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Minimum Dissipation Conditions of the Mass Transfer and Optimal Separation Sequence Selection for Multicomponent Mixtures I

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Additional information is available at the end of the chapter

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1. Introduction

1.1. The mass transfer process with minimum irreversibility

In many processes, heat and mass transfer are distributed in time or space. The problem of thermodynamically perfect organization lies in the choice of such concentration and temperature change, in space or time, laws to minimize the entropy production σ . Below we consider stationary processes and a spatial distribution, for definiteness.

1.1.1. Optimal organization of an irreversible mass transfer process

Consider the irreversible process of mass transfer, in which from one flow to another one substance is transmitted. The problem of minimal irreversibility of this process at a given average intensity of mass transfer takes the form:

$$\sigma = \int_0^L \frac{g(c_1, c_2)}{T} (\mu_1(c_1) - \mu_2(c_2)) dl \rightarrow \min \quad (1)$$

under conditions

$$\int_0^L g(c_1, c_2) dl = \bar{g}; \quad (2)$$

$$\frac{d(G_1 c_1)}{dl} = \frac{dN_1}{dl} = -g(c_1, c_2); \quad N_1(0) = N_1^0. \quad (3)$$

The minimum is searched by selecting the concentration $c_2(l)$. change law. (In the equation (1) $\mu_i(c_i)$ denotes the chemical potential of the i -th flow dependence on the concentration of the redistributed substance in it). Here G_1 and c_1 is an amount and molarity of the redistributed substance respectively, N_1 -number of moles of that component.

Minimal irreversibility conditions of mass transfer arise from the solution of (1) — (3). They can be described as follows [24]: *In the mass transfer process with minimum irreversibility the ratio of flow g and chemical potential μ_2 derivatives with respect to the concentration c_2 is proportional to the ratio of relative flow g square to the temperature, in any cross-section of l .*

$$\frac{\partial g / \partial c_2}{\partial \mu_2 / \partial c_2} = \xi \frac{g^2}{T} \quad (4)$$

Indeed, the entropy production after transition from dt to dN is:

$$\sigma = \int_{N_1^0}^{N_1^L} -\frac{1}{T} (\mu_1(c_1) - \mu_2(c_2)) dN_1 \rightarrow \min \quad (5)$$

under the condition

$$\int_{N_1^0}^{N_1^L} -\frac{1}{g(c_1, c_2)} dN_1 = L. \quad (6)$$

The Lagrange function of problem (5), (6) takes the form

$$R = \frac{1}{T} (\mu_1(c_1) - \mu_2(c_2)) + \lambda \frac{1}{g(c_1, c_2)}, \quad (7)$$

stationarity conditions with respect to c_2 :

$$\frac{\partial R}{\partial c_2} = 0 \rightarrow \frac{1}{T} \frac{\partial \mu_2}{\partial c_2} + \lambda \frac{1}{g^2(c_1, c_2)} \frac{\partial g}{\partial c_2} = 0 \quad (8)$$

lead to the equation (4). The proportionality coefficient ξ in (4) is defined from the initial data of the current problem.

For a specific task $g(c_1, c_2)$ condition (4) allows us to find a relation between the c_1 and c_2 for the optimal mass transfer organization. For example, if

$$g = k \left(\frac{\mu_1(c_1)}{T} - \frac{\mu_2(c_2)}{T} \right), \quad (9)$$

we'll get the following equation from (4) :

$$\mu_1(c_1) - \mu_2(c_2) = \text{const}. \quad (10)$$

At the constant temperature and pressure, this condition leads to the equation

$$c_1(l)/c_2(l) = \text{const} \quad (11)$$

and the constancy of flow $g(c_1, c_2)$ for any l .

For the mass transfer law of the form

$$g = k(c_1(l) - c_2(l)) \quad (12)$$

Derivatives are

$$\partial g / \partial c_2 = -K; \quad \frac{\partial \mu_2}{\partial c_2} = \frac{RT}{c_2}. \quad (13)$$

After their substitution into (4), we obtain

$$(c_1(l) - c_2(l))^2 / c_2(l) = \text{const}. \quad (14)$$

During the mass transfer between phases the driving force of the process is expressed as the difference between the concentration of a redistributed component in one phase c_1 and the equilibrium concentration $c_1^p(c_2)$ linearly independent of c_2 (concentration of the same component in another phase). In this case, c_1^p is substituted in (11) or (14) instead of concentration c_2 .

1.1.2. Example

Let optimality conditions of irreversible mass transfer have the form (11). From the view of flow $\bar{g} = \bar{g} / L$ constancy from (3) follows:

$$c_1^*(l) = c_1^0 - \frac{\bar{g}}{rL}; \quad c_1^{p*}(l) = c_1^0 - \frac{c_1^*(l)}{M}, \quad (15)$$

where M denotes the right side of (11). Substituting c_1^* and c_1^{p*} in the expression for the mass flux and taking the constancy of this flux into account, we obtain

$$\frac{k}{T}(\mu_1(c_1^*) - \mu_1(c_1^{p*})) = \frac{\bar{g}}{L}, \quad (16)$$

Or $kR \ln M = \bar{g} / L$, from which $M = e^{\bar{g}/kLR}$.

Assuming a linear dependence

$$c_1^p(c_2) = ac_2 + b, \quad (17)$$

where a, b — are some constants determined by processing experimental data of the equilibrium. Then, find the optimum profile

$$c_2^*(l) = \frac{c_1^0 rL - \bar{g}l}{arL} e^{-\bar{g}/kRL} - \frac{b}{a}. \quad (18)$$

2. Irreversible work of separation and heat-driven separation

2.1. Introduction

The minimal amount of energy needed for separation a mixture with a given composition can be estimated using reversible thermodynamics. These estimates turn out to be very loose and unrealistic. They also do not take into account kinetic factors (laws and coefficients of heat and mass transfer, productivity of the system, etc.). In this paper we derive irreversible estimates of the work of separation that take into account all these factors.

The majority of separation systems are open systems that exchange mass and energy with the environment. If mass and heat transfer coefficients (determined by the size and construction of the apparatus) are finite and if the productivity of the system is finite then the processes in such systems are reversible. The energy flows, the compositions of the mass flows, and the

productivity of the system are linked via the balance equations of energy, mass, and entropy. The latter also includes entropy production in the system. Minimal energy used for separation corresponds to minimal entropy production in the system subject to various constraints. This allows us to estimate this minimal energy.

There is a qualitative as well as a quantitative difference between the reversible and irreversible estimates obtained in this paper. For example, the irreversible estimate of the work of separation for poor mixtures (where the concentration of one of the components is close to one) tends to a finite nonzero limit, which depends on the kinetics factors. The reversible work of separation for such mixtures tends to zero. The reversible estimate differs from the amount of energy needed in practice for separation of poor mixtures by a factor of 10^5 .

For heat-driven separation processes the novel results obtained in this paper include the estimate of the minimal heat consumption as a function of kinetic factors and the thermodynamic limit on the productivity of a heat-driven separation.

2.2. Thermodynamic balances of Separation Processes and the Link between Energy Consumption and Entropy Production

Consider the system, shown in Figure 1, where the flow of mixture with rate g_0 , composition x_0 , temperature T_0 , and pressure P_0 is separated into two flows with the corresponding parameters g_i , x_i , T_i , P_i ($i=1, 2$). The flow of heat q_+ with the temperature T_+ can be supplied, and the flow of heat q_- with the temperature T_- can be removed. The mechanical work with the rate (power) p can be supplied.

In centrifuging, membrane separation, and adsorption–desorption cycles that are driven by pressure variations, no heat is supplied/removed and only mechanical work is spent. In absorption–desorption cycles, distillation, and so forth, no mechanical work is spent, only heat is consumed (heat-driven separation). In some cases the number of input and output flows can be larger. As a rule one can still represent the system as an assembly of separate blocks, whose structure is shown in Figure 1.

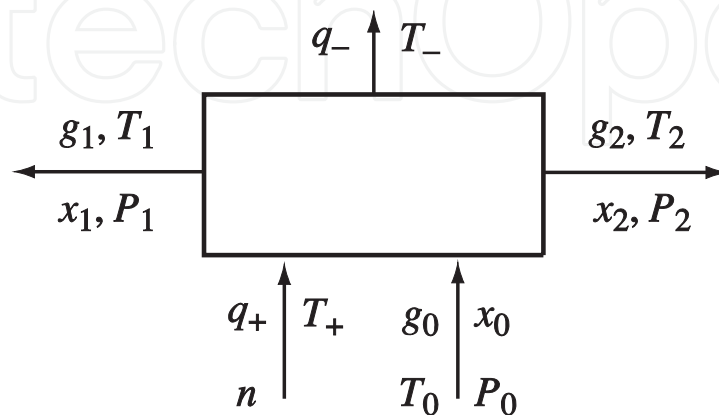


Figure 1. Simplified schematic of thermodynamic balances for separation processes.

2.2.1. Heat-driven separation

Consider a heat-driven separation ($p=0$) and assume that each of the vectors $x_i = (x_{i1}, \dots, x_{ij}, \dots, x_{ik})$ $i=0, 1, 2$ consists of k components which denote the molar fraction of the j -th substance in the i -th flow. The thermodynamic balance equations of mass, energy, and entropy here take the following form

$$g_0 x_{0j} - g_1 x_{1j} - g_2 x_{2j} = 0, \quad j = 1, \dots, k \quad (19)$$

$$\sum_{j=1}^k x_{ij} = 1, \quad i = 0, 1, 2 \quad (20)$$

$$q_+ - q_- + g_0 h_0 - g_1 h_1 - g_2 h_2 = 0 \quad (21)$$

where h_i is the enthalpy of the i -th flow;

$$\frac{q_+}{T_+} - \frac{q_-}{T_-} + g_0 s_0 - g_1 s_1 - g_2 s_2 + \sigma = 0 \quad (22)$$

σ denotes entropy production. From eq (19), eq (20) follows that $g_0 = g_1 + g_2$. After elimination of g_0 from eqs (21) and (22) and introduction of enthalpy increments Δh and entropy increment Δs we get

$$q_+ - q_- + g_1 \Delta h_{01} + g_2 \Delta h_{02} = 0 \quad (23)$$

$$g_2 \Delta s_{02} + g_1 \Delta s_{01} + \frac{q_+}{T_+} - \frac{q_-}{T_-} + \sigma = 0 \quad (24)$$

Here, $\Delta h_{0i} = h_0 - h_i$, $\Delta s_{0i} = s_0 - s_i$ ($i=1, 2$).

Elimination of q_- using eq (23) and its substitution into eq (24) yields

$$\sum_{i=1}^2 g_i \left(\Delta s_{0i} - \frac{\Delta h_{0i}}{T_-} \right) + q_+ \left(\frac{1}{T_+} - \frac{1}{T_-} \right) + \sigma = 0$$

and the flow of used heat for heat-driven separation is

$$q_+ = \frac{T_+}{T_+ - T_-} \left[\sum_{i=1}^2 g_i (\Delta s_{0i} T_- - \Delta h_{0i}) + \sigma T_- \right] \quad (25)$$

The first term in the square brackets depends only on the parameters of the input and output flows and represents the reversible work of separation per unit of time (reversible power of separation). The second term there represents the process kinetics and corresponding energy dissipation.

For mixtures that are close to ideal gases and ideal solutions, molar enthalpies and entropies h_i and s_i in the eqs (21) and (22) can be expressed in terms of compositions and specific enthalpies and entropies of the pure substances. We obtain for each of the flows

$$\begin{aligned}\Delta h_{0i} &= \sum_{j=1}^k [x_{0j} h_j(T_0, P_0) - x_{ij} h_j(T_i, P_i)] \\ \Delta s_{0i} &= \sum_{j=1}^k [x_{0j} s_j^0(T_0, P_0) - x_{ij} s_j^0(T_i, P_i) - R(x_{0j} \ln x_{0j} - x_{ij} \ln x_{ij})], \quad i = 1, 2\end{aligned}\quad (26)$$

where R is the universal gas constant. The reversible energy consumption here is

$$q_+^0 = \frac{1}{\eta_k} \sum_{i=1}^2 g_i \sum_{j=1}^k [x_{0j} s_j^0(T_0, P_0) - x_{ij} s_j^0(T_i, P_i) - R(x_{0j} \ln x_{0j} - x_{ij} \ln x_{ij})] T_- + x_{ij} h_j(T_i, P_i) - x_{0j} h_j(T_0, P_0)] \quad (27)$$

We denote here the Carnot efficiency of the ideal cycle of the heat engine as

$$\eta_C = \frac{T_+ - T_-}{T_+}$$

Condition (25) can be rewritten as

$$q_+ = \frac{1}{\eta_C} (p^0 + \sigma T_-) \quad (28)$$

Here, p_0 is the reversible power of separation that is equal to the reversible flow of heat given by eq (27) multiplied by the Carnot efficiency. When eq (28) was derived we took into account only the irreversibility σ of the separation process (the irreversibility of the heat transfer was not taken into account). In reality heat can be supplied/removed with a finite rate only irreversibly. Any transformation of heat into work with finite heat transfer coefficients and finite power is irreversible. This leads to a lower efficiency than the Carnot efficiency. The closed form expression for this efficiency was obtained in ref [16]. It depends on the power p and on heat transfer coefficients for heat supply and heat removal α_+ and α_- . For the Newton (linear) law of heat transfer it has the form

$$\eta_p = \max \frac{p}{q_+} = 1 - \frac{1}{2T_+} \left(T_+ + T_- - \frac{4p}{\alpha} - \sqrt{(T_+ - T_-)^2 + \left(\frac{4p}{\alpha} \right)^2} - 8 \frac{p}{\alpha} (T_+ + T_-) \right) \quad (29)$$

where it is assumed that there is constant contact of the working body with the heat reservoirs and

$$\alpha = \frac{4\alpha_+\alpha_-}{\alpha_+ + \alpha_-} \quad (30)$$

It is easy to show that if $p \rightarrow 0$ then η_p tends to the Carnot efficiency.

Substitution of η_p instead of η_C in eq (28) allows us to derive a tighter estimate for the heat consumption in heat-driven separation processes by finding the minimal possible entropy production σ subject to various constraints

$$q_+ \geq q_+^{\min} = \frac{p^{\min}}{\eta_p(p^{\min}, \alpha, T_+, T_-)} \quad (31)$$

where

$$p^{\min} = p^0 + \sigma^{\min} T_- \quad (32)$$

Conditions (29-31) single out the area of thermodynamically feasible heat-driven separation systems.

Expressions (27) and (28) and eq (25) can be further specified by assuming the constancy of heat capacities, that the mixture is binary, and so forth.

2.2.2. Mechanical separation

Consider a separation system that uses mechanical work with rate p . Assume that no heat is supplied/removed ($q_+ = q_- = 0$) and that input and output flows have the same temperature T and the same pressure. Multiplication of eq (24) by T and subtraction of the result from the energy balance eq (23), where $(q_+ - q_-)$ is replaced with the supplied power p , yields

$$p = T\sigma + g_0 \sum_{i=1}^2 \gamma_i (T\Delta s_{0i} - \Delta h_{0i}) \quad (33)$$

here $\gamma_i = g_i / g_0$

After taking into account eq (27) that the enthalpy increment Δh_{0i} in a mechanical separation is zero, we get

$$p = g_0 RT \left[\sum_{i=1}^2 \gamma_i \sum_{j=1}^k x_{ij} \ln x_{ij} - \sum_{j=1}^k x_{0j} \ln x_{0j} \right] + T\sigma = p^0 + T\sigma \quad (34)$$

The first term in this expression represents the minimal power for separation that corresponds to the reversible process ($\sigma=0$). This power p^0 is equal to the difference between the reversible power for complete separation of the input flow $p_0^0 = -g_0 RT \sum_j x_{0j} \ln x_{0j}$ and the combined reversible power of separation of the output flows p_1^0 and p_2^0 .

