Finite-time thermodynamics: Multistage separation processes consuming mechanical energy ☆

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HIGHLIGHTS

- Isotope separation is a very important process in nuclear engineering.
- Classical estimations of energy costs for such processes are very rough.
- Finite-time thermodynamics allows to obtain more realistic estimates.

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ABSTRACT

We analyze limiting capabilities of mechanical separation processes using finite-time thermodynamics and obtain estimates for the lower bound of the energy consumption for systems of a given productivity. We show that this consumption does not tend to zero when the molar fraction of one of the components tends to unity. The estimates obtained are used to analyze multistage separation processes, containing recycles, especially, isotope separation systems. For such systems we obtain relations between fluxes, mass transfer surfaces, and stage number. These relations are deduced from the condition of minimum dissipation, assuming that the enrichment factor is constant. We also obtain the optimality condition for the sequence of separations needed for a multicomponent mixture in a mechanical separation systems.

1. Introduction

Despite the fact that the first works on optimization thermodynamics (thermodynamics at finite time) were published in the early 1960s, and since then this section of irreversible thermodynamics has been actively developing (Andresen, 1983; Andresen, 2011), this field of thermodynamics and its applications to technological systems are far from being exhausted.

Works considering the shape of heat engine cycles, for which their output power is maximum were published in France at the end of the nineteenth century (Moutier, 1872). However it was only in connection with the development of nuclear energy that this problem acquired practical importance and, starting with the well-known article by I. I. Novikov in the Journal of Nuclear Energy (Novikov, 1954), a huge number of studies were devoted to the limiting capabilities and optimal cycles of thermal machines. Later, largely thanks to the efforts of the schools of S. Berry in the USA and L. Rozonoer in Russia, the problems of the limiting capabilities of thermodynamic systems of different nature with nonzero fluxes were recognized as a separate area of thermodynamics (Andresen et al., 2000).

Humanity spends a significant part of its energy consumption on separation processes. These processes are very diverse in terms of the nature of the energy used and in terms of design. Absorption- and adsorption–desorption cycles, distillation, evaporation, drying, zone melting, etc. use thermal energy for separation (they are called *thermal*); in centrifugation and membrane separation mechanical energy is being utilized (these systems are called *mechanical*). Bosnjakovic (Bosnjakovic, 1965) pointed out that the

Nomenclature

α	ratio of enrichment factors	k	mass transfer coefficients, mol^2·K/(J·s)
η	efficiency	K	specific mass transfer coefficients, mol^2·K/(J·s·m^2)
γ	fraction	L	Lagrange function
λ	Lagrange multipliers	m, n	number of steps/stages
μ	chemical potentials, J/mol	M	square of the reduced flux, W·m^2/K
σ	entropy generation rate, W/s	N	numbers of moles, mol
τ	time, s	p	power outputs, W
φ	dissipation factors, J/(mol·K)	P	pressure, Pa
A	molar energies, J/mol	R	gas constant, 8.31 J/(K·mol)
c, d	characteristic coefficients	S	total entropy generation, J/K
C	mole fraction	T	temperatures, K
F	size of a stage	x	enrichment factor
g	material fluxes, mol/s		

largest unproductive energy losses in industry are in chemical and metallurgical processes. For example, separating oil takes about six percent of the energy it contains.

Analyses of energy losses in these industries were carried out using so-called exergy analysis (El-Sayed and Gaggioli, 1989). The exergy approach allows one to find irreversible losses in a designed or operating system and thus to compare systems in terms of the magnitude of these losses. However, this does not say anything about how and to what limit irreversible losses can be reduced, taking into account restrictions on the size of devices and their performance, nor how to organize the process to keep these losses to a minimum.

An estimate of the minimum energy required to separate a mixture of a given composition can be obtained using the methods of reversible thermodynamics. These estimates are usually quite rough, and they do not take into account kinetic factors (laws and coefficients of heat and mass transfer, system performance, etc.). In some cases, irreversible estimates differ not only quantitatively, but also qualitatively from reversible ones. E.g. for diluted mixtures in which the molar fraction of one of components is close to unity, irreversible estimates in contrast to reversible estimates do not tend to zero but to a finite limit depending on the kinetic coefficients. This fact finds confirmation in real systems, where for diluted mixtures, for example for separation of uranium isotopes, the actual energy consumption exceeds the reversible estimates by thousands of times (Chambadal, 1958). Figuratively speaking, it is extremely difficult to find a needle in a haystack.

Thermodynamic balances (material, energy and entropy) of mechanical and thermal separation systems are different since in the first case the flux of expended energy is not coupled with the flux of entropy and is not included in the entropy balance of the system (Tsirlin and Sukin, 2014).

Typically, processes in mechanical systems may be considered isothermal. In thermal systems, the energy flux is supplied to the system at one temperature and removed at a different temperature and is coupled with entropy supply and removal. Irreversible losses associated with the supply and removal of heat increase the work of separation, so that for thermal separation processes the productivity reaches a maximum with an increase in heat fluxes and then decreases.

