest unproductive energy losses in industry occur in chemical and metallurgical processes. For example, about six percent of the energy contained in oil is spent on its separation.

An analysis of energy losses in the indicated industries is carried out using the concept of exergy [4]. The exergy approach makes it possible to find losses due to irreversibility in a designed or operating system and to compare the systems by the magnitude of these losses, but it does not say anything about how and how much irreversible losses can be reduced with account for the limitations on the dimensions of apparatuses and their performance, and how to organize the process in such a way as to minimize these losses.

An estimate of the minimum energy needed to separate a mixture of a particular composition can be obtained using the methods of reversible thermodynamics, however, these estimates are very rough and do not take into account kinetic factors (the laws and coefficients of heat and mass transfer and the system performance). In a number of cases, irreversible

estimates not only quantitatively but also qualitatively differ from reversible ones. So, for "poor" mixtures, i.e., mixtures in which the concentration of one of the components is close to unity, the irreversible estimate, in contrast to the reversible one, tends not to zero, but to a finite limit, which depends on the kinetic coefficients. This fact is confirmed in real apparatuses, where for "poor" mixtures, for example, in the process of separation of uranium isotopes, the actual energy expenditures exceed their reversible estimates by thousands of times [5] (recall how it is difficult to find a needle in a haystack).

The thermodynamic balances (material, energy, and entropy ones) of mechanical and thermal separation systems are different, because in the first case, the flow of expended energy is not conjugated with the entropy flow and is not included into the entropy balance of the system. Usually processes in mechanical systems can be considered isothermal. In thermal systems, the energy flow is supplied to the system at one temperature, and is removed at another, and is associated with the supply and removal of entropy. Irreversible losses associated with the supply and removal of heat reduce the separation work, so that for thermal separation processes the productivity reaches a maximum with increasing heat flows and then decreases.

Account for the irreversibility and its minimization allow one not only to obtain an estimate for minimum expenditures of heat at a fixed productivity, but also to find the thermodynamic limit of productivity, above which it cannot exist at any heat losses. The dependence of the maximum productivity of the process on energy expenditures or the minimum energy expenditures on the productivity is the thermodynamic boundary of the multitude of realizable modes of the process (realizability set).

The aim of the present work is to obtain the lower limit for the work of mixture separation in mechanical multistage systems, such as diffusion isotope separation systems and isotope separation systems using centrifuges, with account for the irreversibility factors, construction of a realizability set for them, and obtaining a rule for choosing the order of separation of multicomponent mixtures, which minimizes energy expenditures, on the basis of the general methodology of thermodynamics at a finite time [6–12]. Such kind of problems are solved in two stages: 1) the sought estimates of the intensity of flows are expressed in terms of the production or increase of entropy with the use of the equations of thermodynamic balances of matter, energy, and entropy, and 2) the minimum possible production of entropy σ_{min} is determined as a function of the intensity of the flows at the given restrictions posed on the heat and mass transfer surface and on the intensity of some flows. The substitution of the found dependences into the equations of thermodynamic balances determines the limit of possibilities of the thermodynamic system.

The Set of Realizability of Mechanical Separation Systems. *Assumptions and formulation of the problem.* Let us consider an initially reversible isothermal process of mixture separation. We will assume that the mixture and its components are close in their properties to ideal gases. With this assumption taken into account, the chemical potential of the ith component will have the form

$$\mu_i(T, P, C_i) = \mu_{0i}(T) + RT \ln PC_i , \quad i = 1, \dots, n , \tag{1}$$

where C_i is the concentration of the ith component, T and P are the temperature and pressure in the system.

Let us assume that the temperature and pressure in the system before and after the end of the separation process are the same, and the system is adiabatically isolated (no heat is supplied or removed). The work of separating a mole of a mixture in such a system with an arbitrarily slow process is equal to the change in the free energy of the mixture (of the Gibbs energy), i.e., for one mole of the mixture, to the total increment of its chemical potentials [3]. This work can be expressed in terms of the initial concentration of the mixture $C^0 = (C_1^0, \dots, C_i^0, \dots, C_n^0)$ and the concentration of the mixture in those two subsystems where it entered after the separation: $C_1 = (C_{11}, \dots, C_{1i}, \dots, C_{1n})$ and $C_2 = (C_{21}, \dots, C_{2i}, \dots, C_{2n})$.

Let the fraction of the mixture that enters the first subsystem be equal to γ and the fraction that enters the second subsystem be equal to $1 - \gamma$. Then the change in the molar energy of the mixture will be equal to

$$\Delta A_0 = \sum_{i=1}^{n} (\gamma C_{1i} \mu_i(T, P, C_{1i}) + (1 - \gamma) C_{2i} \mu_i(T, P, C_{2i}) - C_{0i} \mu_i(T, P, C_{0i})) . \tag{2}$$

If we substitute the expressions for the chemical potentials of the mixture into (2) and take into account that for any component of the mixture the material balance conditions are valid:

$$\gamma C_{1i} + (1 - \gamma) C_{2i} = C_{0i} , \quad i = 1, \dots, n , \tag{3}$$

then the terms μ_{0i} and $RT \ln P$ cancel out, and expression (2) takes the form
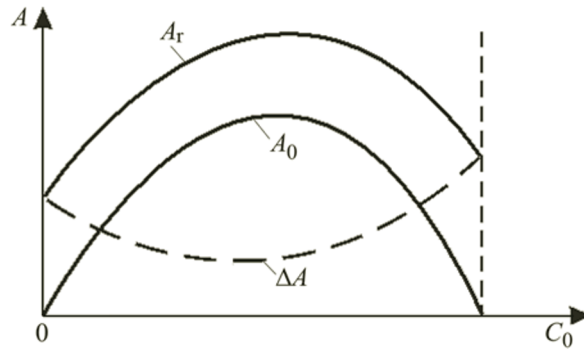
Fig. 1. Dependence of the reversible, A_0, and irreversible, A_r, estimates of the minimum work of separation of a binary mixture on the concentration of one of the components.