Here

$$p_i^0(x_i) = -RT g_0 \gamma_i \sum_{j=1}^k x_{ij} \ln x_{ij}, \quad i = 0, 1, 2 \quad (35)$$

is the reversible power of separation of the i -th flow into pure substances.

2.3. Minimal work of separation in irreversible processes

2.3.1. Assumptions and problem formulation

Assume that the components of the input mixture are close to ideal gases or ideal solutions. The chemical potential of the i -th component can then be written in the following form

$$\mu_i(T, P) = \mu_0(T, P) + RT \ln x_i, \quad i = 1, \dots, k \quad (36)$$

where x_i is the concentration of the i -th component.

First we consider a system that includes three elements, a reservoir with the time independent temperature T , pressure P , and vector of concentrations $x_0 = \{x_{01}, \dots, x_{0k}\}$ (therefore its chemical potential μ_0 is also time independent), the finite capacity output subsystem with chemical potential μ_1 that depends on the current compositions of the mixture and of the working body that has controllable values of chemical potential μ_0^w and μ_1^w , at the points of contact with reservoir and output subsystem. At the time the intensive variables of the output subsystem coincide with the values of the reservoir's intensive variables, and the number of moles in it is given and equal to N_0 . At time τ the number of moles $N(\tau)$ and the composition $x(\tau)$ in the output subsystem are given. The mass transfer coefficients between the reservoir and the working body and the working body and the output subsystem are finite and fixed. The minimal necessary work required for the separation is sought.

We do not consider here how to implement the derived optimal dependence of the chemical potential of the working body because of two reasons. First, our main objective is to derive a

lower bound on the work of separation. However, imposing constraints on feasible variations of chemical potential would lead to an increase in energy consumption. Second, we will demonstrate that for the majority of mass transfer laws the optimal mass transfer flow is time independent, and its implementation is straightforward.

The work of separation in an isothermal process for an adiabatically insulated system can be found using the Stodola formula in terms of the reversible work A_0 and the entropy increment ΔS

$$A = A_0 + T\Delta S \quad (37)$$

The reversible work is equal to the increment of the system's internal energy. Since as a result of the process $(N(\tau) - N(0))$ moles of mixture with the composition x_0 is removed from the reservoir, and the energy of the output subsystem rises because of the increase of the amount of moles in it from $N(0)$ to $N(\tau)$ and its composition from x_0 to x_τ , the total change of the system's internal energy is

$$A_0 = N(\tau) \sum_{i=1}^k \Delta\mu_i = N(\tau) RT \sum_{i=1}^k [x_i(\tau) \ln x_i(\tau) - x_{i0} \ln x_{i0}] \quad (38)$$

and it is independent of $N(0)$. Because A_0 is determined by N , $x(\tau)$, $x(0)$, the minimum of A corresponds to the minimum of the entropy increment

$$\begin{aligned} \Delta S &= \frac{1}{T} \int_0^\tau \sum_{i=1}^k [g_{0i}(\mu_{0i} - \mu_i^w) + g_{1i}(\mu_i^w - \mu_{1i})] dt \\ &= \frac{1}{T} \int_0^\tau \sum_{i=1}^k (g_{0i} \Delta\mu_{0i} + g_{1i} \Delta\mu_{1i}) dt \end{aligned} \quad (39)$$

Because the working body's parameters have the same values at the beginning and at the end of a cycle

$$\begin{aligned} \int_0^\tau g_{i0} dt &= \int_0^\tau g_{i1} dt \\ N(\tau)x_i(\tau) - N(0)x_i(0) &= \Delta(Nx_i), \quad i = 1, 2, \dots, k \end{aligned} \quad (40)$$

2.3.2. Optimal solution

The problem of minimization of ΔS subject to constraints eq (40) on $g_{0i} \geq 0$, $g_{1i} \geq 0$ becomes simpler in a common case where the chemical potentials' increments $\Delta\mu_{0i}$, $\Delta\mu_{1i}$ are unique

functions of flows g_{0i} and g_{1i} , correspondingly. If processes are close to equilibrium then this dependence is linear.

Assume

$$\Delta\mu_{0i} = \phi_{0i}(g_{0i}), \quad \Delta\mu_{1i} = \phi_{1i}(g_{1i})$$

then the problems (39) and (40) can be decomposed into $2k$ problems

$$\Delta S_{ji} = \int_0^\tau \sigma_{ji}(g_{ji}) dt \rightarrow \min / \int_0^\tau g_{ji} dt = \Delta(Nx_i) \quad j=0,1, \quad i=1,2,\dots,k \quad (41)$$

where $\sigma_{ji} = g_{ji} \phi_{ji}(g_{ji})$ is the function that determines dissipation.

Problems eq (41) are averaged nonlinear programming problems. Their optimal solutions g_{ji}^* are either constants and equal to

$$g_{ji}^* = g_{1i}^* = \frac{\Delta(Nx_i)}{\tau} \quad (42)$$

or switches between two so-called basic values on the interval $(0, \tau)$, the solution eq (42) corresponding to the case where the convex envelope of the function $\sigma_{ji}(g_{ji})$ is lower than the value of this function at g_{ji}^* . Characteristic forms of the function $\sigma_{ji}(g_{ji})$ for the constant and switching regimes are shown in Figure 2.

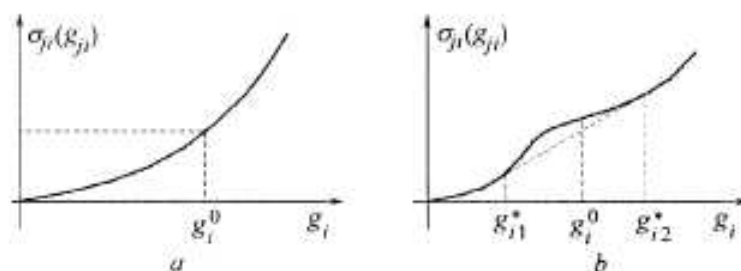


Figure 2. Dependence of the entropy production on the rate for the constant (a) and switching (b) solutions (g_{1i}^* and g_{2i}^* are the basic values of the rate).

If the function σ_{ji} is concave then the optimal rate g_{ji} is always constant. Let us calculate the second derivative of σ on g (we omit subscripts for simplicity). If it is positive then the constancy of the rate in the optimal process is guaranteed.

$$\sigma''(g) = 2\phi'(g) + g\phi''(g) \geq 0 \quad (43)$$

The first term in this expression is always positive because the chemical potentials' difference is the driving force of mass transfer and monotonically depends on the flow. For the majority of laws of mass transfer the inequality eq (43) holds. In particular, it holds if the flow of mass transfer is proportional to the difference of chemical potentials in any positive degree.

Consider mass transfer flow that depends linearly on the chemical potential difference for all i, j . Then

$$g_{ji} = \alpha_{ji} \Delta \mu_{ji} \rightarrow \phi_{ji} = \frac{g_{ji}}{\alpha_{ji}} \quad (44)$$

It is clear that the conditions eq (43) hold and the optimal rates of flows obey equalities (42).

Equalities (42) hold for any nonswitching solution. The minimal increment of the entropy production for such solution is

$$\Delta S^{\min} = \sum_{ij} \Delta S_{ji}^{\min} = \tau \sum_{ij} \sigma_{ji} \left(\frac{\Delta(Nx_i)}{\tau} \right) \quad (45)$$

and the minimal work of separation is

$$A_{\min} = A_0 + \tau T \sum_{ij} \sigma_{ji} \left(\frac{\Delta(Nx_i)}{\tau} \right) \quad (46)$$

The optimal rates are determined by the initial and final states which allows us to specify the estimate eq (46).

Near equilibrium the flows obey Onsanger's kinetics eq (44), and from eq (46) it follows that

$$A_{\min} = A_0 + \tau \sum_{i=1}^k g_i^2 \left(\frac{1}{\alpha_{0i}} + \frac{1}{\alpha_{1i}} \right) = A_0 + \frac{1}{\tau} \sum_{i=1}^k \frac{\Delta^2(Nx_i)}{\bar{\alpha}_i} \quad (47)$$

$$\bar{\alpha}_i = \frac{\alpha_{0i} \alpha_{1i}}{\alpha_{0i} + \alpha_{1i}} \quad (48)$$

is the equivalent mass transfer coefficient on the i -th component and the minimal entropy production is

$$\sigma_{\min} = \frac{1}{T\tau^2} \sum_{i=1}^k \frac{\Delta^2(Nx_i)}{\bar{\alpha}_i} \quad (49)$$

The lower bound for the average power of separation is

$$p_{\min} = \frac{A_{\min}}{\tau} = \frac{A_0}{\tau} + \frac{1}{\tau^2} \sum_{i=1}^k \frac{\Delta^2(Nx_i)}{\bar{\alpha}_i} \quad (50)$$

$p_0 = A_0/\tau$ is the reversible power of separation.

If

$$N(0)=0, \quad \Delta(Nx_i)=Nx_i(\tau)$$

then expressions (47) and (50) take the form

$$A_{\min} = A_0 + \frac{N^2}{\tau} \sum_{i=1}^k \frac{x_i^2(\tau)}{\bar{\alpha}_i} \quad (51)$$

$$p_{\min} = p_0 + g^2 \sum_{i=1}^k \frac{x_i^2(\tau)}{\bar{\alpha}_i} \quad (52)$$

Where

$$A_0 = NRT \sum_{i=1}^k [x_i(\tau) \ln x_i(\tau) - x_i \ln x_i] \quad (53)$$

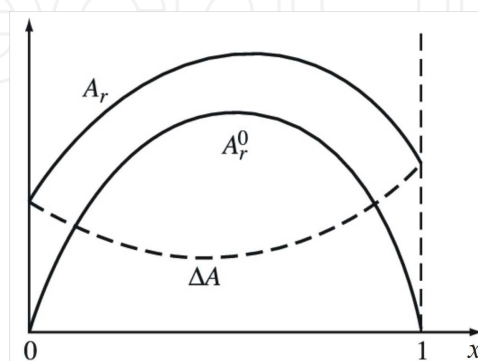


Figure 3. Reversible (A_0) and irreversible (A_r) estimates of the minimal work of separation of binary mixture as functions of key component's concentrations.

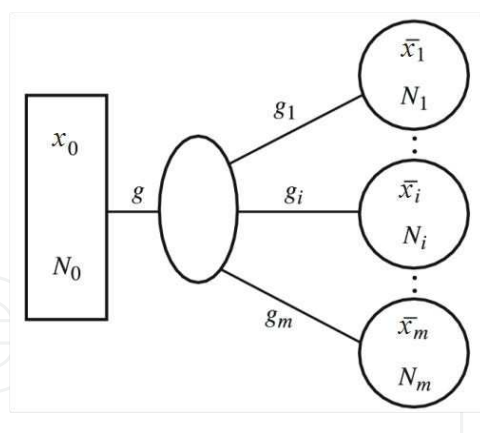


Figure 4. Separation of the system with finite capacity on m subsystems.

Note that the irreversible estimate of the work of separation eq (51) does not tend to zero for poor mixtures when the concentration of one of the components tends to one (Figure 3).

If system includes not one but a number of output subsystems then it is clear that the estimate for the minimal work of separation is equal to the sum of the estimates for each subsystem.

$$A_{\min} = \sum_{j=1} A_{\min}^j, \quad p_{\min} = \sum_{j=1} p_{\min}^j \quad (54)$$

The superscript j here denotes the subsystems.

2.3.3. Separation of a System with finite capacity into m subsystems

Consider a system that is shown in Figure 4. Its initial state is described by the vector of concentrations x_0 , the number of moles of the mixture N_0 , and its final state by the number of moles N_j , $j=1, \dots, m$ in each of the subsystems and their concentrations, \bar{x}_j . The mass balances yields

$$\begin{aligned} \sum_{j=1}^m \bar{N}_j &= N_0 \\ \sum_{j=1}^m \bar{N}_j \bar{x}_{ji} &= N_0 x_{0i}, \quad i = 1, 2, \dots, k \end{aligned} \quad (55)$$

The work in the reversible separation process here is

$$A_r^0(x_0, \bar{x}) = RT \left[\sum_{j=1}^m \bar{N}_j \sum_i \bar{x}_{ji} \ln \bar{x}_{ji} - N_0 \sum_i x_{0i} \ln x_{0i} \right] = A_{r0}^0(x_0, N_0) - \sum_{j=1}^m A_{rj}^0(\bar{x}_j, \bar{N}_j) \quad (56)$$

The reversible work of separation is equal to the difference of the reversible work of separation of the initial mixture into pure components and the reversible work of separation for mixtures in each of the subsystems.

We again assume that flows g_j have components g_{ji} proportional to the difference of the chemical potential of the subsystem and the working body with the coefficient α_{ji} . Here, the condition of minimal work of separation corresponds to the condition of flow constancy

$$g_{ji} = \frac{\bar{N}_j \bar{x}_{ji}}{\tau}, \quad i = 1, 2, \dots, k, \quad j = 1, \dots, m \quad (57)$$

$$\Delta\mu_{ji} = \frac{g_{ji}}{\bar{\alpha}_{ji}}, \quad j = 0, 1, \dots, m \quad (58)$$

Here, $\bar{\alpha}_{ji}$ is the equivalent mass transfer coefficient calculated using eq (48) for the flow into the j -th output subsystem of the i -th component. Similarly as was done above for the system with the reservoir and one finite capacity output subsystem and flows proportional to the final concentrations eq (57), these concentrations in the output subsystems are time independent and equal to \bar{x}_j , correspondingly, and the number of moles $\bar{N}_j(t)$ depends linearly on time. The power p here is constant

$$p = \frac{RT}{\tau} \sum_{j=1}^m \bar{N}_j \sum_i \bar{x}_{ji} \ln \frac{\bar{x}_{ji}}{x_{0i}} + \frac{1}{\tau^2} \sum_{j=1}^m N_j^2 \sum_i \bar{x}_{ji}^2 / \bar{\alpha}_{ji} \quad (59)$$

The minimal work of separation for the mixture with concentrations x_0 into m subsystems with concentrations \bar{x}_i over the time τ is

$$A_r = RTN_0 \sum_{j=1}^m \gamma_j \sum_i \bar{x}_{ji} \ln \frac{\bar{x}_{ji}}{x_{0i}} + \frac{N_0^2}{\tau} \sum_{j=1}^m \gamma_j^2 \sum_i \bar{x}_{ji}^2 / \bar{\alpha}_{ji} \quad (60)$$

Here, $\gamma_j = N_j / N_0$, $\bar{\alpha}_{ji} = \alpha_{ji} \alpha_{0i} / (\alpha_{0i} + \alpha_{ji})$

The first term here coincides with the reversible work of separation A_r^0 of the mixture of N_0 moles with concentration x_0 into subsystems with number of moles \bar{N}_j and concentrations \bar{x}_j . The second term takes into account irreversibility of the process. A_r decreases monotonically and tends to A_r^0 when process duration τ and mass transfer coefficient $\bar{\alpha}_{ji}$ increases.

2.3.4. Example

Consider separation of the binary mixture into pure components in time τ . In this case $N_1 = x_0 N_0$, $N_2 = (1 - x_0) N_0$, where x_0 is the concentration of the key component, $\bar{x}_{11} = \bar{x}_{22} = 1$. From the formula (60) we get

$$A_r = -RTN_0(x_0 \ln x_0 + (1 - x_0) \ln(1 - x_0)) + \frac{N_0^2}{\tau} \left(\frac{x_0^2}{\bar{\alpha}_{11}} + \frac{(1 - x_0)^2}{\bar{\alpha}_{22}} \right) = A_r^0(x_0) + \frac{N_0^2}{\tau} \left(\frac{x_0^2}{\bar{\alpha}_{11}} + \frac{(1 - x_0)^2}{\bar{\alpha}_{22}} \right) \quad (61)$$

The estimate eq (61) was derived in ref [1] by solving the problem of optimal separation of the binary mixture in the given time τ in Van't Hoff's thought experiment with movable pistons and semitransparent membrane where $\bar{\alpha}_{11}$ and $\bar{\alpha}_{22}$ are the permeability coefficients on the first and second component. If flows do not depend explicitly on the chemical potentials' differentials, for example, are proportional to the concentrations' differential, then an estimate similar to the one obtained above can be constructed by solving the following auxiliary nonlinear programming problem

$$\Delta\mu_i(P_0^i, P_i) \rightarrow \min_{P_0^i, P_i} / g_i(P_0^i, P_i) = g_i, \quad i = 1, 2, \dots \quad (62)$$

Here, (P_0^i, P_i) are partial pressures of the components in contacting subsystems that depend on the chemical potentials' differentials $\Delta\mu_i$. The flow g_i depends on the same differentials. Minimums in these problems are sought for different values of constant $g_i > 0$ and nonpositive P_0^i and P_i . We denote the minimal values of the objective in each of these problems $\Delta\mu_i^{\min}(g_i)$ as $\Delta\mu_i^*(g_i)$. This dependence can be used in the estimate eq (41) of the irreversible work of separation.