Taking into account and minimizing irreversibility not only allows one to obtain an estimate of the minimal expended heat for a fixed productivity, but also to find the thermodynamic limit of productivity above which the process cannot operate at any heat input. The dependence of the maximum process productivity on energy consumption or the minimum energy consumption on productivity is the thermodynamic boundary of the set of realizable process modes (reachable set).

The purpose of this work is to obtain such a lower estimate, taking into account irreversibility factors, for separation operation in mechanical multistage systems, such as diffusion and centrifugal isotope separation systems. Further, it will construct a feasibility set for them, as well as to obtain a rule for choosing the order of separations of multicomponent mixtures while minimizing energy costs.

We follow the general methodology of finite-time thermodynamics (Berry et al., 1999; Amelkin et al., 2001). The algorithm of solving such problems consists of two stages:

- express the sought-for estimates of the flux intensity through the generation of entropy using the equations of thermodynamic balances for matter, energy, and entropy;
- find the minimum possible entropy generation σ_{min} as a function of the fluxes at given constraints (on the surface of heat and mass transfer, on the intensity of some flows, etc.).

Substitution of the resulting relations into the thermodynamic balance equations determines the limit of the capabilities of the thermodynamic system.

This procedure is very general and can be applied to any physical system. It was shown (Rozonoer and Tsirlin, 1983) that there are two important categories of such systems: thermal ones, where the energy supplied is heat (e.g. distillation and thermal diffusion), and mechanical ones, where energy supplied is work (e.g. mechanical or electric). Many problems considering optimization of systems of the first kind were stated and solved in previous works by the present authors (Schaller et al., 2002; Tsirlin and Sukin, 2014) as well as by colleagues (Dhole and Linnhoff, 1993; Rivero, 1995; Schack et al., 2020).

2. Reachable set of mechanical separation systems

Assumptions and problem statement. Consider the initially reversible isothermal separation process. We will assume that the mixture and its components are close in their properties to ideal gases, so that the chemical potential of the i-th component can be written in the form

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

where C_i is the mole fraction of the i-th component, T and P — the temperature and pressure of the mixture.

We assume that the temperature and pressure of the system do not change during the separation process and it is adiabatic (heat is not 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 its free energy (Gibbs energy), i.e. for one mole of

the mixture, the total increment of chemical potentials (Bosnjakovic, 1965). This work can be expressed through the vector of initial mole fractions $C_0 = (C_{01}, \ldots, C_{0i}, \ldots, C_{0n})$ and the vectors of mole fractions in the products after separation $C_1 = (C_{11}, \ldots, C_{1i}, \ldots, C_{1n})$ and $C_2 = (C_{21}, \ldots, C_{2i}, \ldots, C_{2n})$.

Let us denote by γ the fraction of the mixture that entered the first subsystem, and by $(1 - \gamma)$ the fraction that entered the second subsystem. Then the change in molar energy is

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

If we substitute expressions for chemical potentials in (2) and take into account that the material balance conditions must be satisfied for all components

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

then the terms μ_{0i} and $RT \ln P$ will cancel and the expression (2) takes the form

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

The product fraction is related to the mole fractions of flows as:

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

For complete separation, i.e. when one component is selected for each of the subsystems, its initial fraction is $\gamma_i = C_{0i}$, and final the mole fraction is $C_{ii} = 1$. From formula (4) we obtain the work of separating the mixture into pure components in a reversible process (Gibbs reversible work of separation):

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

By comparing (4) and (6) it follows that the reversible work of incomplete separation is equal to the difference between the reversible work of complete separation of the initial mixture and the average with weights γ and $(1 - \gamma)$ reversible work of complete separation of the mixture into subsystems 1 and 2

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

The separation energy costs thus found represent a reversible lower estimate of the actual costs. For separation of a mixture of two components (binary), this estimate depends on the mole fraction of C_0 of one of them in the initial mixture as shown in Fig. 1 (curve A_{irr}).
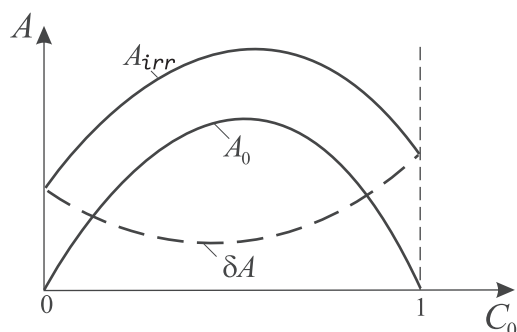
Reversible estimates do not take into account kinetic factors (heat and mass transfer coefficients, flow rates, etc). They depend only on the composition of the mixture before and after separation. Meanwhile, taking into account these factors leads to the irreversibility of the processes, and, consequently, to an increase in energy costs. Separation work in an isothermal process for an adiabatically isolated system can be expressed by the Stodola formula (Bosnjakovic, 1965) through the reversible work A_0 and the increase in the entropy of the system ΔS, as

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

where T is the environmental temperature.

The expression for δA as a function of the mixture composition and of the duration of the process is obtained below.