$$\Delta A_0 = RT \sum_{i=1}^{n} (\gamma C_{1i} \ln C_{1i} + (1 - \gamma)C_{2i} \ln C_{2i} - C_{0i} \ln C_{0i}) . \tag{4}$$

The fraction withdrawn from the mixture is related to the flow concentrations as

$$\gamma = \frac{C_{0i} - C_{2i}}{C_{1i} - C_{2i}} . \tag{5}$$

On complete separation of the mixture, when one of its components is taken into each of the subsystems and its amount and concentration are equal to $\gamma_i = C_{0i}$ and $C_{ii} = 1$, formula (4) can be used to calculate the work of mixture separation into pure components in a reversible process (the reversible work of Gibbs separation):

$$A_0 = RT \sum_{i=1}^{n} C_{0i} \ln C_{0i} . \tag{6}$$

It follows from comparing Eqs. (4) and (6) that the reversible work of incomplete separation of the mixture is equal to the difference between the reversible work of complete separation of the initial mixture and the average reversible work of complete separation of the mixture in subsystems 1 and 2 with weights γ and $1 - \gamma$:

$$\Delta A_0 = A_0 - \gamma A_{01} - (1 - \gamma)A_{02} . \tag{7}$$

The thus-found energy expenditures for the separation of the mixture represent a reversible lower limit of the actual energy expenditures. For the separation of a mixture of two-components (of binary mixture) this estimate depends on the concentration C^0 of one of the components in the initial mixture in the way as is shown in Fig. 1 (curve A_0).

Example 1. Let us calculate the reversible energy expenditures on the separation of a binary mixture with $N = 3$, in which the initial concentrations of the components are equal to $C_{01} = 0.2$ and $C_{02} = 0.8$ at the temperature $T = 300$ K into two parts, in one of which the concentration of the first component C_{11} is equal to 0.1, and in the other is $C_{21} = 0.9$. From the material balance condition we have $\gamma = 0.875$. Taking into account the fact that the concentrations of the second component before separation and after separation are defined as $C_{j2} = 1 - C_{j1}, j = 0, 1, 2$, and $R = 8.29$ J/(mole·K), we obtain $\Delta A_0 = 1321$ J by formulas (6) and (7), after multiplying the molar work of separation by three. In this case, the reversible work of mixture separation into pure components will be $A_0^0 = 3745$ J.

Reversible estimates do not take into account kinetic factors (heat and mass transfer coefficients, intensities of flows). They depend only on the mixture composition before and after separation. Meanwhile, account for the indicated factors leads to the irreversibility of the processes and, consequently, to an increase in energy expenditures. The work of mixture separation in an irreversible isothermal process in an adiabatically isolated system can be expressed in terms of the reversible work A_0 and the increase in the entropy of the system ΔS with the use of Stodola's formula [3]:

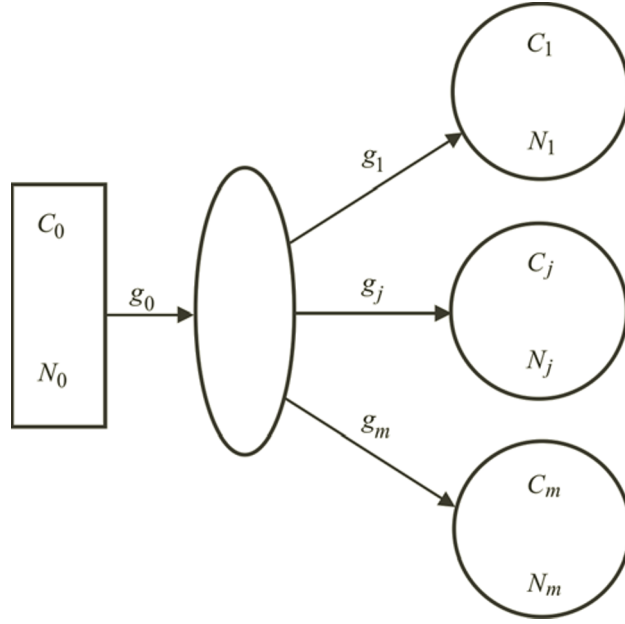$$A_r = A_0 + T\Delta S = A_0 + \delta A , \tag{8}$$

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Fig. 2. Scheme of mixture separation into m subsystems.

where T is the ambient temperature. If we go over from quantities to flows, the power expended on mixture separation in such a system will be determined as

$$p_\mathrm{r} = p_0 + T\sigma , \qquad (9)$$

where σ is the entropy production in the system and p_0 is the reversible power. The concept of reversible power requires clarification, since in reversible processes the intensity of flows is arbitrarily small. However, reversible flows can be understood as flows for which the entropy production associated with them is arbitrarily small. This corresponds to arbitrarily large heat and mass transfer coefficients. Therefore, the reversible power is the power expended on the separation of a mixture in a system of arbitrarily large dimensions with kinetic coefficients proportional to these dimensions.

