Finite-Time Thermodynamics: Limiting Possibilities of Irreversible Separation Processes[†]

Anatoliy M. Tsirlin,[‡,#] Vladimir Kazakov,[*,§] and Dmitrii V. Zubov[‡]

Program System Institute, Russian Academy of Science, set.“Botic”, Perejaslavl-Zalesky 152020, Russia, and School of Finance and Economics, Faculty of Business, University of Technology, Sydney, PO Box 123, Broadway, NSW 2007, Australia

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In this paper, new thermodynamic limits on the performance of irreversible separation processes are derived, including work of separation in finite time (a generalization of Van't Hoff reversible work of separation for finite rate processes), maximal productivity of heat-driven separation process (an analogue of Novikov−Curzon−Ahlborn maximal power of a heat engine), and the minimal possible dissipation in an irreversible distillation column, the ideal operating line, for which this dissipation level is achieved, the profile of heat supply/removal that realizes the ideal operating line, and the distillation column’s maximal productivity.

1. Introduction

Separation processes are among the most energy-consuming and least energy-efficient technological processes. Various types of separation are widely used in industry, including membrane separation, absorption−desorption cycles, distillation, centrifugation, evaporation, etc. Their importance as baseline processes explain the everlasting interest in the study of their efficiency and especially in finding in-principle performance limits imposed on separation by thermodynamics. Classical thermodynamics provide reversible estimates of these limits. However, these reversible estimates are significantly understated and do not take into account kinetics of separation, so their usefulness is limited.

Exergy analysis is often used to determine the thermodynamic quality of separation processes.[1−3] Still, the exergy loss itself does not characterize the degree of thermodynamic perfection to this process. In finite-time thermodynamics (FTT), it is shown that if the productivity of the system is given and heat and mass transfer coefficients are finite then some minimal possible unavoidable dissipative losses (entropy production) in the system exist. Therefore, the natural way to evaluate the degree of thermodynamic perfection of a process with a given productivity is by comparing the actual dissipative losses with this minimal possible dissipation. In this paper, the minimal possible entropy production, $\sigma_{\min}$, and its dependence on heat and mass transfer coefficients is found for a number of irreversible gas and liquid separation processes. Thermodynamic balances are then used to obtain the minimal possible energy/work of separation.

First, gas separation is considered. The lower bound on the power of gas separation with given productivity and fixed compositions of the input and output fluxes is derived.

Second, a general heat-driven separation process (we shall call it thermal separation) is considered. It is shown that the productivity (rate) of thermal separation is limited. That is, if the heat flux supplied to the system is higher than some given value, then as the flux becomes higher, the productivity of thermal separation becomes lower.

Third, an irreversible binary distillation column is considered. A new estimate on minimal possible entropy production and the ideal operating line, at which this minimal possible entropy production is achieved, are derived. A stronger bound than the one for a general thermal separation is obtained for the maximal productivity of binary distillation.

2. Thermodynamic Balances of Separation Processes

Consider the system shown in Figure 1. Here, the flux of mixture with the rate g_0, composition x_0, temperature T_0, and pressure P_0 is separated in two fluxes with parameters g_i, x_i, T_i, and P_i ($i = 1, 2$). The flow of heat q_+ with the temperature T_+ is supplied to the system, and the flow of heat q_- with temperature T_- is removed from it. The mechanical work with the power p is also supplied to the system.

In a stationary regime, the thermodynamic balance equations for such a system have the following form:

The Mass Balance

$$g_0x_{0j} - g_1x_{1j} - g_2x_{2j} = 0, \quad j = 1, ..., k \tag{1}$$

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

The Energy Balance

$$p + q_+ - q_- + g_0h_0 - g_1h_1 - g_2h_2 = 0 \tag{3}$$

where h_i is the molar enthalpy of the ith flux, and

The Entropy Balance

$$\frac{q_+}{T_+} - \frac{q_-}{T_-} + g_0s_0 - g_1s_1 - g_2s_2 + \sigma = 0 \tag{4}$$

Here, s_i is the molar entropy of the ith flux.

From eqs 1 and 2, it follows that $g_0 = g_1 + g_2$. After elimination of g_0 from eqs 3 and 4 and introduction of enthalpy

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[*] To whom correspondence should be addressed. E-mail: kaz@arch.usyd.edu.au.