2.3.5. Example

Assume $\Delta\mu = RT \ln(P_0/P)$, $g(P_0, P) = (P_0 - P)/\alpha$, and $0 < P < P_{\max}$. Let us express P_0 in terms of g and P :

$$P_{0i} = \alpha_i g_i + P_i, \quad i = 1, 2$$

$$\Delta\mu = RT \ln(\alpha g / P + 1) \text{ attains its minimum at } P = P_{\max} \forall g.$$

$$\text{Therefore, } \Delta\mu_i^*(g_i) = RT \ln(\alpha_i g_i / P_{\max} + 1).$$

2.4. Potential application of obtained estimates

We will illustrate the possibilities of the application of the derived estimates.

2.4.1. Estimate of the power of separation in a continuous separation system

Consider a continuous separation system with the input flow g_0 with concentration x_0 and m output flows $g_j (j=1, \dots, m)$ with concentrations $x_j = \{x_{j0}, x_{j1}, \dots, x_{jk}\}$. Here, the temperatures on the input and output flows are close to each other.

Equation (59) allows us to estimate the minimal power required for continuous separation in such system

$$p_{\min} = \sum_{j=1}^m p_{0j} + g_0^2 \sum_{j=1}^m \gamma_j^2 \sum_{i=1}^k \frac{x_{ji}^2}{\alpha_{ji}} \quad (63)$$

Where

$$\gamma_j = \frac{g_j}{g_0} \geq 0, \quad \sum_{j=1}^m \gamma_j = 1 \quad (64)$$

$$p_{0j} = g_0 \gamma_j RT \sum_{i=1}^k [x_{ji} \ln x_{ji} - x_{0i} \ln x_{0i}] p_{0j} = \gamma_j M_j (g_0, x_j) \quad (65)$$

Mass balance equations yield

$$\begin{aligned} \sum_{j=1}^m \gamma_j x_{ji} &= x_{0i}, \quad i=1, \dots, k-1, \\ \sum_{i=1}^k x_{ji} &= 1, \quad j=0, \dots, m \end{aligned} \quad (66)$$

The number of conditions eq (66) is $k-1$, because the concentration of one of the components is determined by the conditions eq (64).

If the number of flows $m > k$, and their compositions are given, then the removal fractions can be chosen in such a way that the power of separation is minimal subject to constraints eqs (64) and (66). The Lagrange function of this problem is

$$L = \sum_{j=1}^m \left\{ \gamma_j M_j + \gamma_j^2 r_j - \lambda_0 \gamma_j - \sum_{i=1}^k \lambda_i \gamma_j x_{ji} \right\} \quad (67)$$

here

$$r_j(g_0, x_j) = g_0^2 \sum_{i=1}^k \frac{x_{ji}}{\alpha_{ji}}$$

L is the concave function on γ_j , and its conditions of stationarity determine the flows that minimize the power for separation for a given flow's compositions

$$\gamma_j^* = \frac{\lambda_0 - M_j + \sum_{i=1}^{k-1} \lambda_i x_{ji}}{2r_j}, \quad j = 1, \dots, m \quad (68)$$

We have k linear equations for λ_0 and λ_i

$$\frac{1}{2} \left[\sum_{j=1}^m \frac{\lambda_0 - M_j}{r_j} + \sum_{i=1}^{k-1} \lambda_i \sum_{j=1}^m \frac{x_{ji}}{r_j} \right] = 1 \quad (69)$$

$$\frac{1}{2} \left[\sum_{j=1}^m x_{ji} \left(\frac{\lambda_0 - M_j}{r_j} + \frac{1}{r_j} \sum_{i=1}^{k-1} \lambda_i x_{ji} \right) \right] = x_{0i}, \quad i = 1, \dots, k-1 \quad (70)$$

2.4.2. Example

Assume $m=3$, $k=2$, $g_0=1$ mol/s, $T=300$ K, and the compositions and transfer coefficients are

$$x_{01}=x_{02}=0.5$$

$$x_{11}=0.9; \quad x_{12}=0.1; \quad \bar{\alpha}_{11}=\bar{\alpha}_{12}=0.004 \text{ mol}^2/(\text{J s})$$

$$x_{21}=0.3; \quad x_{22}=0.7; \quad \bar{\alpha}_{21}=\bar{\alpha}_{22}=0.01 \text{ mol}^2/(\text{J s})$$

$$x_{31}=0.1; \quad x_{32}=0.9; \quad \bar{\alpha}_{31}=\bar{\alpha}_{32}=0.06 \text{ mol}^2/(\text{J s})$$

From eq (65) we obtain $M_1=910$, $M_2=197$, $M_3=910$, and $r_1=205$, $r_2=580$, $r_3=137$.

Equations (69) and (70) for λ -multipliers take the form

$$\frac{1}{2} \left[\frac{\lambda_0 - M_1}{r_1} + \frac{\lambda_0 - M_2}{r_2} + \frac{\lambda_0 - M_3}{r_3} + \lambda \left(\frac{x_{11}}{r_1} + \frac{x_{21}}{r_2} + \frac{x_{31}}{r_3} \right) \right] = 1$$

$$\frac{1}{2} \left[x_{11} \left(\frac{\lambda_0 - M_1}{r_1} + \frac{\lambda_1 x_{11}}{r_1} \right) + x_{21} \left(\frac{\lambda_0 - M_2}{r_2} + \frac{\lambda_1 x_{21}}{r_2} \right) + x_{31} \left(\frac{\lambda_0 - M_3}{r_3} + \frac{\lambda_1 x_{31}}{r_3} \right) \right] = x_{01}$$

We obtain $\lambda_0=894$, $\lambda_1=183$. Their substitution in eq (68) yields $\gamma_1^*=0.36$, $\gamma_2^*=0.64$, $\gamma_3^*=0$ and the corresponding estimate for the minimal irreversible power of separation eq (63) is

$$p_{\min} = 718 \text{ wt}$$

2.4.3. The selection of the separation sequence for a multicomponent mixture

In practice, separation of multicomponent mixtures is often realized via a sequence of binary separations. So, a three-component mixture is first separated into two flows, one of which does not contain one of the components. The second flow is then separated into two unicomponent flows. The reversible work of separation (that corresponds to the power p_0) does not depend on the sequence of separation, because p_0 is determined by the rates and compositions of the input and output flows of the system as a whole. The irreversible component of the power Δp in eq (63) depends on the sequence of separation and can be used to find the optimal one.

Consider a three-component mixture with concentration $x_0 = (x_{01}, x_{02}, x_{03})$, and rate g_0 we set to one. We denote the mass transfer coefficients at the first and second stages of separation as α_1 and α_2 . They depend on the construction of the apparatus. First, we assume for simplicity that these coefficients do not depend on the mixture's composition (in the general case they do depend on it). We consider irreversible power consumption for two cases:

- a. The first component is first separated, then the second and the third are separated.
- b. The second component is separated, and then the first and the third are separated.

We assume that the separation at each stage is complete. We get up to the constant multiplier

$$\Delta p_a = \Delta p_{a1} + \Delta p_{a2} = x_{01}^2 / \alpha_1 + \frac{(x_{02} + x_{03})^2}{\alpha_1} + (x_{02} + x_{03})^2 + (x_{02}^2 / \alpha_2 + x_{03}^2 / \alpha_3) \quad (71)$$

The first two terms in this sum represent the loss of irreversibility during the first stage of separation. For $g_0=1$ and complete separation the output rates of this stage g_1 and g_2 are x_{01} and $(x_{02} + x_{03})$, correspondingly.

Consider the first stage of case a for $g_0=1$ and complete separation and view the second and third component as the same substance with the output rate $x_{02} + x_{03} = 1 - x_{01}$. The irreversible expenses eq (63) are

$$\Delta p_{a1} = \frac{x_{01}^2}{\alpha_1} + \frac{(1 - x_{01})^2}{\alpha_1} = \frac{2x_{01}^2 + 1 - 2x_{01}}{\alpha_1} \quad (72)$$

When the second flow is separated into two flows their rates are

$$g_{22} = \frac{x_{02}}{(1 - x_{01})}, \quad g_{23} = \frac{x_{03}}{(1 - x_{01})}$$

and the irreversible power is

$$\Delta p_{a2} = \frac{1}{\alpha_2(1-x_{01})^2} (x_{02}^2 + x_{03}^2)$$

The combined irreversible power is

$$\Delta p_a(x_{01}, x_{02}) = \frac{2x_{01}^2 - 2x_{01} + 1}{\alpha_1} + \frac{x_{02}^2 + (1-x_{01}-x_{02})^2}{\alpha_2(1-x_{01})^2}$$

Similarly in case b we get

$$\Delta p_b(x_{01}, x_{02}) = \frac{2x_{02}^2 - 2x_{02} + 1}{\alpha_1} + \frac{x_{01}^2 + (1-x_{01}-x_{02})^2}{\alpha_2(1-x_{02})^2}$$

The differential between these two values is

$$\Delta p_{ab} = \Delta p_a - \Delta p_b = \frac{2}{\alpha_1} [(x_{01}^2 - x_{02}^2) - (x_{01} - x_{02})] + \frac{1}{\alpha_2(1-x_{01})(1-x_{02})} [(1-x_{02})^2(x_{02}^2 + x_{03}^2) - (1-x_{01})^2(x_{01}^2 + x_{03}^2)] \quad (73)$$

If $\Delta p_{ab} > 0$, then sequence b is preferable.

Note that it is not possible to formulate the general rule to choose the optimal separation sequence for a multicomponent mixture, in particular, on the basis of the reversible work of separation. It is necessary here to compare irreversible losses for each sequence.

2.4.4. Example

Assume that the composition of the input three component mixture is $x_{01}=0.6$, $x_{02}=0.3$, $x_{03}=1-x_{01}-x_{02}$; the mass transfer coefficients are $\alpha_1=0.01\text{mol}^2/(\text{J s})$, $\alpha_2=0.02\text{mol}^2/(\text{J s})$. From (eq 73) we find that the difference in power between sequences *a* and *b* is

$$\Delta p_{ab} = \Delta p_a - \Delta p_b = -7.82 \text{ J}$$

The comparison of the combined minimal irreversible power for the same initial data shows that the power for separation of a mixture using sequence *b* is higher than the power used for sequence *a*, that is, $\Delta p_{ab} < 0$.

Thus, sequence *a* is preferable, and it is better to perform the complete separation by separating the first component.

2.5. Limiting productivity and minimal heat consumption for a heat-driven separation

In many separation processes a heat engine is used to create the differential of the chemical potential between the working body and the reservoirs (the driving force of mass transfer). Here, the working body is heated during contact with one reservoir and is cooled during contact with the other reservoir. One can represent the heat-driven separation system as a transformer of heat into the work of separation that generates power *p*, consumes heat flow

from hot reservoir g_+ and rejects flow g_- to the cold reservoir. Heat transfer coefficients for contacts with the hot and cold reservoir α_+ and α_- are fixed.

It was shown in refs [12] and [6] that the potential of the direct transformation of heat to work is limited and the maximal generated power for the working body with the distributed parameters is

$$p_{\max} = \bar{\alpha}(\sqrt{T_+} - \sqrt{T_-})^2 \quad (74)$$

In this expression $\bar{\alpha} = (\alpha_+ \alpha_-) / (\alpha_+ + \alpha_-)$ is the equivalent heat transfer coefficient for continuous contact with the reservoirs; $\bar{\alpha} = (\alpha_+ \alpha_-) / (\sqrt{\alpha_+} + \sqrt{\alpha_-})^2$ is the equivalent heat transfer coefficient for sequential contact.

The maximal power determines the heat flow consumed from the hot reservoir. Further increase of heat consumption for given values of heat transfer coefficients requires an increase of the temperature differential between the reservoirs and the working body and reduces the power.

The dependence of the used power on the productivity of irreversible separation processes is monotonic eq (63). Therefore, the limiting productivity of heat-driven separation processes corresponds to the maximal possible power produced by transformation of heat into work. Further increase of heat consumption q_+ reduces power and therefore reduces the productivity of separation process.

For the Newton (linear) law of mass transfer and heat-work transformer the dependence of the power on the heat used is

$$q^+(p) = \frac{p}{\eta_p} = \frac{2p}{\left(\frac{p}{\bar{\alpha}T_+} + \eta_C \right) + \sqrt{\left(\frac{p}{\bar{\alpha}T_+} + \eta_C \right)^2 - \frac{4p}{\bar{\alpha}T_+}}} \quad (75)$$

Here, $\eta_C = (T_+ - T_-) / T_+$ is the Carnot efficiency, T_+ and T_- are the hot and cold reservoir's temperatures, and $\bar{\alpha} = (\alpha_+ \alpha_-) / (\alpha_+ + \alpha_-)$ is the equivalent heat transfer coefficient.

The minimal heat consumption q_+ as a function of productivity g_0 for a heat-driven separation can be obtained by substituting expression (75) instead of p in the right-hand side of eq (63). The result holds for $p \leq p_{\max}$ and therefore for $g_0 \leq g_{0\max}$. The duration here must not exceed the maximal possible duration.

Substitution of the right-hand side of eq (74) instead of p in eq (63) yields the maximal possible productivity of the system (where $\bar{\alpha}$ is chosen according to the type of contact between the transformer and reservoir). We denote

$$B = RT \sum_j \gamma_j^2 \sum_i x_{ji} \ln \frac{x_{ji}}{x_{0i}}, \quad D = T \sum_j \gamma_j^2 \sum_i \ln \frac{x_{ji}^2}{\alpha_{ji}} \quad (76)$$

We obtain

$$p_{\max} = \bar{\alpha} (\sqrt{T_+} - \sqrt{T_-})^2 = B g_{\max} + D g_{0\max}^2$$

and the limiting productivity is

$$g_{0\max} = \frac{-B + \sqrt{B^2 + 4\bar{\alpha}D(\sqrt{T_+} - \sqrt{T_-})^2}}{2D} \quad (77)$$

Formulas (76) and (77) allow us to estimate the limiting productivity of a heat-driven separation process for Newton's laws of heat transfer between the working body and reservoirs and mass transfer proportional to the differentials in chemical potentials (mass transfer is close to isothermal with the temperature T).

2.5.1. Example

Consider heat-driven monoethanamide gas cleansing. One of the components is absorbed by the cold solution from the input gas mixture. This solution is then heated and this component is vaporized. The input mixture's parameters are $\bar{T}=350$ K, the key component's molar concentration $x=0.5$, the rate of mixture $g_0=5$ mol/s. The temperatures of heat supplied/removed are correspondingly $T_h=400$ K, $T_c=300$ K, and the heat transfer coefficients are $\alpha_+=8.368$ kJ/(s K) and $\alpha_-=16.736$ kJ/(s K). The concentrations of the key components in the output flows are $x_1=0.9$, $x_2=0.1$; the mass transfer coefficients for each of the components (integral values over the whole contact surface) for the hot and cold reservoir's contacts are $\alpha_1=0.07$ mol²/(kg s), $\alpha_2=0.03$ mol²/(kg s).