If we go from quantities to fluxes, then the separation power in such a system is

$$p_{irr} = p_0 + T \sigma, \tag{9}$$

where σ is the entropy generation rate in the system and p_0 is the reversible separation power.

The concept of reversible power requires an explanation, since for a reversible process we usually take the intensity of flows to be vanishingly small. However, we could also achieve a vanishingly small entropy production with a system of arbitrarily large size and kinetic coefficients proportional to this size while keeping the total turnover constant. This allows a non-vanishing reversible power even in the reversible limit.

To estimate the energy consumption for separation in the class of irreversible processes, it is necessary to find the minimum entropy generation for a given process duration or a given flow rate as well as given heat and mass transfer coefficients and then use the formulas (8), (9).

Let us consider the design scheme (Fig. 2), consisting of the initial mixture and m subsystems into which flows are directed after separation, connected by a device that implements the separation process (we will call it "separation device").

The separation device receives energy from the outside and creates fluxes of matter. We will assume that the composition C_0 and the total number of moles N to be separated at the beginning of the process, the composition of the mixture in each jth subsystem C_j at the end of the process, and the number of moles N_j arriving to each subsystem, as well as the duration of the process τ are set and satisfy the material balance conditions (3).

The driving force for the fluxes of matter is the chemical potential difference between the separation device and the initial mixture and between the separation device and the subsystems. In

Fig. 1. The minimum work of complete separation A of a binary mixture as a function of the initial mole fraction of one of its components C_0. The curve A_0 assumes reversible operation, A_{irr} is an example of irreversible operation with δA being the difference between the two, i.e. the cost of the irreversibility.
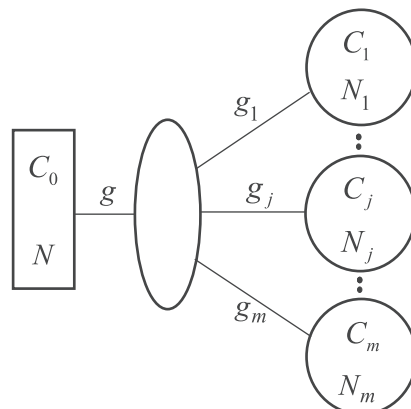

Fig. 2. Scheme of mixture separation into m subsystems. C and N are the mole fractions of one of the components and the number of moles treated, respectively, of the input (0) and output fractions (j). g are the fluxes of the respective flows.

an isothermal process, the chemical potential can be controlled by changing the pressure.

2.1. Separation into two streams

For simplicity, we will consider only two subsystems and a binary mixture. The composition of the mixture in the second subsystem is completely determined by its initial composition and the composition of the separated flow obtained in the first subsystem due to mass balance. The sum of the mole fractions of two substances in each subsystem is equal to unity ($C_2 = 1 - C_1$). Let us denote by N the number of moles of the mixture to be separated, and by γ the fraction of the product that ends up in the first subsystem.

Let us denote the difference in chemical potentials for the i-th substance as

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

Here, the index w marks the chemical potentials of the separation device at the boundaries of its contact with the reservoir and subsystem.

The entropy generation associated with the creation of a flux from the reservoir to the first subsystem is

$$\Delta S_{01} = \frac{1}{T} \int_0^\tau \sum_{i=1}^2 (g_{01}\Delta\mu_{0i} + g_{11}\Delta\mu_{1i})dt. \tag{10}$$

where g_{j1} are the fluxes of components 0/1 from the source to subsystem 1.

The parameters of the separation device do not change, so that

$$\int_0^\tau g_{0i}dt = \int_0^\tau g_{1i}dt, \quad i = 1, 2. \tag{11}$$

The total amount of the i-th substance transferred to the subsystem during the τ time is given and is equal to the product of the number of moles $N(\tau)\gamma$ transferred to the subsystem by the mole fraction $C_{1i}(\tau)$.

Optimal solution

The problem of the minimum of ΔS_1 under the conditions (11) with controls $g_{0i} \geq 0, g_{1i} \geq 0$, in the general case turns out to be a problem of optimal control, since μ_1 depends on the mole fraction vector C_1 of the mixture in subsystem, and that, in turn, changes depending on the composition and intensity of the flow $g_1(t)$. However, this problem is greatly simplified in the common case, when the differences in chemical potentials $\Delta\mu_{0i}$ and $\Delta\mu_{1i}$ are uniquely related to the fluxes g_{0i} and g_{1i}, respectively. In all cases where the processes are close to equilibrium, the fluxes are proportional to the driving forces (Onsager kinetics).

More generally

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

where $\varphi(g)$ is a dissipation factor that relates the dissipation to the flux g. This depends on the type of flux, mechanical details, and the substance.

The problem (10), (11) breaks down into subproblems of the form

$$\Delta S_i = \frac{1}{T} \int_0^\tau \sigma_i(g_i)dt \to \min / \begin{array}{l} \int_0^\tau g_i dt = N_1 C_{1i} \\ v = 0, 1, \quad i = 1, 2, \end{array} \tag{12}$$

where $\sigma_i = g_{vi}\varphi_i(g_i)$ is a function that determines the dissipation.