Dependence of δA on the initial mixture parameters and on the duration of the process. To evaluate energy expenditures on mixture separation in the class of irreversible processes, it is necessary to find the minimum increase in entropy or the minimum production of entropy at a given duration of the process or a given intensity of flows and at the given heat and mass transfer coefficients, using formulas (8) and (9).

Let us consider the computational scheme (Fig. 2) that represents the initial mixture and m subsystems, into which the streams are directed after separation, as well as the device that implements the separation process (further called the "working body"). The working body receives energy from outside and creates flows of matter. Let us assume that the composition and total number of moles of the mixture at the beginning of the process of its separation C_0 and N_0, the composition of the mixture in each jth subsystem C_j at the end of the process, the number of moles entering each subsystem, N_j, and the duration of the process τ are assigned and satisfy the material balance conditions (3). The driving force that creates the flows of matter is the difference in chemical potentials between the working body and the initial mixture and between the working body and subsystems. In an isothermal process, the magnitude of the chemical potential can be controlled by changing the pressure.

Separation into two flows. For simplicity, we will consider only two subsystems and a binary mixture. The composition of the mixture in the second subsystem is determined completely by its initial composition and by the composition of the separated flow obtained in the first subsystem. The sum of the concentrations of two substances in each subsystem is equal to unity: $C_2 = 1 - C_1$. Let us determine the difference of chemical potentials for the ith substance:

$$\Delta\mu_{0i} = (\mu_{0i} - \mu_{0i}^\mathrm{w}) , \quad \Delta\mu_{1i} = (\mu_{1i}^\mathrm{w} - \mu_{1i}) , \quad i = 1, 2 ,$$

where μ_{0i}^{w} and μ_{1i}^{w} are the chemical potentials of the working body at the boundaries of its contact with the reservoir and subsystem. The increase in entropy associated with the creation of the flow coming from the reservoir into the first subsystem is equal to

$$\Delta S_{01} = \frac{1}{T} \int_{0}^{\tau} \sum_{i=1}^{2} (g_{01}\Delta\mu_{0i} + g_{11}\Delta\mu_{1i}) \, dt \, . \tag{10}$$

The parameters of the working body do not change during the cycle, therefore the following condition is fulfilled:

$$\int_{0}^{\tau} g_{0i} dt = \int_{0}^{\tau} g_{1i} \, dt \, , \quad i = 1, 2 \, . \tag{11}$$

The total quantity of the ith substance transferred to the subsystem in time τ is given and equal to the product of the number of moles $N(\tau)\gamma$, transferred to the subsystem, by the concentration $C_{1i}(\tau)$.

Optimal solution. The problem on the minimum of ΔS_1 in the case of fulfillment of condition (11) at $g_{0i} \geq 0$ and $g_{1i} \geq 0$ is reduced to the optimal control problem, since μ_1 depends on the concentration C_1 of mixture in the subsystem, which, in turn, varies depending on the composition and flow intensity $g_1(t)$. However, this problem is greatly simplified in that widespread case, in which the differences of the chemical potentials $\Delta\mu_{0i}$ and $\Delta\mu_{1i}$ are uniquely related to flows g_{0i} and g_{1i}, respectively. In all of the cases where the processes are close to equilibrium, the flows are proportional to the driving forces (Onsager kinetics). In a more general case, we have

$$\frac{\Delta\mu_{0i}}{T} = \varphi_{0i}(g_{0i}) \, , \quad \frac{\Delta\mu_{1i}}{T} = \varphi_{1i}(g_{1i}) \, , \quad \frac{d\varphi}{dg} > 0 \, .$$

Problem (10), (11) is divided into subproblems:

$$\Delta S_i = \frac{1}{T} \int_{0}^{\tau} \sigma_i(g_i) dt \rightarrow \min \Bigg/ \int_{0}^{\tau} g_i dt = N_1 C_{1i} \, , \quad \nu = 0, 1 \, , \quad i = 1, 2 \, , \tag{12}$$

where $\sigma_i = \sum_{\nu} g_{\nu i}\varphi_{\nu i}(g_{\nu i})$ is the entropy production. In the case of optimum solution of problem (12), the Lagrange function

$$L = \sum_{i} (\sigma_i(g_i) + \lambda g_i)$$

is stationary with respect to g_i. The function σ_i is convex down the g_i, since it is the product of the expenditure of substance into the driving force φ_i, which increases monotonically with g_i. For this reason L has the only minimum, and the optimal flow rate g_i is constant and equal to $NC_i\gamma/\tau$ for any dependence $\varphi_i(g)$, which increases with the flow rate.

Let us consider the Onsager kinetics, when the mass transfer flux is proportional to the thermodynamic driving force, i.e., to the difference of chemical potentials divided by the temperature T. In this case

$$g_i = k_i \frac{\Delta\mu_i}{T} \Rightarrow \varphi_i = \frac{g_i}{k_i} \, . \tag{13}$$

For isothermal processes occurring in membrane systems and mixtures of ideal gases, the difference of chemical potentials of the ith component is equal to the logarithm of the ratio of its partial pressures on both sides of the membrane. In centrifugation systems, the difference in pressures is created by centrifugal forces depending on the speed of the rotation of centrifuges and on the molecular weight of the components [13, 14]. In both cases, the values of the effective mass transfer coefficients, defined as the ratio of the mass transfer flux to the difference in the pressure logarithms, can be found from experimental data.