Because the solution circulates and is heated and cooled in turns, the limiting power for transformation of heat into work is given by the expression (74) with the corresponding $\bar{\alpha}$

$$p_{\max}=20.711 \text{ kJ/s}$$

The power for separation is given by eq (63).

We have

$$p^0 = RT g_0 \sum_{j=1}^m \gamma_j \sum_i x_{ji} \ln \frac{x_{ji}}{x_{0i}} = 5.397 \text{ kJ/s}$$

The minimal work required for a system with Onsanger's equations are (see eq (63))

$$\Delta p = g_0^2 \sum_{j=1}^m \gamma_j^2 \sum_i \frac{x_{ji}^2}{\alpha_{ji}} = 7.238 \text{ kJ/s}$$

Thus, $p = p^0 + \Delta p = 12.636 \text{ kJ/s} < p_{\max}$. The work needed for separation does not exceed the maximal possible value for given heat transfer coefficients.

Let us estimate the minimal heat consumption. From eq (75) we get

$$q_+ = 32.426 \text{ kJ/s}$$

If the temperatures of the input and output flows are not the same then the minimal energy required for separation can be estimated using the thermodynamic balance equations (31) and (32) and the expression for σ^{\min} eq (49).

2.6. Conclusion

New irreversible estimates of the in-principle limiting possibilities of separation processes are derived in this paper. They take into account the unavoidable irreversibility caused by the finite rate of flows and heat and mass transfer coefficients. They also allow us to estimate the limiting productivity of a heat-driven separation and to find the most energy efficient separation sequence/regime of separation for a multicomponent mixture.

3. Optimization of membrane separations

3.1. Introduction

As the properties of membranes improve, the membrane separation of liquids and gases is more widely used in chemical engineering [8,10,11,20]. Since the mathematical modeling of membrane separations is simpler than that for most of the other separation processes, they could be controlled by varying the pressure, contact surface area, and the like during the separation process.

The minimal work needed to separate mixtures into pure components or into mixtures of given compositions can be minorized using well-known relationships of reversible thermodynamics [15]. However, this estimate is not accurate because it ignores the mass transfer laws and the properties of membranes, process productivity, possible intermediate processes of mixing, and so on. The estimates based on reversible thermodynamics are not suitable for determining the optimal sequence of operations in the separation of multicomponent systems, because they depend only on the compositions of feeds and end products and do not reflect the sequence of operations in which the end product was obtained. The work needed for separation consists of its reversible work and irreversible energy losses. The losses are equal to ΔST , where ΔS is the increment of the system entropy due to the irreversibility of the process. Below, the minimum possible production of entropy (that is, the minimal additional separation work) will be found for the separation of one component at a specified production rate and transport coefficients. Also, we will determine the dependence of this minimum on the input data for one or another process flowsheet at a fixed production rate.

3.2. Batch membrane separation

We will first consider a batch separation of a mixture in a system consisting of two chambers separated by a membrane permeable to only one active (to be separated) component of the mixture (Fig. 5). Let and $G_i(t)$, $C_i(t)$, $\mu_i(C_i)$, and P_i denote the amount, the concentration of the active component, and its chemical potential in chamber i , respectively. These parameters can be varied during the process. At the initial moment of time ($t=0$), the parameters that are specified include the mixture amount $G_1(0)=G_{10}$ in chamber 1 and the concentration $C_1(0)=C_{10}$ of the active component passing through membrane 3 at a mass transfer rate g , which depends on its chemical potentials on both membrane sides, μ_1 and μ_2 . In turn, the potentials depend on the variation of the pressure and mixture composition in the first and second chambers. The pressure in the first chamber can be varied using piston 4. The process is isothermal, and the temperature T is specified and remains unchanged.

The intensive variables in the second chamber are the pressure $P_2(t)$ and the chemical potential $\mu_2(t)$, which varies with time due to the accumulation of the active component in the chamber and the variation of the external conditions. Assume that the laws of this variation are known. The specification of the initial composition of the mixture C_{10} , the number of moles G of the component that passed through the membrane in time τ , and the initial number of moles G_{10} determines the final composition in the first chamber,

$$C_1(\tau) = \frac{G_{10}C_{10} - G}{G_{10} - G},$$

and, hence, the reversible work of separation, which is equal to the increment of the free energy of the system:

$$A^0 = -G_{10}RT[C_{10} \ln C_{10} + (1 - C_{10}) \ln(1 - C_{10})] + (G_{10} - G)RT\{C_1(\tau) \ln C_1(\tau) + [1 - C_1(\tau)] \ln[1 - C_1(\tau)]\}. \quad (78)$$

Consequently, the minimum of the produced work corresponds to the minimum of the irreversible losses of energy, which is proportional to ΔS .

The increment of entropy in the system, the minimum of which should be determined for a separation process of duration τ , is equal to the product of the flux and driving force:

$$\Delta S = \frac{1}{T} \int_0^\tau g(\mu_1, \mu_2)(\mu_1 - \mu_2) dt \rightarrow \min. \quad (79)$$

The amount of the active component that passed through the membrane is written as

$$G = \int_0^\tau g(\mu_1, \mu_2) dt. \quad (80)$$

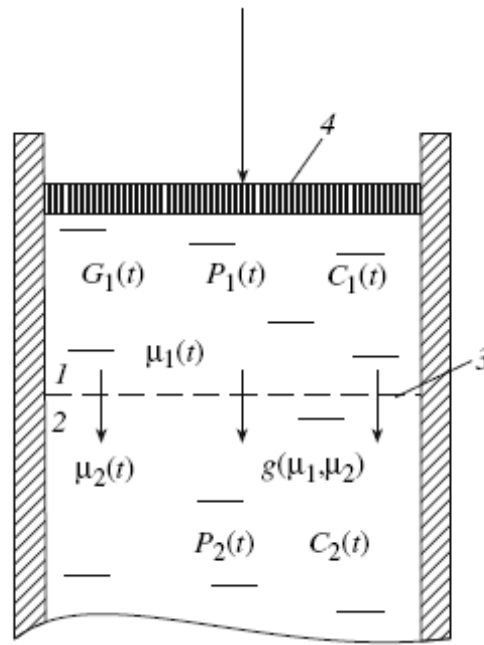


Figure 5. Batch separation of a mixture: 1, chamber with the mixture to be separated; 2, chamber to which the active component passes; 3, membrane; 4, piston.

The process duration τ will be fixed.

The variation of G_1 and concentration C_1 are determined by the equation:

$$\frac{d(G_1 C_1)}{dt} = \frac{dG_1}{dt} = -g(\mu_1, \mu_2). \quad (81)$$

It follows from Eq. (81) that $\frac{d[G_1(1-C_1)]}{dt} = 0$, implying that $G_1(t)(1-C_1(t)) = \text{const}$ for any moment of time. The latter is equal to the amount of the “inert” component of the mixture in the first chamber. It will be denoted as $\tilde{G} = G_1(0)[1-C_1(0)]$.

The solution of Eq. (81) determines the dependence of the mixture amount in the first chamber on the active component concentration $G_1(C_1)$:

$$G_1(t) = \frac{\tilde{G}}{1-C_1(t)}. \quad (82)$$

After expression (82) is substituted into Eq. (81), the latter takes the form

$$\frac{dC_1}{dt} = -\frac{1}{\tilde{G}_1} (1-C_1)^2 g(\mu_1, \mu_2), \quad C_1(10) = C_{10}. \quad (83)$$

First, we will find such time variation of, chemical potential $\mu_1(t)$ that the increment of entropy takes the minimum value at a specified value of G . Then, for a specific form of chemical potential, we will find the time variation of pressure $P_1(t)$ corresponding to the found optimal variation of the chemical potential.

We will write the Lagrangian function F for the problem given by Eqs. (79) and (80) in view of the fact that the constant factor $1/T$ does not affect the optimality condition:

$$F = g(\mu_1, \mu_2)(\mu_1 - \mu_2 - \lambda).$$

The mass transfer rate g is equal to zero when $\mu_1 = \mu_2$ and increases monotonically with increasing μ_1 . As a result, the function F is, as a rule, convex with respect to μ_1 . Consequently, this dictates the stationarity of F in the solution of the problem and this solution is unique:

$$\frac{\partial F}{\partial \mu_1} = 0 \rightarrow \frac{\partial g}{\partial \mu_1}(\mu_1 - \mu_2 - \lambda) = -g(\mu_1, \mu_2).$$

To cancel out λ , we integrate the both sides of this equality from zero to τ in view of Eq. (80) to obtain

$$\lambda = \frac{G + \int_0^\tau \frac{\partial g}{\partial \mu_1}(\mu_1 - \mu_2) dt}{\int_0^\tau \frac{\partial g}{\partial \mu_1} dt}.$$

Consequently, to determine $\mu_1(t)$ with a convex function F , we have the equation determining the optimal variation of $\mu_2(t)$ in the function $g(\mu_1, \mu_2)$ for any $\mu_1(t)$ and mass transfer law $\mu_2(t)$:

$$g(\mu_1, \mu_2) = \frac{\partial g}{\partial \mu_1} \left[\frac{G + \int_0^\tau \frac{\partial g}{\partial \mu_1}(\mu_1 - \mu_2) dt}{\int_0^\tau \frac{\partial g}{\partial \mu_1} dt} - (\mu_1 - \mu_2) \right]. \quad (84)$$

If the flux is proportional to the difference of chemical potentials,

$$g = \alpha(\mu_1 - \mu_2), \quad (85)$$

it follows from optimality condition (84) that

$$\mu_1^*(t) = \mu_2(t) + \frac{G}{\tau\alpha}, \quad g^* = \frac{G}{\tau} = \text{const.} \quad (86)$$

The variation of $P_1(t)$ corresponding to $\mu_1^*(t)$ depends on the form of the chemical potential.

For mixtures close in properties to ideal gases, the chemical potential (molar Gibbs energy) of the active component of the mixture is written as

$$\mu_1 = \mu_{11}(T, P_1) + RT \ln C_1 = \mu_{01}(T) + RT \ln P_1 + RT \ln C_1, \quad (87)$$

where μ_{01} is the standard chemical potential for $P_1 = C_1 = 1$.

The variation of $C_1^*(t)$ (t) is determined by Eq. (83) with known mass transfer rate g . After $C_1^*(t)$ and $\mu_1^*(t)$ are substituted into Eq. (87), we obtain an expression for the pressure in the first chamber:

$$P_1^*(t) = \frac{1}{C_1^*(t)} \exp \left[\frac{\mu_1^*(t) - \mu_{01}(T)}{RT} \right]. \quad (88)$$

For the flux defined by Eq. (85) and defined by Eq. (86), Eq. (83) takes the form:

$$\frac{dC_1}{dt} = -\frac{G(1-C_1)^2}{\tau G_1} = \frac{G(1-C_1)^2}{G_{10}(1-C_{10})\tau}, \quad C_1(0) = C_{10}.$$

The solution to this equation is written as

$$C_1^*(t) = \frac{G_{10}C_{10} - \frac{G}{\tau}t}{G_{10} - \frac{G}{\tau}t}. \quad (89)$$

Substituting the latter into Eq. (88) gives the time variation of the pressure:

$$P_1^*(t) = \frac{G_{10} - \frac{G}{\tau}t}{G_{10}C_1(0) - \frac{G}{\tau}t} \exp \left(\frac{\mu_2 + \frac{G}{\alpha\tau} - \mu_{10}(T)}{RT} \right).$$

After the optimal variation of $\mu_1^*(t)$, or optimal value of this chemical potential, is found, we can determine ΔS_{\min} by substituting μ_1^* and μ_2 into Eq. (79). Using the flux defined by Eq. (85) and relationship (79), we obtain

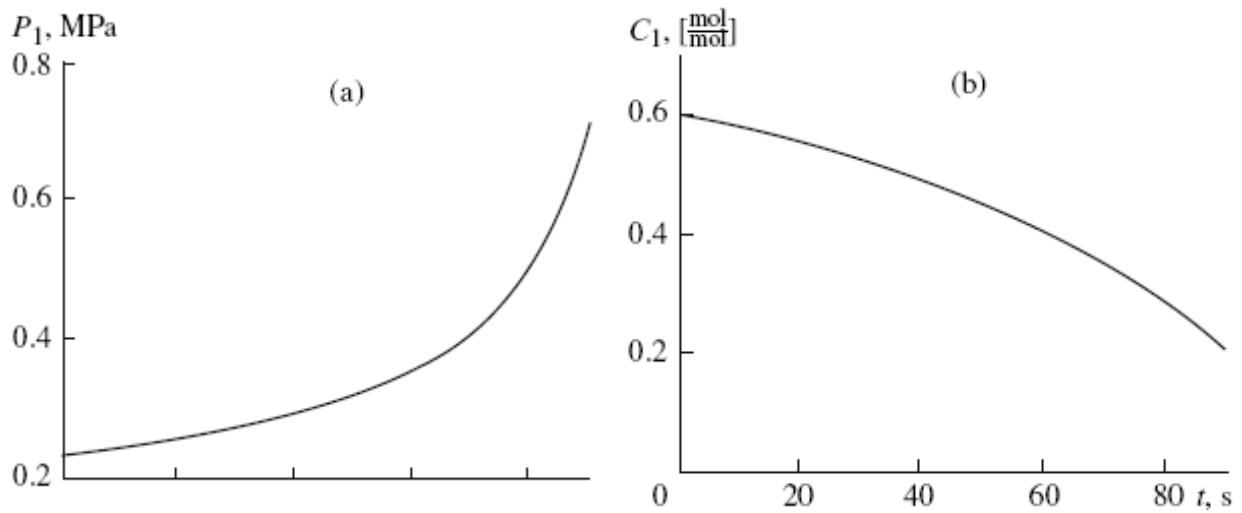


Figure 6. Optimal time variation of (a) pressure and (b) mole fraction of the active component in the first chamber for a gas mixture.

$$\Delta S_{\min} = \frac{G^2}{T\alpha\tau}.$$

The optimal variation of the pressure and mole fraction of oxygen in the first chamber is shown in Fig. 6. It corresponds to the separation of a gas mixture composed of carbon dioxide, 120 moles of CO_2 , and oxygen, 180 moles of O_2 (active component), when $G_{10}=300$ moles, $C_{10}=0.6$, $G=150$ moles, $\tau=90$ s, $\alpha=2.13 \times 10^{-3} \text{ mol}^2/(\text{s J})$, $P_2=101330$ Pa, $C_2=1.0$, and $T=283$ K. At the moment when the process is terminated, $C(\tau)=0.2$. The production of entropy is $\Delta S = \Delta S_{\min} = 415$ J/K.

The produced work is $A = A^0 + T\Delta S = 415730$ J, where according to Eq. (78) $A_0 = 298300$ J.