Along the optimal solution of the problem (12), its Lagrange function

$$L = \sum_i (\sigma_i(g_i) + \lambda g_i)$$

is stationary with respect to g_i.

The function σ_i is concave with respect to g_i, since it is the product of the flux and its driving force φ_i, which monotonically increases with g_i. Therefore, L has a single minimum, and the optimal flux g_i is constant and equal to $\frac{NC_i\gamma}{\tau}$ for any φ_i that increases with the flow rate.

Consider the Onsager kinetics, when the mass transfer flux is proportional to the thermodynamic driving force, i.e. the chemical potential difference 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 in membrane systems and mixtures of ideal gases, the difference in chemical potentials of the i-th component is equal to the logarithm of the ratio of its partial pressures on both sides of the membrane. In centrifugation systems, the pressure difference is created by centrifugal forces, which depend on the rotational speed of the centrifuges and the molecular weight of the (London, 1961; Halle, 1980) components. In both cases, the values of the effective mass transfer coefficients (the ratio of the mass transfer flow to the difference in logarithms of pressures) can be found from experimental data.

The minimum entropy generation corresponding to the solution (13) is

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

and the minimum work of separation for the first subsystem is

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

Since the optimal flow values are determined through the given initial and the final states of the system, their substitution into the equation $\sigma_{ji}(g_{ji})$ allows one to improve the estimate (15).

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

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

where the equivalent mass transfer coefficient for the i-th component is

$$\overline{k_i} = \frac{k_{0i}k_{1i}}{k_{0i} + k_{1i}}. \tag{17}$$

Expression (16) can be rewritten as

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

where the molar reversible work of separation is

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

In exactly the same way we obtain for the second subsystem:

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

Here the molar reversible work of separation is

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

Further we have $C_{1i}\gamma + C_{2i}(1-\gamma) = C_{0i}, \quad i = 1, 2.$

The total irreversible work of separation has the form corresponding to A_{irr} in Fig. 1.

After passing from molar quantities to fluxes, we obtain an expression for the power needed for separating a binary mixture into two flows by an irreversible process in the form of a parabola:

$$p_{min} = A_0 g + g^2 \left[\gamma^2 \sum_{i=1}^{2} \frac{C_{1i}^2}{\overline{k_{1i}}} + (1-\gamma)^2 \sum_{i=1}^{2} \frac{C_{2i}^2}{\overline{k_{2i}}} \right] = cg + dg^2. \quad (22)$$

Here g is the flux of the mixture to be separated. For definiteness, we will assume that the flow to the first subsystem is enriched with the target component, the mole fraction of which is C_{11}, while $\overline{k_{11}} > \overline{k_{12}}$ (enrichment condition).

The coefficients of the parametrized boundary of the realizability set are

$$c = A_0 = RT \sum_{i=1}^{2} [\gamma C_{1i} \ln C_{1i} + (1-\gamma) C_{2i} \ln C_{2i} - C_{0i} \ln C_{0i}], \quad (23)$$

$$d = \gamma^2 \sum_{i=1}^{2} \frac{C_{1i}^2}{\overline{k_{1i}}} + (1-\gamma)^2 \sum_{i=1}^{2} \frac{C_{2i}^2}{\overline{k_{2i}}}. $$

Some mass transfer coefficients can be close to zero (the component cannot be separated from the mixture) or to infinity (creating a component flow does not require energy consumption).

Only those processes are realizable for which the energy consumption is not lower than the one calculated by the formula (22). The realizable processes lie above the boundary shown in Fig. 3.

The reversible efficiency of the process (number of moles of the separated mixture per unit of consumed energy) $\eta^0 = \frac{1}{c}$. Taking into account the irreversibility, the efficiency of the process is equal to:

$$\eta = \frac{g}{p} = \frac{1}{c + dg}. \quad (24)$$

Note that the irreversible estimate of the molar work of separation calculated by Eq. (18) is discontinuous. It is equal to zero for the case when the mole fraction of one of the components is zero, but at an arbitrarily low mole fraction of any component (for diluted mixtures) it takes a finite value (see the A_{irr} curve in Fig. 1). This explains why the inaccuracy of reversible estimates is especially large for such dilute mixtures.

The result that the dependence of the system performance on energy consumption is close to parabola makes it possible to find the coefficients c and d from experimental data and use the resulting dependence when solving problems of structure optimization for many separation systems.
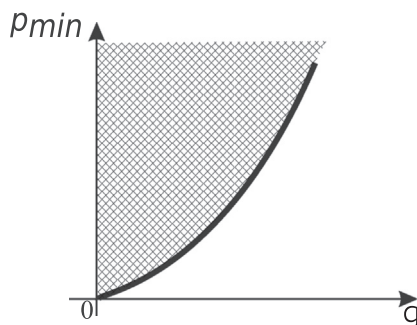

Fig. 3. The reachable set for mechanical separation systems is the hatched area above the curve. At a certain operation flux g the minimal dissipation is at least p_{min}.