[‡] Russian Academy of Science.

[#] E-mail: tsirlin@sarc.botik.ru.

[§] University of Technology, Sydney.

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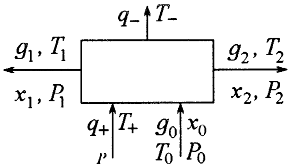

Figure 1. Computational schema of a separation process.

and entropy increments Δs and Δh, we get

$$p + q_+ - q_- + g_1\Delta h_{01} + g_2\Delta h_{02} = 0 \tag{5}$$

$$g_2\Delta s_{02} + g_1\Delta s_{01} + \frac{q_+}{T_+} - \frac{q_-}{T_-} + \sigma = 0 \tag{6}$$

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

After elimination of q_- from eq 5 and substitution of the obtained expression in eq 6, we get

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

Therefore, the flux of heat used in thermal separation ($p = 0$) is

$$q_+ = \frac{T_+}{T_+ - T_-}\left[\sum_{i=1}^{2} g_i(\Delta s_{0i}T_- - \Delta h_{0i}) + \sigma T_-\right] \tag{7}$$

Similarly, for mechanical separation ($q_+ = q_- = 0$),

$$p = \sum_{i=1}^{2} g_i(\Delta s_{0i}T_- - \Delta h_{0i}) + \sigma T_- \tag{8}$$

The first term in the right-hand side of this equality depends only on the parameters of the input and output fluxes. It represents the reversible work of separation per unit of time, p^0 (reversible power of separation). The second term describes the kinetics of the process and dissipation caused by it.

For mixtures that are close to ideal gases and ideal solutions, the molar enthalpies and entropies, h_i and s_i in eqs 3 and 4, can be written in the following form

$$h_i(T_i,P_i,x_i) = \sum_{j=1}^{k} x_{ij}h_j(T_i,P_i) \tag{9}$$

$$s_i(T_i,P_i,x_i) = \sum_{j=1}^{k} x_{ij}[s_j^0(T_i,P_i) - R\ln x_{ij}], \quad i = 0, 1, 2 \tag{10}$$

Here, R is the universal gas constant. In this case, the reversible estimate of heat used in separation is

$$q_+^0 = \frac{1}{\eta_{\mathrm{Carnot}}}\sum_{i=1}^{2} g_i \sum_{j=1}^{k}\{[x_{0j}s_j^0(T_0,P_0) - x_{ij}s_j^0(T_i,P_i) - R(x_{0j}\ln x_{0j} - x_{ij}\ln x_{ij})]T_- + x_{ij}h_j(T_i,P_i) - x_{0j}h_j(T_0,P_0)\} \tag{11}$$

η_{Carnot} is the Carnot efficiency of the ideal cycle of a heat engine

$$\eta_{\mathrm{Carnot}} = \frac{T_+ - T_-}{T_+}$$

The condition in eq 7 can be rewritten as

$$q_+ = q_+^0 + \frac{1}{\eta_{\mathrm{Carnot}}}\sigma T_- \tag{12}$$

If minimal entropy productions for thermal, $\sigma_{\mathrm{min}}^{\mathrm{T}}$, and mechanical, $\sigma_{\mathrm{min}}^{\mathrm{M}}$, separations are found, then the inequalities

$$q_+ \geq q_+^0 + \frac{1}{\eta_{\mathrm{Carnot}}}\sigma_{\mathrm{min}}^{\mathrm{T}}T_-$$
$$p \geq p^0 + \sigma_{\mathrm{min}}^{\mathrm{M}}T_- \tag{13}$$

determine irreversible estimates of minimal energy consumption for each type of separation.

3. Mechanical Processes of Gas Separation

Consider a separation system that uses the work with power p and has no heat supplied or removed ($q^+ = q^- = 0$). Assume that the input and output fluxes have the same temperature ($T_+ = T_- = T$) and pressure. After taking into account eq 10 and the fact that for mechanical separation enthalpy increments Δh_{0i} are equal to zero, the equality in eq 8 can be rewritten as

$$p = g_0RT\left[\sum_{i=1}^{2}\epsilon_i\sum_{j=1}^{k}x_{ij}\ln x_{ij} - \sum_{j=1}^{k}x_{0j}\ln x_{0j}\right] + T\sigma = p^0 + T\sigma \tag{14}$$