Although the chemical potential for ideal solutions is written like Eq. (87), the function $\mu_{11}(T, P_1)$ for them takes a different form. This is caused by the fact that the chemical potential $\mu_1(T, P_1, x_1)$ is the molar Gibbs energy of the active component and the derivative of the chemical potential with respect to pressure is the molar volume of this component v_1 [15]. In contrast to gases, the molar volume of liquids is virtually independent of pressure and varies very little with temperature. As

$$\frac{\partial \mu_1}{\partial P_1} = \frac{\partial \mu_{11}}{\partial P_1} = v,$$

we obtain

$$\mu_1(T, P_1, x_1) = \mu_{01}(T) + vP_1 + RT \ln C_1. \quad (90)$$

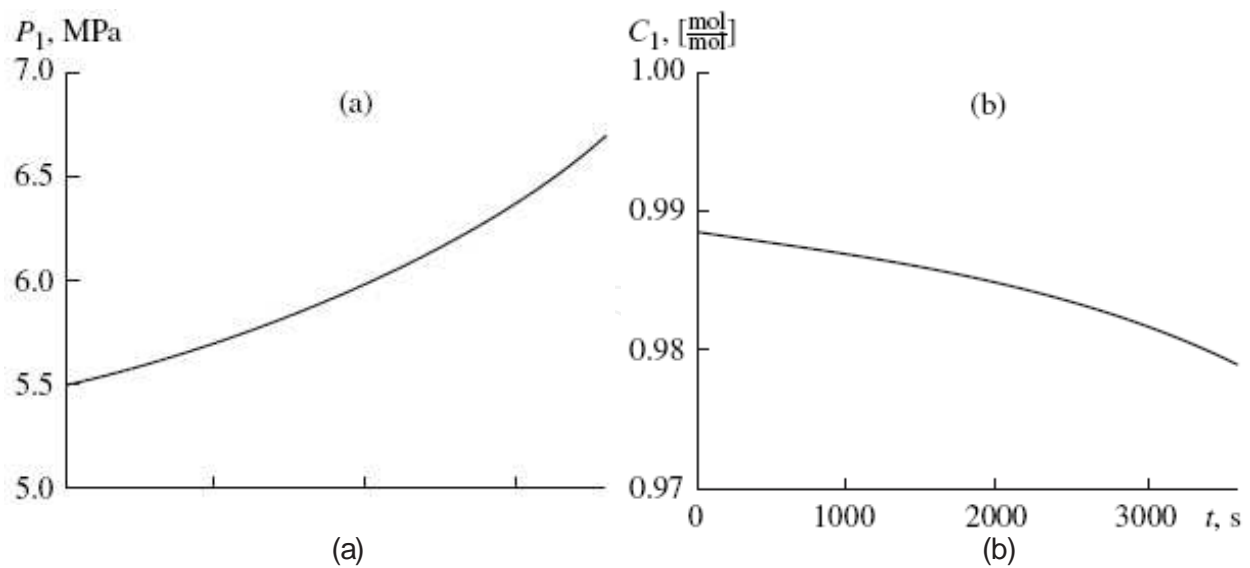


Figure 7. Optimal time variation of (a) pressure and (b) the mole fraction of the active component in the first chamber for a near-ideal solution.

For the flux defined by Eq. (85) and μ_1^* defined by Eq. (86), the variation of $C_1^*(t)$ for liquids can be written in the same way as for gases in Eq. (89). After $\mu_1^*(t)$ and $C_1^*(t)$ are substituted into Eq. (90), we obtain an equation for the optimal variation of pressure in the first chamber:

$$P_1^*(t) = \frac{1}{v_1} \left[\mu_2 + \frac{G}{\tau \alpha} - \mu_{01}(T) - RT \ln \left(\frac{G_{10} C_1(0) - \frac{G}{\tau} t}{G_{10} - \frac{G}{\tau} t} \right) \right].$$

For illustration, we considered the separation of water with a high salt concentration. Like ocean water, it contained 36 g/l of salt (inert component). The other process parameters were $G_{10} = 552.3$ moles, $C_{10} = 0.989$, $G = 250$ moles, $\tau = 3600$ s, $\alpha = 9.92 \times 10^{-4} \text{ mol}^2/(\text{s J})$, $P_2 = 101330 \text{ Pa}$, $C_2 = 1.0$, and $T = 283 \text{ K}$. The time variation of the optimal pressure of the liquid and the mole fraction of water in the first chamber are illustrated in Fig. 7. At the moment when the process is terminated, $C(\tau) = 0.979$. The production of entropy is $\Delta S = \Delta S_{\min} = 61.8 \text{ J/K}$. The produced work is $A = A^0 + T\Delta S = 26470 \text{ J}$, where according to Eq. (78) $A_0 = 8973 \text{ J}$.

3.3. Membrane separation process distributed along the filter

The parameters of the system can vary with length rather than with time, as in the previous system. The flow diagram of this system is shown in Fig. 8. The mixture to be separated, which is characterized by a molar flux $g_1(0) = g_{10}$ and concentration $C_1(0) = C_{10}$, is continuously supplied to the first chamber, the overall length of which is L . As the mixture travels over the length l , the active component passes across the membrane into the second chamber. The concentration of the active component in the mixture to be separated at the outlet of the first chamber is $C_1(L) = C_{1L}$. The chemical potential of this component in the second chamber,

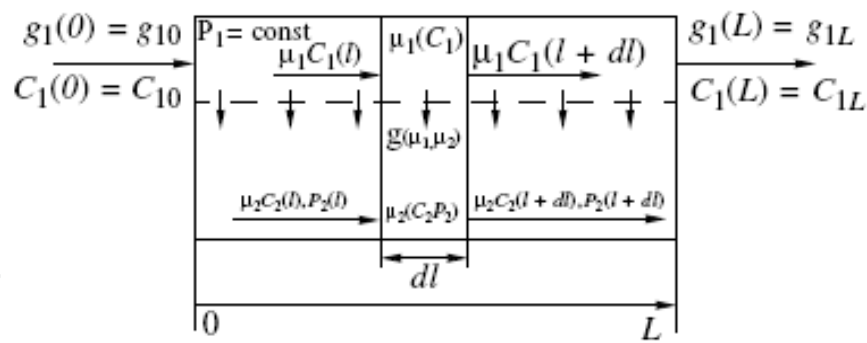


Figure 8. Continuous separation of a mixture.

$\mu_2(l)$, should be chosen so that in the isothermal process the increment of entropy in the system should be a minimum for the specified values of production rate \bar{g} and total membrane surface area $s(L)$. In irreversible continuous separation, the power p expended for separation is the sum of the reversible component

$$p^0 = -g_1(0)RT[C_{10} \ln C_{10} + (1 - C_{10}) \ln(1 - C_{10})] + (g_1(0) - \bar{g})RT[C_1(L) \ln C_1(L) + (1 - C_1(L)) \ln(1 - C_1(L))], \quad (91)$$

which is determined at the given conditions, and the irreversible losses $p_H = T\sigma$. Consequently, the minimal production of entropy σ corresponds to the minimal separation work p .

The flux of the component to be distributed at section l is equal to $g[\mu_1(l), \mu_2(l)]$. The production rate is specified as

$$\int_0^L g(\mu_1, \mu_2) dl = \bar{g}. \quad (92)$$

The production of entropy is determined by the expression

$$\sigma = \frac{1}{T} \int_0^L g(\mu_1, \mu_2)(\mu_1 - \mu_2) dl \rightarrow \min_{\mu_2(l)}. \quad (93)$$

Assume that $\mu_2(l)$ is the control parameter.

If the operating regime in the first chamber is close to plug flow, the material balance equations for section l give equations analogous to Eqs. (81).

$$\frac{d}{dl}(C_1 g_1) = \frac{d}{dl} g_1 = -g(\mu_1, \mu_2). \quad (94)$$

The above equation can be used to obtain a relationship analogous to Eq. (83):

$$\begin{aligned}\frac{dC_1}{dl} &= -\frac{(1-C_1)^2}{\tilde{g}_1} g(\mu_1, \mu_2), \\ C_1(0) &= C_{10}, \quad g_1(l) = \frac{\tilde{g}_1}{1-C_1(l)},\end{aligned}\tag{95}$$

where $\tilde{g}_1 = g_1(0)(1-C_{10})$ is the molar flux of the inert component through the first chamber.

Equations (92), (93), and (95) represent an optimal control problem in which C_1 is the state coordinate and the potential μ_2 is the control action. This problem can be simplified using the fact that for optimal processes the right-hand side of Eq. (95) never change the sign and C_1 monotonically varies with time. The independent variable l can be replaced by C_1 . It follows from Eq. (95) that

$$dl = -\frac{\tilde{g}_1 dC_1}{(1-C_1)^2 g(\mu_1, \mu_2)}.$$

In view of this replacement, the problem given by Eqs. (92), (93), and (95) can be written as

$$\sigma = \frac{\tilde{g}_1}{T} \int_{C_{1L}}^{C_{10}} (\mu_1 - \mu_2) \frac{dC_1}{(1-C_1)^2} \rightarrow \min_{\mu_2}\tag{96}$$

with the constraints

$$\int_{C_{1L}}^{C_{10}} \frac{dC_1}{(1-C_1)^2} = \frac{\bar{g}}{\tilde{g}_1},\tag{97}$$

$$\int_{C_{1L}}^{C_{10}} \frac{dC_1}{(1-C_1)^2 g(\mu_1, \mu_2)} = \frac{L}{\tilde{g}_1}.\tag{98}$$

The concentration C_{1L} is determined by the initial concentration C_{10} and production rate \bar{g} in constraint (97) or (94). Using constraint (94), we obtain

$$C_{1L} g_1(L) = C_{10} g_1(0) - \bar{g}, \quad g_1(L) = g_1(0) - \bar{g}$$

and, hence,

$$C_{1L} = \frac{C_{10} g_1(0) - \bar{g}}{g_1(0) - \bar{g}}.\tag{99}$$

The same follows from constraint (97) with $\tilde{g}_1[C_{10}, g_1(0)]$. Consequently, after C_{1L} is found using constraint (99), constraint (97) can be ignored.

In distinction to batch membrane processes, the control action in a continuous membrane separation can be additionally represented by the coefficient of heat transfer $\alpha(l)$, because the membrane surface area can be varied from section to section, which corresponds to the variation of heat transfer coefficient α . Let α be a function of C_1 . After $\alpha(C_1)$ and $C_1(l)$ are found, we can pass to $\alpha(l)$. The mass transfer equation can be written as

$$g(\mu_1, \mu_2) = \alpha g_0(\mu_1, \mu_2) \quad (100)$$

where g_0 is called the specific mass transfer rate. In this case, the total surface area of the membrane and, hence, the overall value of the heat transfer coefficient will be bounded:

$$\int_{C_{1L}}^{C_{10}} \alpha(C_1) dC_1 = \bar{\alpha}. \quad (101)$$

In constraint (98), the mass transfer rate can be written as Eq. (100), and equality (101) can be added to the constraints of the problem. The resulting problem, given by Eqs. (96), (98), and (101), is an isoperimetric variation problem. The necessary condition for the optimality of its solution is the requirement that the Lagrangian function should be stationary with respect to μ_2 and α :

$$F = \frac{1}{(1-C_1)^2} \left[\mu_1(C_1) - \mu_2 - \frac{\lambda_1}{\alpha g_0(\mu_1, \mu_2)} \right] - \lambda_2 \alpha,$$

where the multipliers λ_1 and λ_2 correspond to constraints (98) and (101). The conditions for the stationary of F with respect to the desired variables are written as

$$\begin{aligned} \frac{\partial F}{\partial \mu_2} = 0 &\rightarrow \frac{\lambda_1 \partial g_0 / \partial \mu_2}{\alpha g_0^2(\mu_1, \mu_2)} = 1, \\ \frac{\partial F}{\partial \alpha} = 0 &\rightarrow \frac{1}{(1-C_1)^2} \frac{\lambda_1}{\alpha^2 g_0(\mu_1, \mu_2)} = \lambda_2. \end{aligned}$$

The above equations give the process optimality conditions:

$$\frac{\lambda_1 \partial g_0 / \partial \mu_2}{\alpha(C_1) g_0^2(\mu_1, \mu_2)} = \text{const} = \frac{1}{\lambda_1}, \quad (102)$$

$$\alpha^2(C_1)(1-C_1)^2 g_0(\mu_1, \mu_2) = \text{const} = \frac{\lambda_1}{\lambda_2}. \quad (103)$$

From constraints (98) and (103) we obtain

$$\frac{\lambda_1}{\lambda_2} = \frac{\tilde{g}_1 \int_{C_{1L}}^{C_{10}} \alpha(C_1) dC_1}{L} = \frac{\tilde{g}_1 \bar{\alpha}}{L}. \quad (104)$$

It follows from (101) and (102) that

$$\frac{1}{\lambda_1} = \frac{1}{\bar{\alpha}} \int_{C_{1L}}^{C_{10}} \frac{\partial g_0 / \partial \mu_2}{g_0^2(\mu_1, \mu_2)} dC_1. \quad (105)$$

After expressions (105) and (104) are substituted into conditions (102) and (103), respectively, we can use the known function $\mu_1(C_1)$ to find the functions $\mu_2^*(C_1)$ and $\alpha^*(C_1)$ that are optimal in terms of minimal irreversibility, which with the help of Eq. (95) determine $C_1^*(l)$ and, hence, $\mu_2^*(l)$ and $\alpha^*(l)$.

Let us write the above relationships specifically for the function g written as a linear function of the difference of chemical potentials, Eq. (85), and chosen functions $\mu_i(C_i)$. Assume that the specific mass transfer rate takes the form:

$$g_0(\mu_1, \mu_2) = \mu_1 - \mu_2.$$

Constraints (102)–(105) lead to the equations

$$\frac{1}{\alpha(C_1)(\mu_1(C_1) - \mu_2(C_1))^2} = \frac{1}{\bar{\alpha}} \int_{C_{1L}}^{C_{10}} \frac{dC_1}{(\mu_1(C_1) - \mu_2(C_1))^2}, \quad (106)$$

$$\alpha(C_1)(1-C_1)^2 [\mu_1(C_1) - \mu_2(C_1)] = \frac{\tilde{g}_1 \bar{\alpha}}{L}. \quad (107)$$

For brevity, we will introduce the notation $\mu_1 - \mu_2 = \Delta\mu$ and the right-hand sides in constraints (106) and (107) will be denoted as R_1 and R_2 . In this case, the above equations can be written as

$$\frac{1}{\alpha \Delta \mu^2} = R_1, \quad \alpha^2 (1 - C_1) \Delta \mu = R_2,$$

and we obtain

$$\Delta \mu^*(C_1) = \frac{(1 - C_1)^{2/3}}{R_2^{1/3} R_1^{2/3}}, \quad \alpha^*(C_1) = \frac{R_1^{1/3} R_2^{2/3}}{(1 - C_1)^{4/3}}. \quad (108)$$

The concentration of the active component in the first chamber declines with increasing l . Therefore, under optimal operating conditions, $\Delta \mu^*(l) = \Delta \mu^*[C_1(l)]$ increases while the surface area of the membrane, which is proportional to $\alpha^*(l) = \alpha^*[C_1(l)]$, decreases.

To find R_1 , we will substitute Eq. (108) into Eq. (106) to obtain the equation

$$\frac{R_1^{4/3} R_2^{2/3}}{\bar{\alpha}} \int_{C_{1L}}^{C_{10}} \frac{dC_1}{(1 - C_1)^{4/3}} = R_1.$$

The evaluation of the integral gives us the desired formula:

$$R_1 = \frac{\bar{\alpha} L^2}{B^3 \tilde{g}_1^2}, \quad (109)$$

where

$$B = \left(\frac{3}{\sqrt[3]{1 - C_1(0)}} - \frac{3}{\sqrt[3]{1 - C_1(L)}} \right).$$

Equation (108) in view of Eq. (109) yields the optimal dependence of the difference of chemical potentials on the concentration C_1 :

$$\Delta \mu^*(C_1) = \frac{(1 - C_1)^{2/3} B^2 \tilde{g}_1}{\bar{\alpha} L}, \quad (110)$$

$$\alpha^*(C_1) = \frac{\bar{\alpha}}{B(\sqrt[3]{1 - C_1})^4}. \quad (111)$$

Consequently, Eq. (95) takes the form:

$$\frac{dC_1}{dl} = -\frac{(1-C_1)^2}{\tilde{g}_1} \alpha^*(C_1) \Delta\mu^*(C_1) = -\frac{(1-C_1)^{4/3} B}{L}.$$

Integrating this equation with specified initial conditions, we can find the variation of the concentration of the active component over the length of the first chamber under optimal operating conditions:

$$C_1^*(l) = 1 - \frac{27L^3}{\left(\frac{3L}{\sqrt[3]{1-C_1(0)}} - Bl \right)^3}. \quad (112)$$

Substituting this expression into Eqs. (110) and (111) yields the variation of the desired variables over the length:

$$\Delta\mu^*(l) = \frac{9LB^2 \tilde{g}_1}{\bar{\alpha} \left(\frac{3L}{\sqrt[3]{1-C_1(0)}} - Bl \right)^2}, \quad (113)$$

$$\alpha^*(l) = \frac{\bar{\alpha} \left(\frac{3L}{\sqrt[3]{1-C_1(0)}} - Bl \right)^4}{3^4 BL^4}. \quad (114)$$

The minimal value of the production of entropy corresponding to the above solution is written as

$$\bar{\sigma}_{\min} = \frac{\tilde{g}}{T} \int_{C_{1L}}^{C_{10}} \Delta\mu^*(C_1) \frac{dC_1}{(1-C_1)^2} = \frac{\tilde{g}_1^2}{LT\bar{\alpha}} B^3. \quad (115)$$

We will introduce α , the mass transfer coefficient per unit area of the membrane surface, and $ds(l)$, the elementary membrane surface area. If $\alpha = \text{constant}$, then

$$\bar{\alpha} = \alpha \int_0^L ds(l) = \alpha s(L),$$

where $s(L)$ is the total contact surface area.