3. Multistage mechanical systems. Isotope separation

In many cases, the separation process is implemented as a system of successive interconnected stages (Tsirlin et al., 2016). At each stage, the mixture stream entering it is divided into a stream enriched in the target component and one depleted in the target component. There are many well-known processes suitable for isotope separaton: distillation, centrifugation, diffusion, etc. Our purpose is to put several well-known separation methods on the same footing so that an educated quantitative choice between different processes as well as the sequence of multiple separations can be made without recourse to tradition, rule of thumb, and "we usually do".

If a feed stream is fed to the inlet of such a multistage system, then the enriched flow entering each subsequent stage decreases and as its mole fraction increases. At the same time, the mole fraction in the depleted effluent streams of each subsequent stage will exceed the mole fraction in the feed. Therefore, the depleted stream after each stage is recycled, and the feed stream is fed not to the initial, but to an intermediate stage of the cascade matching its molar fraction. The structure of such a multistage system is shown in Fig. 4.

We assume that the given compositions C_0, C_f, C_{out}, and hence the *enrichment factor* $x(C) = \frac{C}{1-C}$ are the mole fraction ratios of the target component to the mole fraction of the remaining component in the binary mixture, for the feed stream and output streams.

Minimum dissipation conditions require that the streams mixing at the feed point and at the points of entry of the recycle streams have the same composition (*uniform mixing condition*). For binary mixtures, this requirement can be fulfilled exactly, but for multicomponent mixtures only approximately.

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

$$g_j + g_j^r = g_{j-1} + g_{j+1}^r, \quad g_j C_j + g_j^r C_{j-2} = \left(g_{j-1} + g_{j+1}^r \right) C_{j-1}, \quad (25)$$

$$C_{j-1} = C_{j+1}^r, C_m = C_{m+2}^r = C_0, \quad j = 2, \ldots m, m+2, \ldots, n-1,$$

where C is the mole fraction of the target component.

The feed is introduced into the system between stages m and $m+1$, the depleted flow (waste) is removed after the first stage, and the target enriched flow after the n-th stage. Like in distillation, the section of the system with the mixture lighter than the feed is called stripping, and the section with the mixture heavier than the feed is called rectifying.

The conditions (25) for the stripping section imply the recurrence relations:

$$g_{j+1}^r = g_j^r \frac{C_j - C_{j-2}}{C_j - C_{j-1}} - g_{j-1}, \quad g_j = g_j^r \frac{C_{j-1} - C_{j-2}}{C_j - C_{j-1}} \quad (26)$$

with boundary conditions for $j = 1$:

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

Taking these conditions into account, we obtain:

$$g_2^r = g_{out} \frac{C_1 - C_{out}}{C_1 - C_2^r}, \quad g_1 = g_{out} \frac{C_2^r - C_{out}}{C_1 - C_2^r}. \quad (27)$$

For a rectifying section it follows from (26) that:

$$g_j^r = g_j \frac{C_j - C_{j-1}}{C_{j-1} - C_{j-2}}, \quad g_{j-1} = g_j^r \frac{C_j - C_{j-2}}{C_j - C_{j-1}} - g_{j+1}^r. \quad (28)$$

Boundary conditions for $j = n$ are $C_n = C_f, g_n = g_f = \gamma g_0, g_{n+1}^r = 0$, thus we obtain
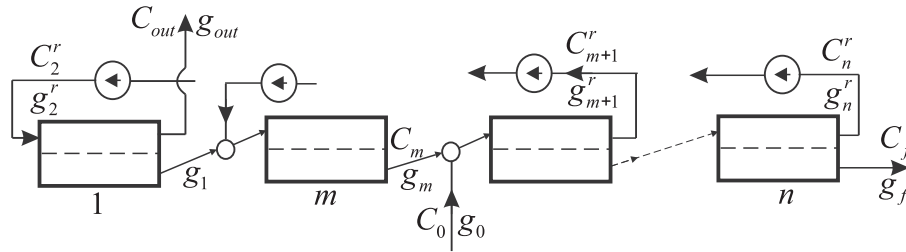
Fig. 4. Structure of a multistage mechanical separation system. The depleted stream after each stage enters the recycle, and the feed stream g_0 with molar fraction of the target component C_0 is fed not to the initial, but to an intermediate stage of the cascade.

$$g_n^r = g_f \frac{C_f - C_{n-1}}{C_{n-1} - C_{n-2}}, \quad g_{n-1} = g_f \frac{C_f - C_{n-2}}{C_{n-1} - C_{n-2}}. \tag{29}$$

The separation factor is used as an indicator of the separation ability of the stage and is equal to the ratio of the enrichment factors at the outlet and at the inlet of the stage $\alpha_j = \frac{x_j}{x_{j-1}}$. It is considered the same for each stage, and under this condition, the system configuration is being calculated.

The mole fraction unambiguously depends on the degree of enrichment:

$$C(x_j) = \frac{x_j}{1 + x_j}, \ldots, C(\alpha^v x_j) = \frac{\alpha^v x_j}{1 + \alpha^v x_j}, \ldots \tag{30}$$

Distribution of membrane surface or number of single devices between individual stages

Since the fluxes and compositions of the separation products change from stage to stage, the size of the stages must also change. The number of single units (e.g. distillation trays, centrifuges, membranes) connected in parallel is typically changed at each separation stage.