The first term in this expression represents the power used for separation in a reversible process ($\sigma = 0$). This power, p^0, is equal to the difference between the reversible power used for complete separation of the input flux and combined reversible power of separation of output fluxes. Here

$$a_i^0(x_i) = -RT\sum_{j=1}^{k}x_{ij}\ln x_{ij}, \quad i = 0, 1, 2 \tag{15}$$

is the reversible work of separation of 1 mol of ith flux on pure components, and $\epsilon_i = g_i/g_0$ is the mass fraction removed by the ith flux. For each of the components, we have

$$\epsilon x_{1j} + (1 - \epsilon)x_{2j} = x_{0j}$$

Irreversible Estimates of Minimal Work of Separation for a Gas Mixture. *Problem Formulation.* Consider N moles of a mixture that is close to ideal gas and contains k components with concentrations x_j ($j = 1, ..., k$). Its separation into pure substances requires that not less mechanical work is used than the reversible work

$$A^0 = -NRT\sum_{j=1}^{k}x_j\ln x_j \tag{16}$$

One of the “methods” of separation of a mixture using mechanical work, A^0, is by using ideal semipermeable membranes.[4] The schematic structure of such a system is shown in Figure 2. The central chamber contains the mixture of two gases. Two semipermeable pistons move toward each other. The left piston is permeable for the first gas only and the right one for the second gas only. When the two pistons touch and the pressures in the left and right chambers become equal, the mixture will be separated. If the movements of the pistons are infinitely slow and the fluxes g_1 and g_2 are infinitely small, then

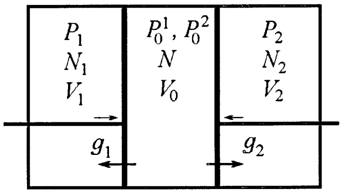

Figure 2. The separation system with two semipermeable membranes.

the work spent is equal to the reversible work of separation

$$A^0 = -NRT[x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)] \qquad (17)$$

Here, the temperature T remains constant and mass transfer coefficients of the membranes do not affect the results. In a more general case, the input mixture with concentrations x_i^0 is separated into two output mixtures with concentrations x_i^1 and x_i^2, correspondingly. That is, there is no complete separation here. In this case, the reversible estimate of the work of separation is equal to the difference between the reversible work of separation of the input mixture and the combined reversible work of separation of each of the output substances with the number of moles N_1 and $1 - N_1$ on pure substances:

$$A^0 = NRT\left[\frac{N_1}{N}\sum_{j=1}^{k} x_j^1 \ln x_j^1 + \left(1 - \frac{N_1}{N}\right)\sum_{j=1}^{k} x_j^2 \ln x_j^2 - \sum_{j=1}^{k} x_j^0 \ln x_j^0\right] \qquad (18)$$

The reversible estimates, eqs 17 and 18, are significantly understated; the actual work of separation can be much higher. That is why it is important to make these estimates more realistic by taking into account the duration of separation and fixed rates of the fluxes in the system.

These estimates are derived by choosing a distribution of mass transfer fluxes over time or along the length of the system, where the work of separation is minimal. But in the majority of separation systems, the possibilities to control distribution of fluxes (profile of concentrations) in the system are very limited. As a rule, only boundary conditions and rates of fluxes are controllable. The Van't Hoff schema with two semipermeable membranes provide more controllable separation. This makes it an important vehicle for derivation of the work of separation in finite time.

The Minimal Work of Separation of a Binary Mixture in Finite Time. Consider the system that includes two ideal semipermeable membranes, Figure 2. The left membrane is permeable for the first component of the initial mixture and the right one for the second component. The fluxes through the membranes, g_i, depend on the partial pressures of the corresponding component on both sides of the membrane:

$$g_1 = g_1(P_0^1, P_1), \quad g_2 = g_2(P_0^2, P_2)$$

The partial pressures are determined by the amount of moles in the central (N), left (N_1), and right ($N_2 = N(0) - N_1$) chambers. The volumes of these chambers are V, V_1, and V_2.