The minimum increase in entropy corresponding to dependence (13) is equal to

$$\Delta S^{\min} = \sum_i \Delta S^{\min_i} = \frac{\tau}{T} \sum_i \sigma_i \left(\frac{NC_i\gamma}{\tau} \right), \tag{14}$$

and the minimum separation work for the first subsystem is given by the relation

$$A_{1\min} = A_0 N\gamma + \tau \sum_i \sigma_i \left(\frac{NC_i\gamma}{\tau} \right). \tag{15}$$

Since the optimal values of the flows are determined through the given initial and final states of the system, the substitution of them into the dependences $\sigma_{ji}(g_{ji})$ allows one to assess (15).

For a process occurring in the vicinity of equilibrium, when the flows obey the Onsager kinetics (13), it follows from (15) that for the first subsystem

$$A_{1\min} = A_{10}N\gamma + \tau \sum_{i=1}^2 g_i^2 \left(\frac{1}{k_{0i}} + \frac{1}{k_{1i}} \right) = A_{10}N\gamma + \frac{1}{\tau} \sum_{i=1}^2 \frac{N^2\gamma^2 C_i^2}{\bar{k}_i}, \tag{16}$$

where the equivalent mass transfer coefficient in the ith component is equal to

$$\bar{k}_i = \frac{k_{0i}k_{1i}}{k_{0i} + k_{1i}}. \tag{17}$$

Expression (16) can be represented as

$$A_{1\min} = A_{10}N(\tau)\gamma + \frac{N^2\gamma^2}{\tau} \sum_{i=1}^2 \frac{C_{1i}^2(\tau)}{\bar{k}_{1i}}, \tag{18}$$

where the molar reversible work of separation is

$$A_{10} = RT \sum_{i=1}^2 \left[C_{1i}(\tau) \ln C_{1i}(\tau) - C_{0i} \ln C_{0i} \right]. \tag{19}$$

Quite similarly, for the second subsystem we obtain the relation

$$A_{2\min} = A_{20}N(\tau)(1-\gamma) + \frac{N^2(1-\gamma)^2}{\tau} \sum_{i=1}^2 \frac{C_{2i}^2(\tau)}{\bar{k}_{2i}}, \tag{20}$$

where the molar reversible work of separation is

$$A_{20} = RT \sum_{i=1}^2 \left[C_{2i}(\tau) \ln C_{2i}(\tau) - C_{0i} \ln C_{0i} \right]. \tag{21}$$

In this case, $C_{1i}\gamma + C_{2i}(1-\gamma) = C_{0i}$, $i = 1, 2$. The total irreversible work of separation is defined as

$$\delta A = \frac{N^2}{\tau} \left[\gamma^2 \sum_{i=1}^2 \frac{C_{1i}^2(\tau)}{\bar{k}_{1i}} + (1-\gamma)^2 \sum_{i=1}^2 \frac{C_{2i}^2(\tau)}{\bar{k}_{2i}} \right], \quad 0 < C_{0i} < 1, \, i = 1, 2, \tag{22}$$

which is equal to zero at $C_{0i} = 1$, $i = 1, 2$. It is shown in Fig. 1.

Going over from quantities to flows, we obtain an expression for the power of separation of a binary mixture into two flows in an irreversible process in the form of a quadratic parabola:

$$p_{\min} = A_0 g + g^2 \left[\gamma^2 \sum_{i=1}^2 \frac{C_{1i}^2}{\bar{k}_{1i}} + (1-\gamma)^2 \sum_{i=1}^2 \frac{C_{2i}^2}{\bar{k}_{2i}} \right] = cg + dg^2. \tag{23}$$
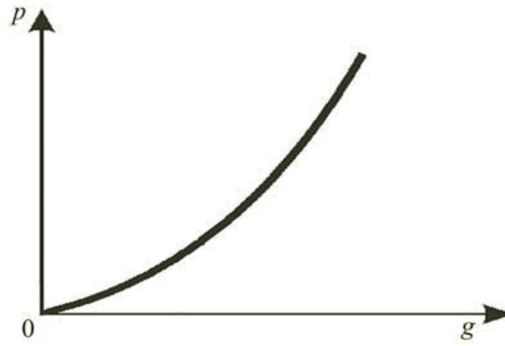
Fig. 3. Form of the realizability set for mechanical separation systems.

For the sake of definiteness, we will assume that the flow into the first subsystem is enriched with the target component with concentration C_{11} with $\bar{k}_{11} > \bar{k}_{12}$ (enrichment condition). The coefficients of the parametrized boundary of the realizability set are defined as

$$c = A_0 = RT\sum_{i=1}^{2}[\gamma C_{1i} \ln C_{1i} + (1-\gamma)C_{2i} \ln C_{2i} - C_{0i} \ln C_{0i}], \quad d = \gamma^2\sum_{i=1}^{2}\frac{C_{1i}^2}{\bar{k}_{1i}} + (1-\gamma)^2\sum_{i=1}^{2}\frac{C_{2i}^2}{\bar{k}_{2i}}. \quad (24)$$

Some of the mass transfer coefficients can be close to zero (the component is inseparable from the mixture) or to infinity (creation of the component flow does not require power consumption). Only those processes are implemented, in which power expenditures are not lower than those calculated by Eq. (23). The realizable processes lie above the boundary shown in Fig. 3.