Let us express the entropy generation σ_j at each stage in terms of flows, component mole fractions and mass transfer coefficients. In this case, we will assume that for the target component at each stage, the mass transfer coefficient is

$$\overline{k}_{1j} = F_j K_1, \quad \overline{k}_{2j} = F_j K_2,$$

where K_1, K_2 are specific mass transfer coefficients for each component, and F_j is the membrane area or the number of standard single pieces of equipment (e.g. centrifuges) at the j-th stage. We will call this value "the size of a stage". Then, for a flux proportional to the difference in chemical potentials, as shown above, the entropy generation can be expressed through the fluxes as:

$$\sigma_j = \frac{g_j^2}{F_j} \left[\frac{C_j^2}{K_1} + \frac{(1 - C_j)^2}{K_2} \right]. \tag{31}$$

To shorten the notation, we introduce M_j as the "square of the reduced flux":

$$M_j = g_j^2 \left[\frac{C_j^2}{K_1} + \frac{(1 - C_j)^2}{K_2} \right] \tag{32}$$

and solve the problem of such a distribution of the total surface or the total number of unit devices F between the steps as specified by

$$\sigma = \sum_j \sigma_j = \sum_j \frac{M_j}{F_j} \to \min / \sum_j F_j = F. \tag{33}$$

The Lagrange function for this problem is

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

Its stationarity conditions are:

$$F_j^* = F \frac{\sqrt{M_j}}{\sum\limits_{v=1}^{n} \sqrt{M_v}}, \quad \frac{F_j^*}{F_{j-1}^*} = \sqrt{\frac{M_j}{M_{j-1}}} \quad j = 1, \ldots, n. \tag{34}$$

After substituting the conditions (34) into the expression for the production of entropy (33) we get:

$$\sigma^* = \frac{1}{F} \left(\sum_j \sqrt{M_j} \right)^2. \tag{35}$$

Thus, since the separation enrichment factor is taken to be constant for all stages, it is necessary to express the costs and mole fractions included in the expression for M_j through the given mole fraction of the output streams and the value of the feed stream and substitute those into the formula (35).

3.1. Calculation formulas for fixed separation factor

In this case, the number of steps to the feed point and the total number of steps are:

$$m = \frac{\ln x_0(C_0) - \ln x_{out}(C_{out})}{\ln \alpha} - 1, \quad n$$

$$= \frac{\ln x_f(C_f) - \ln x_{out}(C_{out})}{\ln \alpha} - 1. \tag{36}$$

To calculate the fluxes at each stage, the mole fractions are substituted into the formulas (27), (26), (28)

$$C_j = C(\alpha^{j+1} x_{out}), \quad C_j^r = C(\alpha^{j-1} x_{out}), \quad C_{j-1} = C_{j+1}^r = C(\alpha^j x_{out}). \tag{37}$$

When $j = m$ we have $C(\alpha^{m+1} x_{out}) = C_0$, and when $j = n$ we have $C(\alpha^{n+1} x_{out}) = C_f$.

Example 1. Let us assume

$$C_0 = 0.007, \quad C_{out} = 0.001, \quad C_f = 0.04,$$

$$\alpha = 1.09, \quad g_0 = 1.0 \, \text{mol/s}, \quad T = 323 \, K.$$

The specific mass transfer coefficients are $K_1 = 1.05, K_2 = 0.95$. Their dimensions are $\frac{mol^2 K}{J \cdot s \cdot m^2}$. The total mass transfer surface is $F = 100 \, \text{m}^2$.

Using formulas (36), (37), (5) we get, rounding to the next large integer:

$$m = 22, n = 43, \gamma = 0.154.$$

The enrichment factor, mole fraction, and flux at the outlet of the first stage according to the formulas (26), (28) are equal to

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

$$C_1 = C(x_{out} \alpha^2) = 0.001188,$$

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

Using (32), we find the "square of the reduced flow" which, through (34) determines the size distribution 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 optimal numerical results for all stages are shown in Table 1. The optimal distribution of contact areas is shown in Fig. 5. The total entropy generation is from (35)

$$\sigma^* = 341.91 \, \text{W/K}.$$

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

$$\Delta A_0 = 8.31 \cdot 323 \cdot (0.154 \cdot 0.04 \cdot \ln(0.04) + 0.154 \cdot (1 - 0.04)$$
$$\cdot \ln(1 - 0.04) + +(1 - 0.154) \cdot 0.001 \cdot \ln(0.001) + (1 - 0.154)$$
$$\cdot(1 - 0.001) \cdot \ln(1 - 0.001) - -0.007 \cdot \ln(0.007) - (1 - 0.007)$$
$$\cdot \ln(1 - 0.007) = 24.64 \, \text{J/mol},$$

whence reversible power:

$$p_0 = \Delta A_0 g = 24.64 \, \text{W}.$$

The irreversible energy consumption is from (9)

$$T\sigma^* = 323 \cdot 341.91 = 110.435 \, \text{kW}.$$

This is 4480 times greater than the reversible power requirement, which is confirmed by the practice of separation of diluted mixtures (Fig. 1, Benedict and Pigford, 1981).