If the specific mass transfer coefficient of the membrane material α and the total contact surface area $s(L)$ are known, we can find the optimal distribution of the membrane surface area over the length of the filter:

$$ds^*(l) = \frac{\alpha^*(l)}{\bar{\alpha}}.$$

For near-ideal gas mixtures, we can write

$$\mu_1(C_1) = \mu_{10}(P_1, T) + RT \ln C_1,$$

where P_1 and T are assumed to be specified, and

$$\mu_2(P_2, T, C_2) = \mu_{20}(T) + RT \ln P_2 + RT \ln C_2. \quad (116)$$

When $\Delta\mu^*(C_1)$ is known, expression (116) can be used to find the pressure function in the second chamber for which σ_{\min} is achieved:

$$P_2^*(C_1, C_2) = \frac{1}{C_2} \exp \left\{ \frac{1}{RT} [\mu_1(C_1) - \mu_{20}(T) - \Delta\mu^*(C_1)] \right\}. \quad (117)$$

The optimal curves for the pressure and mass transfer coefficient are plotted in Fig. 9, in which the data refer to the separation of a gas mixture composed of carbon dioxide CO_2 and oxygen O_2 (active component) when $C_{10}=0.6$, $g_1(0)=3.33\text{mol/s}$, $\bar{g}=1.66\text{mol/s}$, $P_1=2 \times 10^6\text{Pa}$, $\bar{\alpha}=3.18 \times 10^{-4}\text{mol}^2/(\text{s J})$, $\alpha=0.013\text{mol}^2/(\text{s J})$, $L=2.5\text{m}$, and $T=283\text{ K}$.

At the filter outlet, $C_1(L)=0.2$. The production of entropy is $\sigma=\sigma_{\min}=4.6\text{ J}/(\text{s K})$.

The consumed power is $p=p_0+T\sigma=4600\text{ J/s}$, where according to Eq. (91) $p_0=3292\text{ J/s}$.

For ideal solutions, the calculation is almost the same except for the form in which the chemical potentials are written. For the first chamber,

$$\mu_1(C_1) = \mu_{10}(T) + vP_1 + RT \ln C_1,$$

where v is the molar volume of the active component.

For the second chamber,

$$\mu_2(P_2, T, C_2) = \mu_{20}(T) + vP_2 + RT \ln C_2.$$

The dependence of the solution pressure in the second chamber on the concentration is written as

$$P_2^*(C_1, C_2) = \frac{1}{v} [\mu_1(C_1) - \mu_{20}(T) - \Delta\mu^*(C_1) - RT \ln C_2].$$

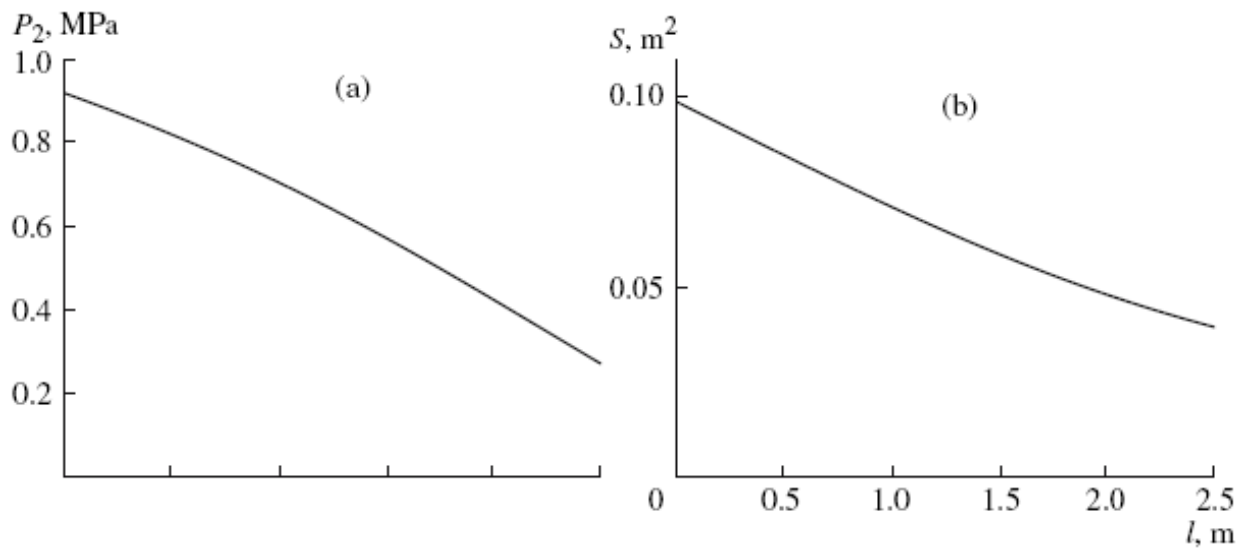


Figure 9. Optimal variation of (a) pressure and (b) the membrane surface area over the filter length for a near-ideal gas mixture.

For illustration, we considered the separation of water with a high salt concentration. Like ocean water, it contained 36 g/l of salt (inert component). The other process parameters were $g_1(0)=0.153$ mol/s, $C_{10}=0.989$, $\bar{g}=1.66$ mol/s, $\bar{\alpha}=2.92 \times 10^{-6}$ mol²/(s J), $\alpha=0.011$ mol²/(s J), $P_1=7.7 \times 10^6$ Pa, $L=3$ m, and $T=283$ K. The profile of optimal pressure in the first chamber and the variation of the mass transfer coefficient over the filter length are illustrated in Fig. 10. At the filter outlet, $C_1(L)=0.979$. The production of entropy is $\sigma=\sigma_{\min}=0.017$ J/(s K).

The consumed power is $p=p_0+T\sigma=7.35$ J/s, where according to Eq. (91) $p_0=2.47$ J/s.

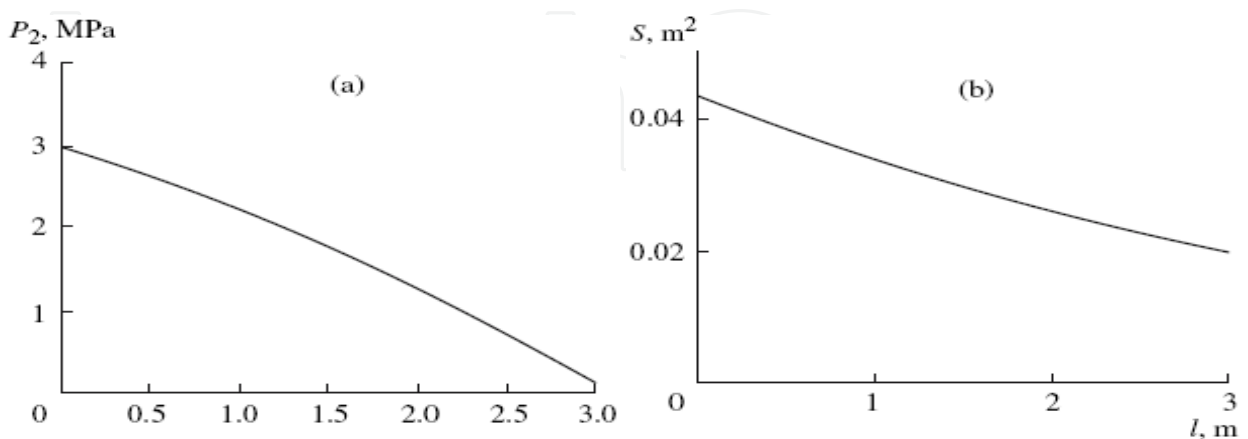


Figure 10. Optimal variation of (a) pressure and (b) membrane surface area over the filter length for a near-ideal solution.

3.4. Conclusion

The minimal losses of energy for irreversible membrane separations with specified production rates are estimated. The variation of the driving force (difference of chemical potentials) and the distribution of the membrane surface area over the filter length corresponding to the process with minimal energy losses are found.

The obtained estimates can be used for assessing the deviation of the actual membrane separation from the optimal process and for comparing the thermodynamic efficiency of membrane separation processes with different flow diagrams, as well as for formulating and solving problems regarding the optimal sequence of operations in the separation of multi-component mixtures.

4. Optimization of diffusion systems

4.1. Introduction

The problem of deriving work from a irreversible thermodynamic system and the inverse problem of maintaining its irreversible state by consuming energy are central in thermodynamics. For systems that are not in equilibrium with respect to temperature, the first (direct) of the above problems is solved using heat engines and the second one (inverse) is solved using heat pumps. For systems that are not in equilibrium with respect to composition, the second problem is solved using separation systems and the first one is solved using diffusion engines. As a rule, separation systems and diffusion engines are based on membranes.

There is a lot of studies of membrane separation systems and diffusion engines in the literature [5,7]. In the present paper, these systems will be considered using the theory of finite-time thermodynamics. The finite-time thermodynamics, which evolved in the past years, studies the limiting performance of irreversible thermodynamic systems when the duration of the processes is finite and the average rate of the streams is specified [14, 17]. For example, some problems for heat engines, such as maximizing the power at given heat transfer coefficients and maximizing the efficiency at given power for different conditions of contact between the working body and surroundings, are already solved. In this case, the irreversible processes of the interaction of subsystems each of which is in internal equilibrium are considered.

For systems that are not uniform in concentration, it is most important to study the limiting performance of separation systems. In this case, however, the inverse problem of studying the performance of diffusion engines is of definite interest as well. The simplest variant of this problem was first formulated by Rozonoer [17]. The review of the literature shows that this problem was discussed rather superficially.

In the present paper, we will study the limiting performance of membrane systems in the separation processes with fixed rates, focusing on the following problems:

1. Minimizing the amount of energy necessary for the separation of a feed mixture with a given composition into separation products with given compositions at a given average production rate.

2. Maximizing the power and efficiency of diffusion engines.

The solution of these problems depends strongly on whether the feed mixture used by the engine is gaseous or liquid because this determines the form of the chemical potentials of components and, hence, the driving forces of the process. For near-ideal gas mixtures, the chemical potential of component I of the mixture takes the form [15]:

$$\mu_i(T, P_i) = \mu_0(T) + RT \ln P_i, \quad i=1, 2, \dots,$$

where P_i is the partial pressure of component I and $\mu_0(T)$ is the chemical potential of the pure component. Assuming that the ratio of the partial pressure to the total pressure is equal to x_i ,

$$P_i = P x_i = P \frac{N_i}{N}, \quad i=1, 2, \dots,$$

we can rewrite the expression for the chemical potential in the form:

$$\mu_i(T, P, x_i) = \mu_1(T, P) + RT \ln x_i, \quad (118)$$

where $\mu_1(T, P) = \mu_0(T) + RT \ln P$.

Although the chemical potential for liquids has the same form as Eq. (118), the form of the function $\mu_1(T, P)$ is different. This is caused by the fact that the chemical potential $\mu_i(T, P, x_i)$ represents the molar Gibbs energy of component I and its derivative with respect to pressure is equal to the molar volume of this component v_i [15]. In contrast to gases, the molar volume of liquids is virtually independent of pressure and weakly dependent on temperature. As

$$\frac{\partial \mu_i}{\partial P} = \frac{\partial \mu_1}{\partial P} = v_i,$$

we obtain

$$\mu_i(T, P, x_i) = \mu_1(T) + RT \ln x_i. \quad (119)$$

It is assumed that the processes are isothermal and the temperatures of all subsystems are equal to T . The problems listed above will be considered for gaseous mixtures and then for liquid solutions.

4.2. Limiting performance of diffusion systems for gaseous mixtures

4.2.1. Maximum work in a membrane process

Consider a system consisting of a thermodynamic reservoir, the intensive variables of which are fixed and are independent of mass transfer fluxes, and a working body, the intensive variables of which can be varied with time by one or another way. The system can consume

external energy or generate work. In the first case, the work will be negative; in the second, positive.

The reservoir and the working body interact through a membrane that is permeable only to one (active) component of the mixture. The mass transfer rate g depends on the chemical potentials of the active component in the reservoir μ_0 and in the working body $\mu(t)$. When these chemical potentials are equal to each other, the flux is equal to zero. In the particular case under consideration,

$$g(\mu_0, \mu) = \alpha(\mu_0 - \mu), \quad (120)$$

where α is the mass transfer coefficient. The working-body temperature T is maintained constant and equal to the reservoir temperature.

When the process duration τ and the total amount of the component G_0 transferred from the reservoir to the working body and in the reverse direction are fixed in the process characterized by a finite mass transfer coefficient, the chemical potentials μ_0 and $\mu(t)$ should differ from each other at every moment of time and the mass transfer process should be irreversible. For definiteness, we assume that $\mu_0 > \mu(0)$ and that the component is transferred from the reservoir to the working body.

The variation of the system entropy will be caused by the decrease in the reservoir entropy, the increase in the entropy of the working body, and the production of entropy due to the irreversible mass transfer σ . For a given initial state of the system (that is, the compositions of mixtures at the initial moment of time, the total amount of the substance in the working body) and a given constant value of the quantity

$$G_0 = \int_0^\tau g[\mu_0, \mu(t)] dt \quad (121)$$

the variation of the entropies of the reservoir and working body with time τ are completely determined and the minimal increase in the system entropy corresponds to the minimum of the entropy production:

$$\bar{\sigma} = \frac{1}{T} \int_0^\tau [\mu_0 - \mu(t)] g[\mu_0, \mu(t)] dt \rightarrow \min. \quad (122)$$

In this case, the function $\mu(t)$ should be chosen.