The reversible efficiency of the process (the number of modes of the mixture to be separated per unit of expended energy) is defined as $\eta^0 = 1/s$. The efficiency of the irreversible process is equal to

$$\eta = \frac{g}{p} = \frac{1}{c + dg}. \quad (25)$$

Note that the irreversible estimate of the molar work of separation calculated by Eq. (18) is not continuous. It is equal to zero for the case where the concentration of one of the components is equal to zero, but at an arbitrarily low concentration of any component (for "lean" mixtures) it takes a finite value (curve A_r in Fig. 1); therefore the inaccuracy of reversible estimates for such mixtures is especially large.

The fact that the dependence of the system performance on the expenditures of energy is close to a quadratic parabola allows one to find the coefficients c and d from the experimental data and to use the dependence obtained in solving the problem of optimization of the separation system structure consisting of several subsystems.

Multistage Mechanical Systems. *Separation of isotopes.* In many cases, the process of mixture separation is implemented in a system of successive interconnected stages. At each stage, the mixture flow entering the system is divided into a flow enriched with the target component and a flow depleted in the target component. If the flow of the raw material is fed to the inlet of such a multistage system, the enriched flow that enters each next stage will decrease and the performance of the system in terms of the flow with a given concentration of the target component will be very small, and its concentration in the outgoing depleted flows will exceed the concentration in the raw material. Therefore, the depleted flow after each stage enters the recycle, and the raw material flow is fed not to the initial, but to the intermediate stage of the cascade. The structure of such a multistage system is shown in Fig. 4.

We will assume that the components of the raw material flow and of outgoing flows C^0, C_f, and C_{out} are given, which means that also the degree of their enrichment, defined as the ratio of the target component concentration to the concentration of the remaining component in the binary mixture: $x(C) = \dfrac{C}{1-C}$. The conditions of the dissipation minimum require that the flows, which mix up at the point of raw material feeding and at the points of entry of recirculating streams, have the same composition (condition of mixing homogeneity). This requirement can be satisfied exactly for binary mixtures, and only approximately for multicomponent ones.
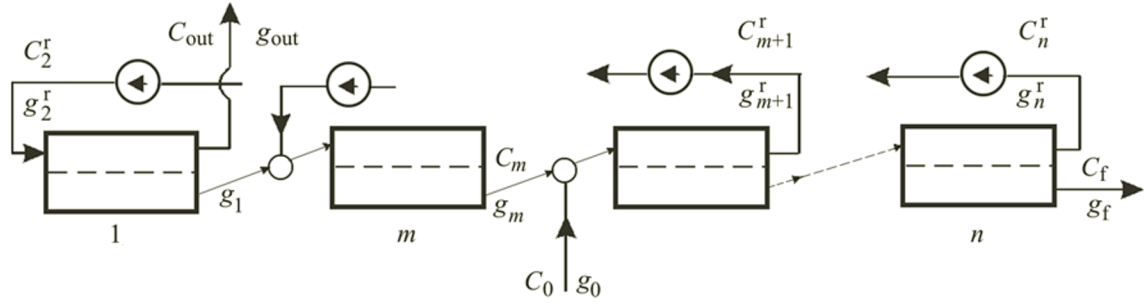
Fig. 4. Structure of the multistage mechanical separation system.

Let us write down the material balance equations for the jth stage, taking into account the condition of mixing homogeneity:

$$g_j + g_j^{\mathrm{r}} = g_{j-1} + g_{j+1}^{\mathrm{r}} \,, \quad g_j C_j + g_j^{\mathrm{r}} C_{j-2} = (g_{j-1} + g_{j+1}^{\mathrm{r}}) C_{j-1} \,,$$

$$C_{j-1} = C_{j+1}^{\mathrm{r}} \,, \quad C_m = C_{m+2}^{\mathrm{r}} = C^0 \,, \quad j = 2, \ldots, m, \, m+2, \ldots, n-1 \,. \tag{26}$$

The system is fed between the stages m and $m + 1$; the lean stream (dump) is put out after the first stage, and the enriched target stream is put out after the nth stage. Like rectification, the section of the system preceding the feeding is called exhaustive and that following the feeding is called reinforcing. For the exhaustive section conditions (26) yield the recurrent relations

$$g_{j+1}^{\mathrm{r}} = g_j^{\mathrm{r}} \frac{C_j - C_{j-2}}{C_j - C_{j-1}} - g_{j-1} \,, \quad g_j = g_j^{\mathrm{r}} \frac{C_{j-1} - C_{j-2}}{C_j - C_{j-1}} \tag{27}$$

with boundary-value conditions for $j = 1$

$$g_{j-1} = 0 \,, \quad C_j^{\mathrm{r}} = C_{\mathrm{out}} \,, \quad g_j^{\mathrm{r}} = g_{\mathrm{out}} = (1 - \gamma) g_0 \,.$$

With account for these conditions we have the relations

$$g_2^{\mathrm{r}} = g_{\mathrm{out}} \frac{C_1 - C_{\mathrm{out}}}{C_1 - C_2^{\mathrm{r}}} \,, \quad g_1 = g_{\mathrm{out}} \frac{C_2^{\mathrm{r}} - C_{\mathrm{out}}}{C_1 - C_2^{\mathrm{r}}} \,. \tag{28}$$

For the reinforcing section Eq. (27) yields

$$g_j^{\mathrm{r}} = g_j \frac{C_j - C_{j-1}}{C_{j-1} - C_{j-2}} \,, \quad g_{j-1} = g_j^{\mathrm{r}} \frac{C_j - C_{j-2}}{C_j - C_{j-1}} - g_{j+1}^{\mathrm{r}} \,. \tag{29}$$