During separation over the time interval τ in addition to the reversible work of separation, the addition energy, ΔA, has to be used. To find a lower estimate of the work of separation, ΔA has to be minimized:

$$\Delta A = \int_0^\tau [g_1(P_0^1, P_1)\Delta\mu_1(P_0^1, P_1) + g_2(P_0^2, P_2)\Delta\mu_2(P_0^2, P_2)\,dt] \rightarrow \min \qquad (19)$$

Here, $\Delta\mu_1$ and $\Delta\mu_2$ are the increments of chemical potentials of the first and second component in the central and side chambers. The problem of minimization of the work of separation on pure components is reduced to the problem of minimization of ΔA subject to constraints that the average rates through membranes are fixed, that is,

$$\int_0^\tau g_1(P_0^1, P_1)\,dt = N_0 x_1(0), \quad \int_0^\tau g_2(P_0^2, P_2)\,dt = N_0 x_2(0) \qquad (20)$$

It is also necessary to include the conditions

$$V_0(t) + V_1(t) + V_2(t) = 1 \qquad (21)$$

$$N(t)x_i(t) + N_i(t) = N_0 x_i(0) \qquad (22)$$

which must hold for each $t \in [0, \tau]$, and

$$P_0^i(t) = \frac{RT}{V_0(t)}N(t)x_i(t), \quad P_i(t) = \frac{RT}{V_i(t)}N_i(t) \qquad (23)$$

$$\frac{dN_i}{dt} = g_i(P_0^i, P_i), \quad N_i(0) = 0, \quad N_i(\tau) = N_0 x_i(0), \quad i = 1, 2 \qquad (24)$$

into the problem in eqs 19 and 20.

In the general case, the problem of eqs 19−24 turns out to be a rather complex optimal control problem. The nonnegative control variables here are $V_1(t)$ and $V_2(t)$, of which the sum must not exceed one (their combined volumes do not exceed the total volume of the system). The important feature of this problem is that the criterion of optimality (eq 19) does not depend on the state variables $N_i(t)$. Another feature is that g_i and $\Delta\mu_i$ depend on the same variables P_0^i and P_i. This allows us to simplify the problem by expressing one of these functions in terms of another.

Conditions of Optimality and Solutions. Consider the case with one-to-one dependence between the increments of chemical potentials and the fluxes, $\Delta\mu_i = \varphi(g_i)$ ($i \in \{1, 2\}$). The irreversible energy losses here take the form

$$\Delta A = \int_0^\tau [g_1\varphi_1(g_1) + g_2\varphi_2(g_2)]\,dt \rightarrow \min \qquad (25)$$

This criterion can be minimized with respect to $g_1 \geq 0$ and $g_2 \geq 0$ and subject to conditions of eq 20 only. The obtained solution gives a lower estimate for ΔA. The substitution of the solution of the problem of eqs 19 and 20, $g_1^*(t)$ and $g_2^*(t)$ into eqs 22 and 24 allows us to check the feasibility of this regime by the constraints of eq 21 and the constraints on $V_1(t)$ and $V_2(t)$.

Note that the problem of eqs 19 and 20 can be decomposed in two subproblems of the following form

$$\int_0^\tau g_i\varphi_i(g_i)\,dt \rightarrow \min_{g_i} \quad \int_0^\tau g_i\,dt = \hat{N}_i \quad i \in \{1, 2\} \qquad (26)$$

where $\hat{N}_1 = N(0)x_1(0)$ and $\hat{N}_2 = N(0)(1 - x_1(0))$. These problems are called the averaged problems of nonlinear programming (NP).[5] Their optimal solutions, $g_i^*(t)$, are the piece-wise constant functions of time, which take not more than two values.

For the optimal rate g_i to be unique, it is sufficient that the Lagrange function

$$L_i = g_i\varphi_i(g_i) - \lambda_i g_i$$

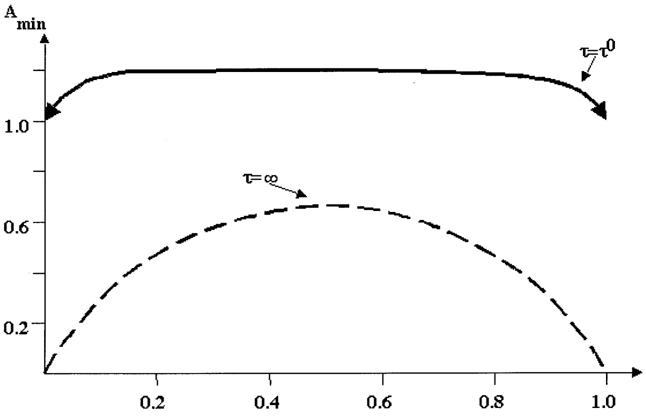

Figure 3. The dependence of the minimal irreversible work of separation on the concentration of the key component in the initial mixture.