Let us find the quantitative relationship between the work A , which can be extracted (consumed) in this process, and the value of $\bar{\sigma}$. For simplicity, we assume that the mixture in the reservoir and working body consists of two components (a more general case can similarly be

considered by introducing an equivalent component). If the concentrations of the active component in the reservoir and working body are x_0 and $x(t)$, the concentrations of the second component will be equal to $1-x_0$ and $1-x(t)$, respectively. The variation of the substance amount G and the concentration $x(t)$ of the active component in the working body are determined by the differential equations:

$$\begin{aligned} \frac{d}{dt}(Gx) &= \frac{dG}{dt} = g(\mu_0, \mu), & G(0) &\rightarrow \text{fix}, \\ x(0) &\rightarrow \text{fix}. \end{aligned} \quad (123)$$

As the amount of the second component is maintained constant, we obtain

$$G(0)[1-x(0)] = [G(0) + G_0][1-x(\tau)]. \quad (124)$$

It follows from (123) and (124) that

$$\begin{aligned} \frac{dx}{dt} &= \frac{1}{G(0)[1-x(0)]} (1-x)^2 g(\mu_0, \mu), \\ x(0) &\rightarrow \text{fix}. \end{aligned} \quad (125)$$

The equations for the material, energy, and entropy balances around the system take the form:

$$G_0 x_0 = G(\tau)x(\tau) - G(0)x(0), \quad (126)$$

$$G_0 h_0 - [G(\tau)h(\tau) - G(0)h(0)] = A, \quad (127)$$

$$G_0 s_0 = [G(\tau)s(\tau) - G(0)s(0)] + \bar{\sigma} = 0, \quad (128)$$

where h_0 and h , s_0 and s are the molar enthalpies and entropies of the mixture in the working body and reservoir, respectively. They are related by the equation [15]:

$$s = \frac{1}{T} \left(h - \sum_{i=1}^2 \mu_i x_i \right), \quad (129)$$

$$s_0 = \frac{1}{T} \left(h_0 - \sum_{i=1}^2 \mu_{i0} x_{i0} \right). \quad (130)$$

The pressure in the working body can vary with time, provided that $P(0)=P(\tau)$. For the chemical potentials defined by Eq. (118), the equation of entropy balance (128) in view of (127), (129), and (130) can be rewritten as

$$\begin{aligned} A/T = & -\bar{\sigma} + R\{G_0[x_0 \ln x_0 + (1-x_0) \ln(1-x_0)] \\ & + G(0)[x(0) \ln x(0) + (1-x(0)) \ln(1-x(0))] \\ & - G(\tau)[x(\tau) \ln x(\tau) + (1-x(\tau)) \ln(1-x(\tau))]\}. \end{aligned} \quad (131)$$

The second term in the right-hand side of this equality can be calculated using G_0 , x_0 , $G(0)$, and $x(0)$. The latter ones are related through (124) and (126) to the values of $G(\tau)$ and $x(\tau)$. Let us denote the second term as $B[G_0, x_0, G(0), x(0)]$. It can be either positive or negative. It follows from equality (131) that

$$A_{\max} = T(B - \bar{\sigma}_{\min}). \quad (132)$$

The maximum of the produced (minimum of the spent) work corresponds to the minimum of entropy production in the mass transfer process.

The problem of finding the minimum of $\bar{\sigma}$ when constraint (121) is valid (or the equivalent problem for the maximum of G_0 at a given constant value of $\bar{\sigma}$) is an averaged nonlinear programming problem [22]. Unlike the problem for the constrained maximum of a function, its optimal solution can vary with time. This solution is a piecewise constant function that can take not more than two values. We will not calculate these values and the fraction of the whole process time during which $\mu^*(t)$ takes each of these values because in the most common case, where the Lagrangian function for the unaveraged problem

$$L = g[\mu_0, \mu(t)][\mu_0 - \mu(t) - \lambda]$$

is convex with respect to μ (second derivative of L with respect to μ is positive), the solution to the formulated problem is constant. Consequently, the constancy condition depends on the validity of the inequality:

$$\frac{\partial^2 g}{\partial \mu^2}(\mu_0 - \mu(t) - \lambda) - 2 \frac{\partial g}{\partial \mu} \geq 0. \quad (133)$$

The multiplier λ , which is equal to the derivative of the minimum value of $\bar{\sigma}$ with respect to G_0 , should be positive due to the physical nature of the problem. The second derivative of L with respect to μ for the mass transfer rate in the form of (120) is equal to $2\lambda\alpha$ and is known to be positive. In all cases where inequality (133) holds, the optimal value of the chemical potential of the active component for the working body is constant and determined by the equation:

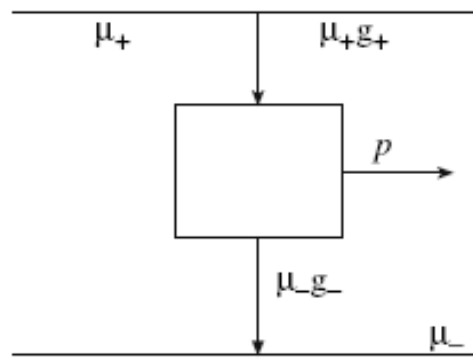


Figure 11. Schematic diagram of a diffusion engine with a constant contact between the working body and sources.

$$g(\mu_0, \mu^*) = \frac{G_0}{\tau}. \quad (134)$$

Consequently, the chemical potential of the active component of the working body for any rate satisfying (133) should be controlled so that the mass transfer rate should be constant.

The law of variation of the control variable, such as the working-body pressure, corresponding to this solution will not be constant in time because the mixture composition is varied during the process according to Eq. (125), in which the flux is determined by Eq. (134).

For mass transfer law (120), the minimal entropy produced is $\bar{\sigma}_{\min} = G_0^2 / \alpha \tau$. It follows from equality (132) that positive work can be extracted from the system under study only when $\tau > \tau_{\min} = G_0^2 / \alpha B$. It is easy to see that the process duration τ^* , for which the average extraction rate of work $A^*(\tau) / \tau$ is maximal, is twice larger than τ_{\min} .

In the case where the system contains a source of a finite capacity at constant temperature and pressure instead of the reservoir (source of an infinite capacity), the fraction of the active component varies according to an equation similar to (125). As a result, the chemical potential μ_0 is changed. However, here also, the minimum of the entropy production for mass transfer law (120) corresponds to such variation of $\mu(t)$ that the mass transfer rate is maintained constant.

Instead of the calendar time, the problem can be studied using the time of contact, when the working body moves and its parameters at every point of the loop remain constant. This can be used to determine the optimal laws of pressure variation for the zones of contact between the working body and source.

4.2.2. Diffusion-mechanical cycle for maximum power

Let us consider the direct cycle of work extraction in a system consisting of a working body and two reservoirs with different chemical potentials. In the first reservoir, the chemical potential of the key element is equal to μ_+ ; in the second, μ_- ; for definiteness, $\mu_+ > \mu_-$ (Fig. 11).

The process is cyclic: the increase in entropy, internal energy, and mass of the key component of the working body around the cycle is equal to zero. The temperatures are the same for all subsystems.

Alternating contact with reservoirs. Consider the case where the working body alternately contacts the first and second reservoirs and its parameters are cyclically varied with time. Let τ stand for the cycle duration and $\mu_0(t)$ stand for the source chemical potential, which can take the values of μ_+ and μ_- . The formulation of the problem dealing with the production of maximum work A in a given time τ takes the form:

$$A = \int_0^\tau \mu g(\mu_0, \mu) dt \rightarrow \max_{\mu_0, \mu} \quad (135)$$

with the constraints placed on the increment in the amount of the working-body:

$$\Delta G = \int_0^\tau g(\mu_0, \mu) dt = 0. \quad (136)$$

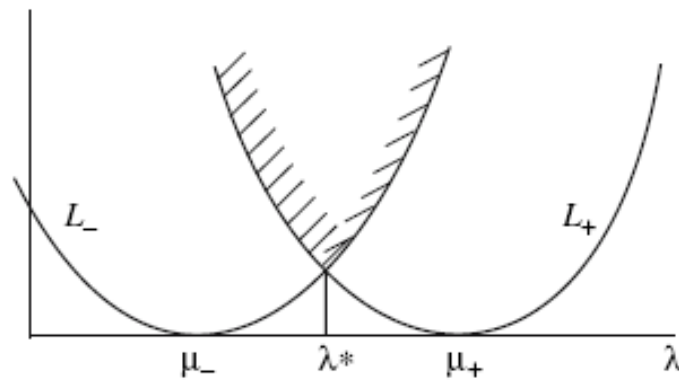


Figure 12. Dependence of the maximum of the Lagrangian function with respect to μ on λ .

To calculate the basic values of μ and μ_0 in the problem given by (135) and (136), we can write the Lagrangian function and find its maximum with respect to μ_0 and μ and its minimum with respect to λ :

$$L = \{g(\mu_0, \mu)(\mu - \lambda)\} \rightarrow \max_{\mu_0, \mu} \min_{\lambda}.$$

The number of basic values of μ_0 is equal to two: one of them corresponds to $\mu_0 = \mu_+$ and the other to $\mu_0 = \mu_-$. For the Lagrangian function L that is strictly convex with respect to μ , the basic values of μ satisfy the conditions:

$$\frac{\partial L}{\partial \mu} = \frac{\partial g}{\partial \mu}(\mu - \lambda) + g(\mu_0, \mu) = 0$$

or

$$\frac{g(\mu_0, \mu)}{(\mu - \lambda)} = - \frac{\partial g(\mu_0, \mu)}{\partial \mu}.$$

The roots for this equation for $\mu_0 = \mu_+$ and $\mu_0 = \mu_-$ will be denoted by μ_1 and μ_2 , respectively. As L is maximal at the basic points, we can write

$$L(\mu_+, \mu_1, \lambda) = L(\mu_-, \mu_2, \lambda), \quad (137)$$

which determines the value of λ .

Let us specify the obtained relations for

$$g(\mu_0, \mu) = \alpha(\mu_0)(\mu_0 - \mu).$$

It follows from (137) that

$$\mu_1 = \frac{\mu_+ + \lambda}{2}, \quad \mu_2 = \frac{\mu_- + \lambda}{2}. \quad (138)$$

Substituting μ_1 and μ_2 into the function L for each basic value gives its dependence on λ :

$$L_+ = L(\mu_+, \mu_1) = \frac{\alpha_+}{4}(\mu_+ \lambda^2,$$

$$L_- = L(\mu_-, \mu_2) = \frac{\alpha_-}{4}(\mu_- \lambda^2.$$

The maximum of L with respect to μ_0 and μ reaches its minimal value with respect to λ (Fig. 12) when

$$L_+(\lambda) = L_-(\lambda) \rightarrow \lambda^* = \frac{\sqrt{\alpha_+} \mu_+ + \sqrt{\alpha_-} \mu_-}{\sqrt{\alpha_+} + \sqrt{\alpha_-}}. \quad (139)$$

The fractions of time τ of contact with reservoirs are determined by Eq. (136) and can be written as

$$\gamma_+ = \frac{\alpha_- \sqrt{\alpha_+}}{\alpha_- \sqrt{\alpha_+} + \alpha_+ \sqrt{\alpha_-}},$$

$$\gamma_- = \frac{\alpha_+ \sqrt{\alpha_-}}{\alpha_- \sqrt{\alpha_+} + \alpha_+ \sqrt{\alpha_-}}.$$

The maximal work in time τ takes the form:

$$A^*(\tau) = \tau[\gamma_+ \mu_1 \alpha_+ (\mu_+ - \mu_1) + \gamma_- \mu_2 \alpha_- (\mu_2 - \mu_-)],$$

where μ_1 and μ_2 can be determined from (138) after the value of λ from (139) is substituted into this expression. The maximal power is equal to

$$\frac{A^*(\tau)}{\tau} = [\gamma_+ \mu_1 \alpha_+ (\mu_+ - \mu_1) + \gamma_- \mu_2 \alpha_- (\mu_2 - \mu_-)].$$

Constant contact with sources. In heat engines, there can be either alternate or constant contact between the working body and sources. In the latter case, the parameters of the working body are distributed and the process in it can be regarded close to reversible if the distribution of the parameters is caused by the conductive flux. Likewise, a constant contact with sources is possible in systems that are not homogeneous in concentration, such as separation systems and diffusion engines.

In this case, the maximal power takes the form of a nonlinear programming problem:

$$p = [g_1(\mu_+, \mu_1)\mu_1 - g_2(\mu_2, \mu_-)\mu_2] \rightarrow \max_{\mu_1, \mu_2}$$

with the constraint

$$g_1(\mu_+, \mu_1) - g_2(\mu_2, \mu_-) = 0. \quad (140)$$

The optimality constraint for this problem leads to the relation:

$$\mu_1 - \mu_2 = \frac{g_2(\mu_2, \mu_-)}{\partial g_2 / \partial \mu_2} - \frac{g_1(\mu_+, \mu_1)}{\partial g_1 / \partial \mu_1}, \quad (141)$$

which together with equality (140) determines the desired variables.

Let g_1 and g_2 are proportional to the difference between the chemical potentials:

$$g_1 = \alpha_1(\mu_+ - \mu_1), \quad g_2 = \alpha_2(\mu_2 - \mu_-).$$

Equality (141) can be written in the form:

$$\mu_1 - \mu_2 = \frac{\mu_+ - \mu_-}{2}. \quad (142)$$

The constraint $g_1 = g_2$ results in

$$\alpha_1 \mu_1 + \alpha_2 \mu_2 = \alpha_1 \mu_+ + \alpha_2 \mu_-. \quad (143)$$

The solution to Eqs. (142) and (143) can be written as

$$\mu_2^* = \frac{1}{2(\alpha_1 + \alpha_2)} [\mu_+ \alpha_1 + \mu_- (\alpha_1 + 2\alpha_2)],$$

$$\mu_1^* = \frac{1}{2(\alpha_1 + \alpha_2)} [\mu_+ (\alpha_2 + 2\alpha_1) + \mu_- \alpha_2].$$

The value of maximal power corresponding to this choice is

$$p_{\max} = \frac{\bar{\alpha}}{4} (\mu_+ - \mu_-)^2,$$

where the equivalent mass transfer coefficient is defined as

$$\bar{\alpha} = \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2}.$$

4.3. Limiting performance of diffusion systems for liquid mixtures

The result obtained above for the membrane systems consisting of a working body and a source of finite or infinite capacity using gaseous mixtures can be translated in the same form to liquid solutions with allowance for the different form of the chemical potential. Diffusion engines are most often designed for the treatment of saline water. Let us consider two flow-sheets of liquid diffusion engines.

4.3.1. Diffusion engine with a constant contact between the working body and the sources

Let the system consist of two liquids with the same temperature separated by a semipermeable membrane. One of the liquids is a pure solvent and the other is a solution in which some substance of concentration C is dissolved. The membrane is permeable only to the solvent. The equilibrium in the system is reached as soon as the chemical potentials calculated by formula (119) become equal to each other:

$$\nu_0 P_0 - \nu_r P_r = -RT \ln x_r.$$

Let the difference of pressure across the membrane be denoted as π . Also, we will keep in mind that the molar volumes ν_0 and ν_r for low concentrations are equal to each other. The mole fraction of the dissolved component will be denoted as x_1 . If its value is low, then $\ln x_r = \ln(1 - x_1) \approx -x_1$. In this case,

$$\pi = RT \frac{x_1}{\nu_0} = -RTC. \quad (144)$$

Equation (144) is called the Van't Hoff equation for osmotic pressure.