For $j = n$ we have the boundary-value conditions $C_n = C_{\mathrm{f}}$, $g_n = g_{\mathrm{f}} = \gamma g_0$ and $g_{n+1}^{\mathrm{r}} = 0$, whence we have

$$g_n^{\mathrm{r}} = g_{\mathrm{f}} \frac{C_f - C_{n-1}}{C_{n-1} - C_{n-2}} \,, \quad g_{n-1} = g_{\mathrm{f}} \frac{C_f - C_{n-2}}{C_{n-1} - C_{n-2}} \,. \tag{30}$$

As an indicator of the separating ability of the stage, use is made of the separation factor equal to the ratio of the degrees of enrichment at the output and input of the stage: $\alpha_j = x_j / x_{j-1}$. It is considered the same for each stage, and under this condition, the system configuration is sought. The concentration of the target component depends unambiguously on the degree of enrichment:

$$C(x_j) = \frac{x_j}{1 + x_j} \,, \ldots, \, C(\alpha^{v} x_j) = \frac{\alpha^{v} x_j}{1 + \alpha^{v} x_j} \,, \ldots. \tag{31}$$

Distribution of the area of membranes or of the number of single apparatuses between individual stages. Since the flows and compositions of the separation products vary from stage to stage, the area of the membranes must vary too. In practice, the number of single apparatuses (centrifuges) connected in parallel at each separation stage is changed. We express the entropy production σ_j at each stage through the flows, concentrations of the components, and mass transfer coefficients. Moreover, we will assume that for the target component at each stage the mass transfer coefficient is equal to

$$\bar{K}_{1j} = S_j k_1 , \quad \bar{K}_{2j} = S_j k_2 ,$$

where k_1 and k_2 are the specific mass transfer coefficients for each component, and S_j is the membrane area or the number of standard single apparatuses (centrifuges) per jth step. Then the entropy production for the flow proportional to the difference of chemical potentials will be determined by the relation

$$\sigma_j = \frac{g_j^2}{S_j} \left[\frac{C_j^2}{k_1} + \frac{(1 - C_j)^2}{k_2} \right] . \tag{32}$$

In order to reduce the notation, we introduce the notation for the "squared reduced flow":

$$M_j = g_j^2 \left[\frac{C_j^2}{k_1} + \frac{(1 - C_j)^2}{k_2} \right] \tag{33}$$

and solve the problem on such a distribution of the total surface or of the total number of single apparatuses S between the stages, for which

$$\sigma = \sum_j \sigma_j = \sum_j \frac{M_j}{S_j} \rightarrow \min \Big/ \sum_j S_j = S . \tag{34}$$

The Lagrange function of this problem is defined by the expression

$$L = \sum_j \left(\frac{M_j}{S_j} + \lambda S_j \right) .$$

From the conditions of its stationarity, we obtain

$$S_j^* = S \frac{\sqrt{M_j}}{\sum\limits_{v=1}^{n} \sqrt{M_v}} , \quad \frac{S_j^*}{S_{j-1}^*} = \sqrt{\frac{M_j}{M_{j-1}}} , \quad j = 1, \dots, n . \tag{35}$$

After the substitution of conditions (35) into the expression for the entropy production (34) we obtain

$$\sigma^* = \frac{1}{S} \Big(\sum_j \sqrt{M_j} \Big)^2 . \tag{36}$$

Thus, for the separating ability constant for all stages, it is necessary to express the expenditures and concentrations included in the expression for M_j in terms of the given concentrations of output flows and the magnitude of the feeding flow and substitute into Eq. (36).

Computational formulas for a fixed separation factor. In this case, the number of stages to the point of power entry and the total number of stages are equal to

$$m = \frac{\ln x_0(C^0) - \ln x_{\text{out}}(C_{\text{out}})}{\ln \alpha} - 1 , \quad n = \frac{\ln x_{\text{f}}(C_{\text{f}}) - \ln x_{\text{out}}(C_{\text{out}})}{\ln \alpha} - 1 . \tag{37}$$

To calculate the flows at each stage, the following concentrations are substituted into formulas (27)–(29):