is strictly concave. If this function is differentiable, then the condition that the optimal flux is constant takes the form

$$\frac{d^2L_i}{dg_i^2} = 2\frac{d\varphi_i}{dg_i} + \frac{d^2\varphi_i}{dg_i^2}g_i > 0 \qquad (27)$$

Note that because the first term in eq 27 is positive, it is sufficient that the second term is nonnegative for the optimal flux to be constant. Let us consider solution of this problem for some particular cases.

Assume that the process is close to equilibrium and the fluxes are proportional to the difference of chemical potentials on both sides of the membrane ($g_i = \alpha_i\Delta\mu_i$, $i = 1, 2$). The coefficients α_i depend on the permeability of membranes and the temperature. Then

$$\Delta\mu_i = \frac{g_i}{\alpha_i}, \quad i = 1, 2 \qquad (28)$$

Let us break the conditions of eqs 21 and 24 and minimize ΔA subject only to the conditions of eq 20, which follow from eq 24. The problem of eqs 19 and 20 is a nonlinear programming problem. Its optimal rates g_1^* and g_2^* are

$$g_i^* = N\frac{x_i}{\tau}$$

and the minimal work of separation is[6]

$$A_{min} = A^0 + \Delta A_{min} = A^0 + \frac{N^2}{\tau}\left[\frac{x_1^{\,2}}{\alpha_1} + \frac{x_2^{\,2}}{\alpha_2}\right] \qquad (29)$$

where A^0 corresponds to the expression in eq 16 and x_i is the initial concentration of the ith component in initial mixture. The minimal entropy production is

$$\sigma_{min}^{M} = \frac{\Delta A_{min}}{\tau T} = \left(\frac{N}{\tau}\right)^2\frac{1}{T}\left[\frac{x_1^{\,2}}{\alpha_1} + \frac{(1-x_1)^2}{\alpha_2}\right] \qquad (30)$$

Characteristic dependence of the minimal irreversible work of separation on the concentration of one of the components in the initial mixture is shown in Figure 3. At $x_1(0) = 0$ and $x_1(0) = 1$, the irreversible estimate of the work of separation has a discontinuity. This explains why the work of separation of poor mixtures (in which the concentration of one of the components is low) is much higher than the reversible estimate. For example, the actual work required to separate uranium isotopes exceeds the reversible estimate by the order of 10^5.[7] The condition of eq 27 holds for the majority of real dependencies $\phi_i(g_i)$. Therefore, the optimal fluxes through membranes are constant.

Incomplete Separation. Assume that the initial concentration of the key component is x in all chambers and its final concentration in the side chambers is x_1 and x_2. For definiteness, we assume that $x_1 > x > x_2$. Assume that initially there are N_{10} and N_{20} moles of input mixture with the concentration of key components x in left and right chambers. In the end, in the left chamber there are $N_{10}(1 - x)$ moles of the second component and $N_{20}x$ moles of the first component. The total amount of moles of mixture that is separated here is

$$N = N^0 + N_1 + N_2 \qquad (31)$$

From the balances, it follows that the ratio of N^0 moles of mixture in the central chamber to the total amount of mixture that is separated is

$$b(x,x_1,x_2) = \frac{N^0}{N} = \frac{(x - x_2)(x_1 - x)}{x(1 - x)(x_1 - x_2)} \qquad (32)$$

Here, x_1 and x_2 are the final concentrations of the key components in the left and right chamber. For the linear law of mass transfer,

$$g_1^* = \frac{N^0x_1}{\tau}, \quad g_2^* = \frac{N^0(1 - x_1)}{\tau}$$

Thus, the minimal work of separation for binary mixture of N moles of gas with the initial composition x into mixtures with compositions x_1 and x_2 in finite time τ is equal to the sum of the reversible work of incomplete separation, A_n^0, and the minimal additional work caused by irreversibility in the system. The latter is determined by the expression in eq 29 (in which it is taken into account that in incomplete separation the volume of the mixture that is separated is N and not N^0).