4. Selection of the separation sequence for multicomponent mixtures

It is assumed above that the mixture being separated is binary and the separation occurs into streams, each of which contains two components. In the case when the mixture is multicomponent and it is required to separate it into several streams, the problem arises of choosing the optimal sequence of separation. In this case, the separation of multicomponent mixtures is realized as sequential separation of mixtures into two streams. So, with complete separation, a mixture of three components is first separated into two streams, one of which contains two components. Then this stream is again separated at the second stage. Both the mass transfer coef-

Table 1

The optimal separation solution for Example 1 with $n = 43$ stages total, $m = 22$ stages in the stripping section, i.e. the feed point, and $\alpha = 1.09$ the separation factor per stage. j is the stage number; x_j the mole fraction of light component leaving that stage; C_j the mole fraction of light component entering the stage; g_j the flux leaving the stage; M_j is the immediate optimization variable "square of the reduced flow"; F_j^* the size of the j-th stage.

| j	x_j	C_j	g_j	M_j	F_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
35	0.022273	0.021788	1.74	3.20	0.97
36	0.024278	0.023703	1.46	2.25	0.81
37	0.026463	0.025781	1.21	1.53	0.67
38	0.028845	0.028036	0.97	0.99	0.54
39	0.031441	0.030482	0.75	0.60	0.42
40	0.034271	0.033135	0.55	0.32	0.31
41	0.037355	0.036010	0.37	0.14	0.20
42	0.040717	0.039124	0.20	0.04	0.11
43	0.044381	0.042495	0.15	0.02	0.09
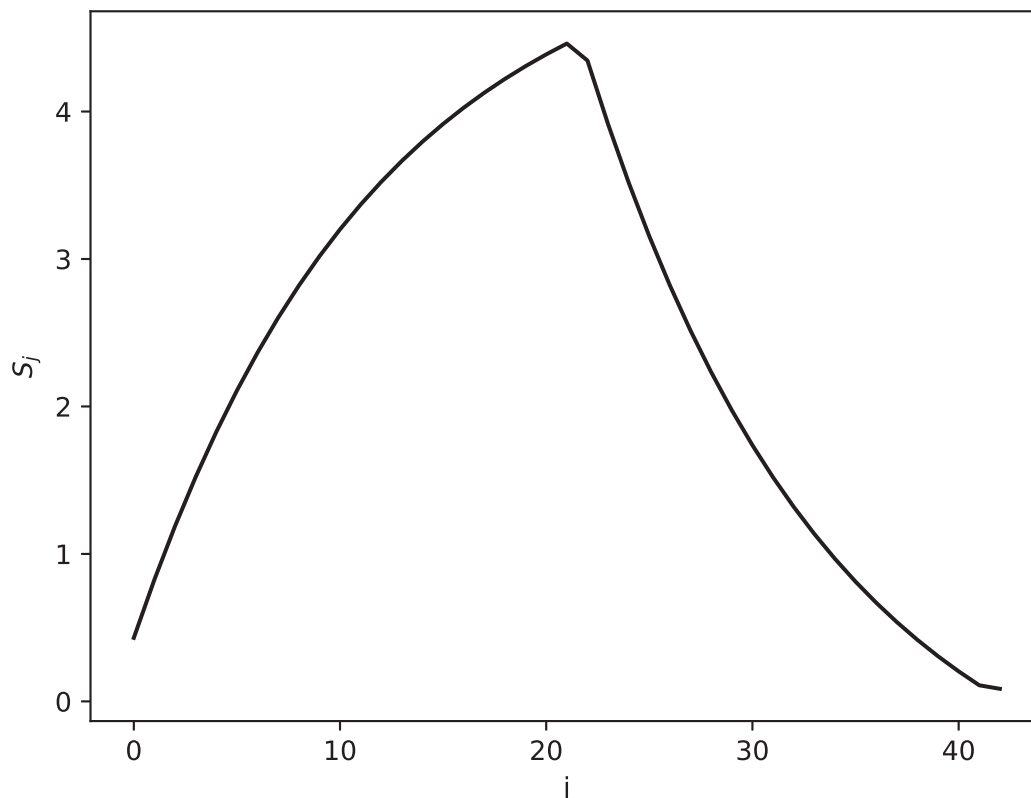
Fig. 5. Optimal distribution of sizes F_j of the stages j in Example 1. As always the largest requirement is at the feed point (22).

ficients and the flow rates of the output streams at each stage depend on the choice of the separation point.

The problem of choosing the separation sequence is solved below under the assumption of complete separation, i.e. when each of the output streams contains only one component. In this case, a stage can be understood as a complex of separating devices with an equivalent coefficient of mass transfer.