TABLE 1. Results of Calculations in Example

| j	x_j	C_j	g_j	M_j	S_j^*
1	0.001189	0.001188	0.78	0.63	0.43
2	0.001296	0.001295	1.49	2.33	0.83
3	0.001413	0.001411	2.14	4.83	1.19
4	0.001540	0.001538	2.74	7.92	1.52
5	0.001679	0.001676	3.29	11.42	1.83
6	0.001830	0.001827	3.80	15.19	2.11
7	0.001995	0.001991	4.26	19.13	2.37
8	0.002174	0.002169	4.69	23.14	2.60
9	0.002370	0.002364	5.08	27.16	2.82
10	0.002583	0.002576	5.44	31.14	3.02
11	0.002815	0.002808	5.77	35.03	3.20
12	0.003069	0.003059	6.07	38.80	3.37
13	0.003345	0.003334	6.35	42.44	3.52
14	0.003646	0.003633	6.61	45.93	3.67
15	0.003974	0.003959	6.84	49.26	3.80
16	0.004332	0.004313	7.06	52.42	3.92
17	0.004722	0.004700	7.26	55.42	4.03
18	0.005147	0.005120	7.44	58.26	4.13
19	0.005610	0.005579	7.61	60.93	4.22
20	0.006115	0.006078	7.76	63.45	4.31
21	0.006665	0.006621	7.91	65.81	4.39
22	0.007265	0.007213	8.04	68.04	4.46
23	0.007919	0.007857	7.83	64.57	4.35
24	0.008632	0.008558	7.05	52.37	3.91
25	0.009409	0.009321	6.34	42.30	3.52
26	0.010255	0.010151	5.68	34.01	3.15
27	0.011178	0.011055	5.08	27.19	2.82
28	0.012184	0.012038	4.53	21.60	2.51
29	0.013281	0.013107	4.02	17.04	2.23
30	0.014476	0.014270	3.56	13.33	1.97
31	0.015779	0.015534	3.13	10.32	1.74
32	0.017199	0.016908	2.74	7.89	1.52
33	0.018747	0.018402	2.38	5.95	1.32
34	0.020434	0.020025	2.05	4.41	1.14
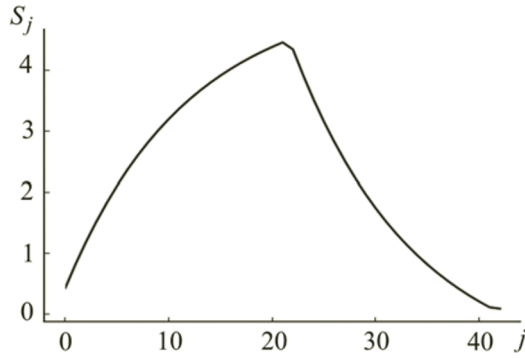
Fig. 5. Optimal distribution of contact areas between stages.

$$C_j = C(\alpha^{j+1} x_{\text{out}}), \quad C_j^{\text{r}} = C(\alpha^{j-1} x_{\text{out}}), \quad C_{j-1} = C_{j+1}^{\text{r}} = C(\alpha^j x_{\text{out}}),\tag{38}$$

where $C(\alpha^{m+1} x_{\text{out}}) = C^0$ at $j = m$ and $C(\alpha^{n+1} x_{\text{out}}) = C_{\text{f}}$ at $j = n$.

Example. $C^0 = 0.007$, $C_{\text{out}} = 0.001$, $C_{\text{f}} = 0.04$, $\alpha = 1.09$, $g_0 = 1.0$ mole/s, $T = 323$ K, and the specific coefficients of mass transfer are equal to: $k_1 = 1.05$ and $k_2 = 0.95$. Their dimensionality is $(\text{mole}^2 \cdot \text{K})/(\text{J} \cdot \text{s} \cdot \text{m}^2)$. The total contact area is equal to $S = 100$ m^2.

Using formulas (37), (38), and (5), we obtain that $m = 22$, $n = 43$, and $\gamma = 0.154$, with rounding off to the larger integer. The enrichment degree, concentrations, and the substance flow at the outlet of the first stage, determined by formulas (27) and (29), are equal to

$$x_{\text{out}} = 0.001001, \quad C_2^{\text{r}} = C(x_{\text{out}}\alpha) = 0.001089, \quad C_1 = C(x_{\text{out}}\alpha^2) = 0.001188,$$

$$g_1 = 0.846 \frac{C(x^{\text{out}}\alpha) - C^{\text{out}}}{C(x^{\text{out}}\alpha^2) - C(x^{\text{out}}\alpha)} = 0.776 \text{ mole/s}.$$

Using formula (33), we find the "square of the reduced flow", and using formula (35), we determine the distribution of the surface between the stages:

$$M_1 = 0.776^2 \left(\frac{0.001188^2}{1.05} + \frac{(1 - 0.001188)^2}{0.95} \right) = 0.632.$$

The results of calculations for all the stages are presented in Table 1. The optimal distribution of the contact areas is shown in Fig. 5. According to Eq. (36), the total production of entropy is $\sigma^* = 341.91$ W/K.

The reversible work of separation of the mole of a mixture can be calculated by formula (4):

$$\Delta A_0 = 8.31 \cdot 323 \cdot (0.154 \cdot 0.04 \cdot \ln (0.04) + 0.154 \cdot (1 - 0.04) \cdot \ln (1 - 0.04)$$

$$+ (1 - 0.154) \cdot 0.001 \cdot \ln (0.001) + (1 - 0.154) \cdot (1 - 0.001) \cdot \ln (1 - 0.001)$$

$$- 0.007 \cdot \ln (0.007) - (1 - 0.007) \cdot \ln (1 - 0.007) = 24.64 \text{ J/mole},$$

whence the reversible power of separation of a mole of a mixture is $p_0 = \Delta A_0 g = 24.64$ W. According to (9), the irreversible power expenditures are equal to $T\sigma^* = 323 \cdot 341.91 = 110.435$ kW. They are 4480 times larger than reversible ones, which is confirmed by the practice of separation of "lean mixtures" (Fig. 1, [17, 18]).

Selection of the Sequence of Separation of Multicomponent Mixtures. It was assumed above that the mixture being separated is binary, and separation occurs into flows, each of which contains two components. In the case that a mixture is multicomponent and it needs to be separated into several flows, the problem arises as to the order of separation. In this case, multicomponent mixtures are separated sequentially into two flows. Thus, mixture of three components is separated first into two flows, one of which contains two components, and then this flow is again separated at the second

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stage. Both the mass transfer coefficients and the flow rates of the output flows at each stage depend on the choice of the separation boundary. The problem of choosing the order of separation was solved under the assumption of complete separation, when each of the output flows contains only one component. Here, by the stage we understand a complex of separating devices with an equivalent mass transfer coefficient.