Consider the system shown in Fig. 13. The chamber to the left of the membrane contains a pure solvent at an environmental pressure equal to P_0 . The chamber of volume V to the right of the membrane contains a continuously replenished solution in which the concentration of the

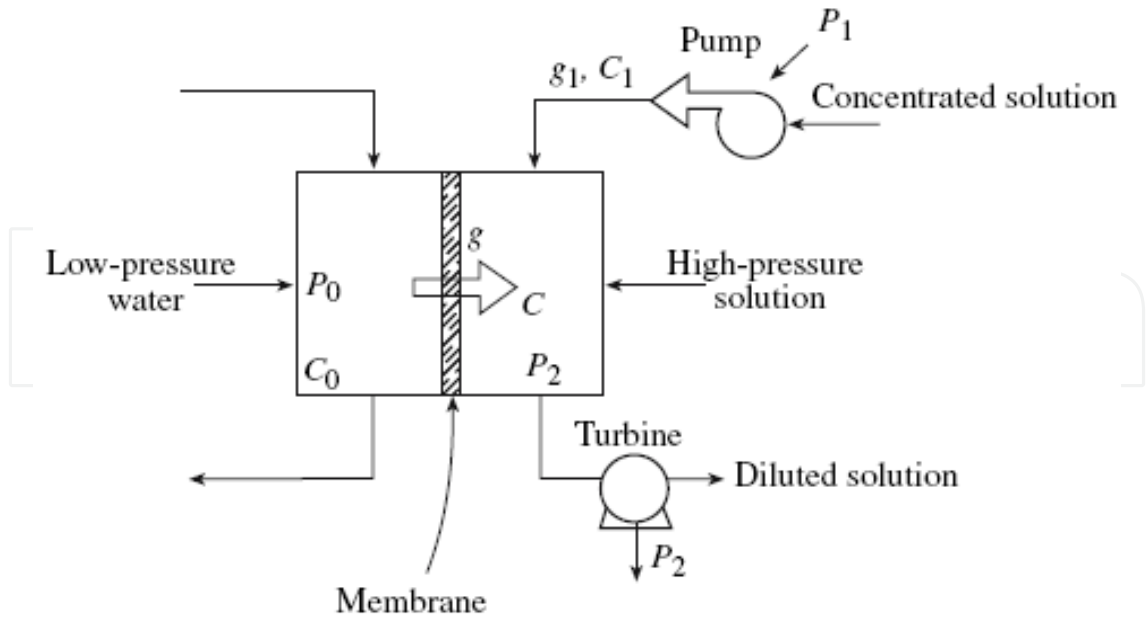


Figure 13. Schematic diagram of a diffusion engine with a constant contact between the working body and sources.

dissolved component is C . The pressure in the right chamber is P_2 and the solution is assumed to be ideal. When an equilibrium is reached in the right chamber (that is, the flux through it is equal to zero), the pressure established in it will exceed P_0 by the value of osmotic pressure π . The osmotic pressure value is related to the concentration and temperature in the chamber by the Van't Hoff equation. When the solution in the chamber is replenished, the pressure $P_2 < P_0 + \pi$, giving rise to a solvent flux g across the semipermeable membrane. Conventionally, the diffusion flux is taken to be equal to the difference between the actual and equilibrium pressures:

$$g = \alpha(P_0 + \pi - P_2) = \alpha(\pi - \Delta P), \quad (145)$$

where $\Delta P = P_2 - P_0$

Let p_1 stand for the power of the pump supplying the concentrated solution, g_1 stand for the flow rate of this solution, and C_1 stand for the solution concentration. Assuming that the pump efficiency is 100%, we obtain

$$p_1 = \Delta P g_1.$$

The additional flux across the membrane increases the volume of the solution, which drives a turbine and generates power p_2 :

$$p_2 = (g_1 + g)\Delta P.$$

Consequently, the power r and efficiency η of the saline diffusion engine can be written as

$$p = p_2 - p_1 = g\Delta P = \alpha(\pi - \Delta P)\Delta P,$$

$$\eta = \frac{P}{g_1} = \frac{\alpha(\pi - \Delta P)\Delta P}{g_1}.$$

where the diffusion engine efficiency is the work extracted from 1 m³ of the concentrated solution. From here on, according to the accepted system of units, the units of power and efficiency referred to a unit membrane surface area are J/(m² s) and J/m³, respectively. If the relationship between π and ΔP is ignored, the power reaches a maximum when $\Delta P = \pi / 2$ and its upper limit is written as

$$\bar{p} = \alpha\pi^2 / 4 = \alpha / 4(CRT)^2.$$

As $C < C_1$, the value of the power is always less than

$$\bar{p}^* = \alpha / 4(C_1RT)^2. \quad (146)$$

which is the upper bound for the maximal power.

The estimate produced by Eq. (146) can be refined if we take into consideration that g , ΔP , and C are related to each other by Eq. (145) and the equation of material balance on the dissolved component

$$(g_1 + g)C = g_1C_1. \quad (147)$$

Expressing C and ΔP in terms of g from Eqs. (145) and (147) and substituting them into p and η , we obtain

$$C = \frac{g_1C_1}{g_1 + g}, \quad \Delta P = CRT - \frac{g}{\alpha}, \quad (148)$$

$$p = g\Delta P = \frac{RTC_1g_1g}{g_1 + g} - \frac{g^2}{\alpha}, \quad (149)$$

$$\eta = \frac{\alpha(\pi - \Delta P)\Delta P}{g_1} = \frac{RTC_1g}{g_1 + g} - \frac{g^2}{\alpha g_1}. \quad (150)$$

The points of maximum with respect to g for two concave functions (149) and (150) coincide. Consequently, to find the optimal value of g^* , we will use one of the functions, specifically the expression for p . The condition for the maximum with respect to g leads to the inequality:

$$g(g_1 + g)^2 = \frac{\alpha RT g_1^2 C_1}{2}. \quad (151)$$

Equation (151) can be rewritten as

$$\frac{g^3}{g_1^2} + 2 \frac{g^2}{g_1} + g = \frac{\alpha RT C_1}{2} \quad (152)$$

and its right-hand side can be denoted for brevity as M . Its solution will be denoted as g^* . It is obvious that it satisfies the inequality:

$$0 < g < M.$$

Numerical solution of Eq. (152) makes it possible to refine the value of the limiting power of the diffusion engine and find the corresponding operating conditions. Equation (151) determines g^* for the chosen values of g_1 and C_1 ; Eq. (148), for C^* and ΔP^* .

It should be noted that the ideal solution bounds the value of the concentration of the working solution:

$$C = C_1 \frac{g_1}{g_1 + g}.$$

The concentration should not be very high: otherwise, the molecules of the dissolved component will interact with each other and relation (144) is upset.

Diffusion Engine with an Alternate Contact between the Working Body and Sources. In the schematic diagram of the diffusion engine discussed in the preceding section, the working body was an open system working in constant contact with two sources under steady-state conditions. One of them supplied a concentrated solution and the other supplied a solvent.

Figure 14 shows the schematic diagram for a diffusion engine in which the working body alternately contacts each of the sources, receiving a solvent through one membrane and giving it up to a concentrated solution through another membrane. In this case, the pressure and flow rate of the working body are periodically varied: pressure increases for a lower flow rate (power p_1 is consumed) and decreases for a higher flow rate (power p_2 is generated).

We will write the balance equations for this diagram and study its limiting performance, ignoring the energy losses for driving the flow of the concentrated solution through the bottom chamber and assuming that the concentration of the dissolved component in the g_2 flow is equal to unity and that the pressure of the surrounding medium is equal to P_0 . For simplicity, flow rates will be used instead of mole fluxes

The engine power is

$$p = p_2 - p_1 = (g_1 + g)\Delta P_{21} - g_1\Delta P_{21} = g\Delta P_{21},$$

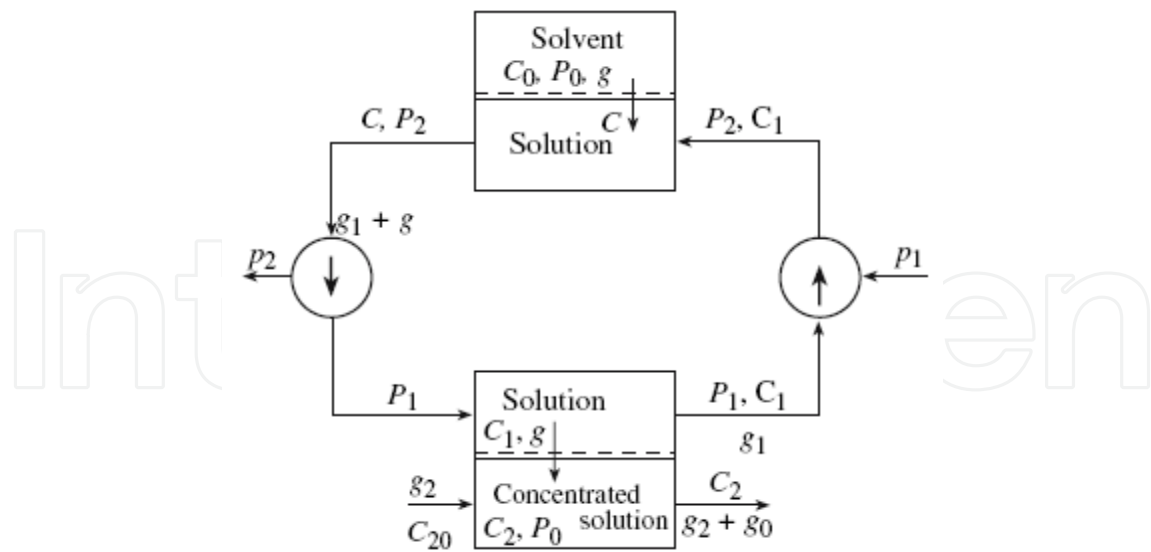


Figure 14. Schematic diagram of a diffusion engine with an alternate contact between the working body and sources.

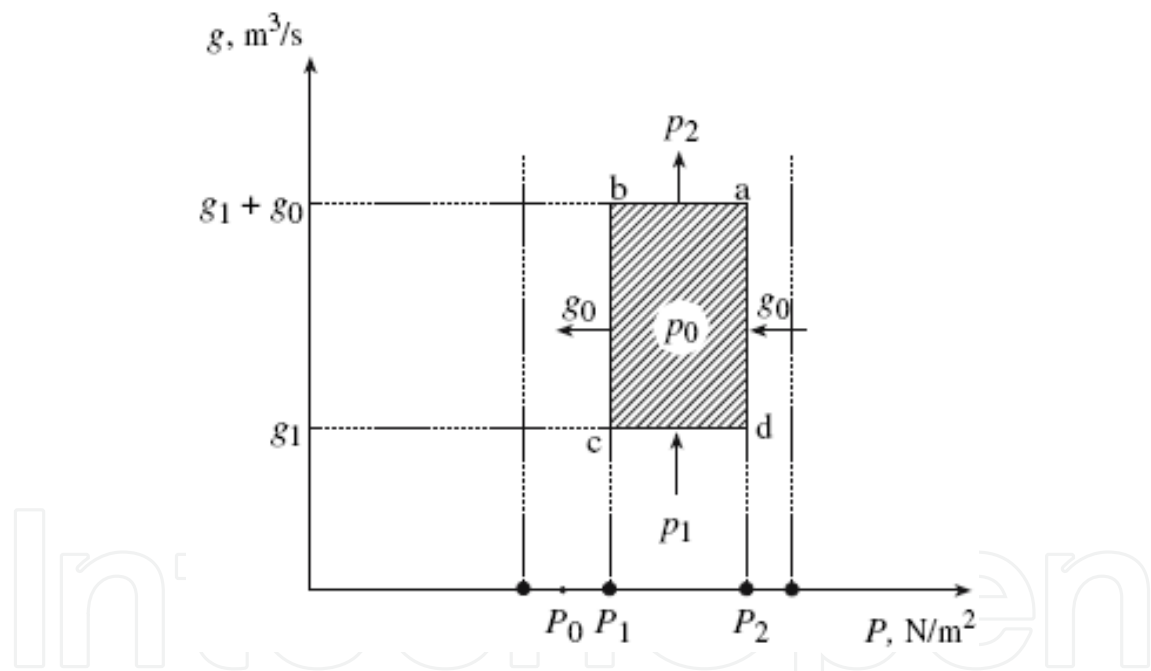


Figure 15. Variation cycle for the parameters of the working body in a diffusion engine.

where

The efficiency will be defined as the ratio of power p to the flow rate g_2 of the dissolved component:

$$h = \frac{p}{g_2} = \frac{g}{g_2} \Delta P_{21}.$$

The rate of mass transfer is determined by the relations:

$$\begin{aligned}
g &= \alpha_1(P_0 + \pi - P_2) = \alpha_1(\pi - \Delta P_{20}) \\
&= \alpha_2[(P_1 + \pi_2) - (P_0 + \pi_1)] = \alpha_2(\Delta\pi_{21} + \Delta P_{10}),
\end{aligned} \tag{153}$$

where $\Delta P_{20} = P_2 - P_0$, $\Delta\pi_{21} = \pi_2 - \pi_1$, $\Delta P_{10} = P_1 - P_0$. Equation (153) corresponds to the condition that the mass of the working body averaged over the cycle is constant.

Figure 15 demonstrates the cycle of the working body of this diffusion engine. The power p_1 is equal to the area of the rectangular P_2dcP_1 , and the power p_2 to the area of P_2abP_1 . The engine power p is equal to the area of the hatched rectangular $abcd$.

The power of the diffusion engine will be determined when the relationship between the osmotic pressures in the chambers and the flow rates is ignored. To do it, we will solve the problem of constrained optimization:

$$p = (P_2 - P_1)g \rightarrow \max_{P_1, P_2}$$

with the constraints:

$$\alpha_1(P_0 + \pi - P_2) = \alpha_2(P_1 - P_0 + \pi_2 - \pi_1) = g. \tag{154}$$

It follows from Eq. (154) that

$$P_1 = \frac{g}{\alpha_2} + P_0 + \pi_1 - \pi_2, \quad P_2 = P_0 + \pi - \frac{g}{\alpha_1}.$$

Let us introduce the equivalent permeability:

$$\bar{\alpha} = \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2}$$

and write the equation:

$$P_2 - P_1 = \pi - \pi_1 + \pi_2 - \frac{g}{\alpha}.$$

Then

$$p = g(\pi - \pi_1 + \pi_2 - \frac{g}{\alpha}) = g(\pi + \Delta\pi_{21} - \frac{g}{\alpha}) \rightarrow \max_g. \tag{155}$$

The maximum of this expression, which is equal to

$$p^* = \frac{\bar{\alpha}(\pi - \pi_1 + \pi_2)^2}{4} = \frac{\alpha(\pi + \Delta\pi_{21})^2}{4},$$

is reached at

$$g^* = \frac{\bar{\alpha}(\pi - \pi_1 + \pi_2)}{2} = \frac{\alpha(\pi + \Delta\pi_{21})}{2}.$$

Keeping in mind that the osmotic pressures in the chambers are related to the concentrations by Van't Hoff equation (144) and the concentrations are related to the flow rates g_1 , g_2 , and g , we obtain

$$\pi = CRT = C_1 \frac{g_1 RT}{g_1 + g},$$

$$\Delta\pi_{21} = (C_2 - C_1)RT = \left(\frac{g_2 C_{20} + g C_1}{g_2 + g} - C_1 \right) RT.$$

In view of these relations, expression (155) for the engine power takes the form:

$$p = g \left[RT \left(\frac{C_1 g_1}{g_1 + g} + \frac{g_2 C_{20} + g C_1}{g_2 + g} - C_1 \right) - \frac{g}{\alpha} \right]$$

$$= g \left[RT \left(\frac{g_2 C_{20} + g C_1}{g_2 + g} - \frac{C_1 g}{g_1 + g} \right) - \frac{g}{\alpha} \right] \rightarrow \max_g. \quad (156)$$

The expression for the efficiency is written as

$$\eta = \frac{g}{g_2} \left[RT \left(\frac{g_2 C_{20} + g C_1}{g_2 + g} - \frac{C_1 g}{g_1 + g} \right) - \frac{g}{\alpha} \right] \rightarrow \max_g. \quad (157)$$

The points of maximum with respect to g for the criteria (156) and (157) coincide. Therefore, we can use either of them in the conditions of optimality to find g^* . The stationarity condition of p with respect to g leads to an equation for the optimal flow rate:

$$g = \frac{\bar{\alpha}RT}{2} \left[\left(\frac{g_2^2 C_{20} + 2gg_2 C_1 + g^2 C_1}{(g_2 + g)^2} \right) - C_1 \frac{g(g + 2g_1)}{(g_1 + g)^2} \right]. \quad (158)$$

The solution to Eq. (158) will be g^* : it is the optimal value of flow rate g at which the efficiency η and power p take their maximal values. The values of flow rate g^* depends on the values of g_1 , g_2 , and C_1 . Its substitution into the equations for p and η determines the maximal power $p^*(g_1, g_2, C_1)$ and efficiency $\eta^*(g_1, g_2, C_1)$. The nonnegative nature of p^* and η^* imposes

constraints on the possible values of g_1 , g_2 , and C_1 . For example, increasing g_1 and g_2 or decreasing C_1 causes an increase in p^* .

4.4. Conclusion

The estimates obtained in the present paper for the limiting performance of diffusion engines can be used to make their reversible-thermodynamics analysis more accurate and consider the influence of the kinetic factors (mass transfer relations, membrane permeabilities) and production flow rate. These estimates can also be used for the optimization of more complex membrane systems. The capacity of membrane systems increases in proportion to the membrane permeability. In this case, the performance of membranes is decreased by the nonuniformity of concentrations in the solution, polarization phenomena, and the other factors ignored in obtaining the above estimates.

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