As already mentioned, for mechanical systems, reversible work (corresponding to the productivity p_0) does not depend on the order in which the separation is organized, since p_0 is determined only by the fluxes and compositions of the input streams and the output of the system as a whole. However the irreversible component of the power Δp in (27) depends on in which sequence, the components are selected and allows one to select this sequence.

A mixture of three components. Consider a mixture of three components with mole fractions $C_0 = (C_{01}, C_{02}, C_{03})$ and the flux g_0, which can be set to unity. In this case, the fluxes can be expressed through their mole fraction in the mixture to be separated. The components are ordered according to the property used for separation (density, membrane permeability coefficient, etc.). Thus e.g. thinking in terms of distillation, component 1 is the most volatile, component 3 the least volatile.

The mass transfer coefficients depend on the choice of the separation point. For the case when the first component is initially separated from the mixture ("direct order of separation"), we denote the mass transfer coefficient by α_1, and for the split between the second and third components, by α_2. Let us find the irreversible energy consumption for the two options:

a. Direct (first separate the first component, then separate the second and third);
b. Reverse (first separate the third component, then the first and second).

Trying to separate off the middle component first is not an option because the components are numbered according to their property used for the separation, e.g. volatility in the case of distillation. Then one always needs to separate from the extreme properties first, either the lightest or the heaviest.

For simplicity, the separation at each stage will be assumed complete. The irreversible power costs for each order of division in accordance with (27) are:

Option a)

$$\Delta p_a = \Delta p_{a1} + \Delta p_{a2} = C_{01}^2/\alpha_1 + \frac{(C_{02} + C_{03})^2}{\alpha_1} + \left(C_{02}^2/\alpha_2 + C_{03}^2/\alpha_2\right). \tag{38}$$

The first two terms in this sum represent losses from irreversibility at the first stage of separation. With $g_0 = 1$ and complete separation, the costs g_1 and g_2 at the exit of this stage are equal to C_{01} and $(C_{02} + C_{03})$ respectively. A mixture of second and third components are considered as one substance with a flux at the outlet $C_{02} + C_{03} = 1 - C_{01}$.

In option b), in a completely similar way, we obtain

$$\Delta p_b = \Delta p_{b1} + \Delta p_{b2} = C_{03}^2/\alpha_2 + \frac{(C_{02} + C_{01})^2}{\alpha_2} + \left(C_{02}^2/\alpha_1 + C_{01}^2/\alpha_1\right). \tag{39}$$

If the difference between these irreversible costs is negative, then the direct splitting order is preferable. This condition

$$\Delta p_{ab} = \Delta p_a - \Delta p_b < 0 \tag{40}$$

after simple calculations leads to the inequality

$$\alpha_1 C_{01}(C_{01} + 2C_{02}) > \alpha_2 C_{03}(C_{03} + 2C_{02}). \tag{41}$$

If the inequality (41) is opposite, then as the first stage of separation it is preferable to choose the reverse splitting order, separating the third component first.

Example 2. Let the composition of the feed three-component mixture be $C_{01} = 0.6, C_{02} = 0.3, C_{03} = 1 - C_{01} - C_{02} = 0.1$ and the mass transfer coefficients: $\alpha_1 = 0.1 \frac{mol^2}{Js}$, $\alpha_2 = 0.2 \frac{mol^2}{Js}$. It is easy to see that the inequality (41) is true (0.072 > 0.032), which means that one first needs to separate off the first component and then split the second and third components.

Multicomponent mixtures. When separating mixtures, consisting of more than three numbers of components, the rule (41) allows one to compare any two possible choices of the separation point, combining several components into one equivalent selection (fraction).

Let the total mole fraction of components with indices from 1 to i be $x_1(i)$, and the mass transfer coefficient corresponding to the i-th separation boundary is α_i. The mass transfer coefficient corresponding to the j-th boundary is α_j. Finally, the total mole fraction of components from $j + 1$ to n is equal to $x_3(j), j > i$. Note that x_1 depends on the choice of the upper bound, and x_3 depends on the choice of the lower one. Finally, $x_2(ij)$ is the mole fraction of the fraction consisting of components located between the i-th and j-th separation boundaries.

At the first stage, it is expedient to choose the i-th separation point if for all values of $j > i$ an inequality similar to (41) holds:

$$\alpha_i x_1(i)[x_1(i) + 2x_2(ij)] > \alpha_j x_3(j)[x_3(j) + 2x_2(ij)]. \tag{42}$$

Let us call the expression

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

the efficiency coefficient corresponding to the i-th separation boundary.

At each stage, the choice of the separation boundary corresponds to the maximum in i of the minimum in $j > i$ of the efficiency coefficient.

5. Conclusion

The boundaries of the reachable sets for mechanical separation systems are obtained and it is revealed how the kinetics of mass transfer processes affects their shape. The distribution of contact surfaces, fluxes of direct flow, and recycle for multistage systems, which satisfies the conditions of minimum dissipation, is obtained under the assumption that the enrichment factor is constant in the stripping and rectifying sections. It is shown that taking into account irreversibility makes it possible to formulate and solve the problem of the order of separation of multicomponent mixtures according to the condition of the minimum irreversible power consumption.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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