As already mentioned, the reversible operation of mechanical systems of power p_0 does not depend on the order in which the separation is organized, since p_0 is determined only by the flow rates and compositions of flows at the inlet and outlet of the scheme as a whole. But according to (28), it is the irreversible component of the power Δp depends on the order, in which the components are selected, that allows one to choose this order.

A mixture of three components. Let us consider a mixture consisting of three components with concentration $C^0 = (C_{01}, C_{02}, C_{03})$ and flow rate g_0, which can be taken as a unit. In this case, the flow rates can be expressed in terms of their concentrations in the mixture being separated. The components are ordered by the property used for separation (density, membrane permeability). The mass transfer coefficients depend on the choice of the separation boundary.

Let us find the irreversible energy expenditures for the case where the first component is initially separated from the mixture (direct separation order) (a) and for the case where the third component is separated first, and then the first and second (reverse order of separation) (b). Let α_1 be the mass transfer coefficient in the direct order of separation and α_2 be the mass transfer coefficient in the reverse order of separation. For the sake of simplicity, the separation at each stage will be assumed to be complete.

In accordance with (28), irreversible energy expenditures for the variant *a* are equal to

$$\Delta p_a = \Delta p_{a1} + \Delta p_{a2} = \frac{C_{01}^2}{\alpha_1} + \frac{(C_{02} + C_{03})^2}{\alpha_1} + (C_{02}^2/\alpha_2 + C_{03}^2/\alpha_2) . \tag{39}$$

The first two terms in this sum represent the losses from irreversibility at the first stage of separation. At $g_0 = 1$ and complete separation, the flow rates g_1 and g_2 at the outlet of this stage are equal to C_{01} and $(C_{02} + C_{03})$, respectively. The mixture of the second and third components is considered to be one substance with the flow rate at the outlet $C_{02} + C_{03} = 1 - C_{01}$. For the variant (b) we obtain a similar relation:

$$\Delta p_b = \Delta p_{b1} + \Delta p_{b2} = \frac{C_{03}^2}{\alpha_2} + \frac{(C_{02} + C_{01})^2}{\alpha_2} + (C_{02}^2/\alpha_1 + C_{01}^2/\alpha_1) . \tag{40}$$

If the difference between these irreversible expenditures is negative, then the direct order of separation is preferable. The condition

$$\Delta p_{ab} = \Delta p_a - \Delta p_b < 0 \tag{41}$$

after simple calculations yields the inequality

$$\alpha_1 C_{01}(C_{01} + 2C_{02}) > \alpha_2 C_{03}(C_{03} + 2C_{02}) . \tag{42}$$

If the sign of inequality in (42) is opposite, then at the first stage of separation it is preferable to separate the third component.

Example 2. Let the initial three-component mixture have the composition $C_{01} = 0.6$, $C_{02} = 0.3$, $C_{03} = 1 - C_{01} - C_{02}$ and the mass transfer coefficients $\alpha_1 = 0.1$ mole^2/(J·s) and $\alpha_2 = 0.2$ mole^2/(J·s). It is easy to see that inequality (42) is valid ($0.072 > 0.032$), which means that first we need to separate the first and then the second and third components.

Multicomponent mixtures. When separating mixtures with more than three components, rule (42) makes it possible to compare any two possible variants for choosing the separation boundary by combining several components into one equivalent selection (fraction).

Let the total concentration of components with subscripts from 1 to i be equal to $x_1(i)$, the mass transfer coefficient corresponding to the ith separation boundary be equal to α_i, the mass transfer coefficient corresponding to the jth boundary be equal to α_j, the total concentration of components from $j + 1$ to n be equal to $x_3(j)$, $j > i$, and $x_2(i, j)$ be the concentration of the fraction consisting of the components located between the ith and jth separation boundaries. Note that x_1 depends on the choice of the upper boundary and x_3 — of the lower one. At the first stage it is advisable to select the ith boundary if for all values of $j > i$ the inequality similar to (42) is satisfied:

$$\alpha_i x_1(i)[x_1(i) + 2x_2(i, j)] > \alpha_j x_3(j)[x_3(j) + 2x_2(i, j)] . \tag{43}$$

Let the expression

$$F_{ij} = \frac{\alpha_i x_1(i)(x_1(i) + 2x_2(ij))}{\alpha_j x_3(j)(x_3(j) + 2x_2(ij))}$$

be called the efficiency ratio corresponding to the ith separation boundary. At each stage, the choice of the separation boundary corresponds to the maximum of the efficiency in i at $j > i$.

Conclusions. The boundaries of the sets of realizable modes for mechanical separation systems have been obtained, and it is determined in which way the kinetics of the mass transfer processes exerts its influence on their shape. The distributions of contact surfaces, flow rates of a direct flow and of the recycle for a multistage isotope separation system that satisfy the conditions of the minimum of energy dissipation in it are obtained on the assumption of constancy of enrichment factors in the reinforcing and exhaustive sections. It is shown that account for the irreversibility of the process of separation of a multicomponent mixture makes it possible to formulate and solve the problem of the order of mixture separation by the condition of the minimum of irreversible energy expenditures.

NOTATION

C, concentration of the target component in the mixture; g, the flow of the mixture to be separated; i, number of the substance component; N, number of moles of the mixture being separated; p, energy of mixture separation; R, universal gas constant; S, entropy of the system; x, degree of substance enrichment; α, mass transfer coefficient; γ, fraction of the mixture taken into the first subsystem. Indices: f, finite; r, reversibility; out, output; w, wall.

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