$$A^* = A_n^0 + \Delta A_{min}\left(\frac{N^0}{N}\right)^2 = A_n^0 + \Delta A_{min}b^2(x,x_1,x_2) \qquad (33)$$

If we denote the reversible work of separation of 1 mol of mixture with concentration x into pure components as

$$a^0(x) = -RT(x \ln x + (1 - x) \ln(1 - x))$$

then the expression in eq 18 for the reversible work of incomplete separation of binary mixture can be rewritten as

$$A^0 = N\left[a_n^0(x) - \frac{x - x_2}{x_1 - x_2}a_n^0(x_1) - \frac{x_1 - x}{x_1 - x_2}a_n^0(x_2)\right] = Na_n^0(x)$$

Here $a_n^0(x)$ is the reversible work of incomplete separation of 1 mol of mixture with composition x into streams with compositions x_1 and x_2.

Power Estimate. The minimal power, p, that has to be spent for separation of a binary mixture is

$$p = \frac{A^*}{\tau} = ga_n^0(x) + g^2d(x)b^2(x,x_1,x_2) \qquad (34)$$

where $g = N/\tau$ is the rate of input mixture and x, x_1, and x_2 are the concentrations of the key component in the input and output fluxes,

$$d(x) = \frac{x^2}{\alpha_1} + \frac{(1-x)^2}{\alpha_2}$$

$b(x,x_1,x_2)$ is determined by the equality of eq 32. It describes the completeness of separation; $b = 1$ corresponds to the complete separation (on the pure components), and $b = 0$ corresponds to no separation at all. The dependence of the minimal power used in the separation of a binary gas mixture on its composition and rate g for fixed mass transfer coefficients and the degree of separation is shown in Figure 4. It is assumed here that there the following relation exists between the degree of separation b and compositions of output fluxes

$$x_1 = x + b(1-x), \quad x_2 = x(1-b)$$

From eq 30, it follows that the minimal entropy production in gas separation driven by mechanical work depends on the rate of mixture and compositions of input and output fluxes as

$$\sigma^{\mathrm{M}}_{\min} = \frac{1}{T}(gb(x,x_1,x_2))^2 d(x,\alpha_1,\alpha_2) \tag{35}$$

Note that if the initial temperatures of the mixture and output products are the same and the components are close to ideal gases then these estimate are also valid for a separation process in which temperature is not constant.

4. Heat Energy Consumption and Limiting Productivity of Thermal Gas Separation

Many separation processes utilize heat energy instead of mechanical energy. They receive heat from the reservoir with the high temperature, T_+, and reject it into the low-temperature reservoir with the temperature, T_-. The derived estimates for irreversible work of separation also allows us to estimate the amount of heat that has to be used in thermal separation.

Assume that the heat transfer coefficients β_+ and β_- for heat supply and removal, correspondingly, are known. Novikov,[8] and later independently Curzon and Ahlborn,[10] derived the expression for maximal power that can be obtained from a heat engine with two reservoirs in irreversible cycle as

$$p_{\max} = \frac{\beta_+\beta_-}{(\sqrt{\beta_+} + \sqrt{\beta_-})^2}(\sqrt{T_+} - \sqrt{T_-})^2 = \beta(\sqrt{T_+} - \sqrt{T_-})^2 \tag{36}$$

The irreversible process with the productivity g and fixed compositions of input and output fluxes can be realized in heat-driven separation schema only if the power p, calculated from eq 34, is lower than $p_{\max}$. If this condition holds, then the heat consumption can be estimated using eq 12, after substitution into it of the minimal entropy production $\sigma^{\mathrm{T}}_{\min}$. In turn, this minimal entropy production depends on the power p used in separation. If the input and output gas fluxes have temperatures that are close to T_-, then the estimate for power is given by eq 34. The minimal entropy production as a function of power was derived in ref 9 and has the form

$$\sigma^{\mathrm{T}}_{\min}(p) = \frac{p}{T_-}\left(\frac{\eta_{\mathrm{Carnot}}}{\eta(p)} - 1\right) \tag{37}$$

According to eq 12, we get

$$q_+ = q^0_+ + \frac{p(\eta_{\mathrm{Carnot}} - \eta(p))}{\eta_{\mathrm{Carnot}}\eta(p)} \tag{38}$$

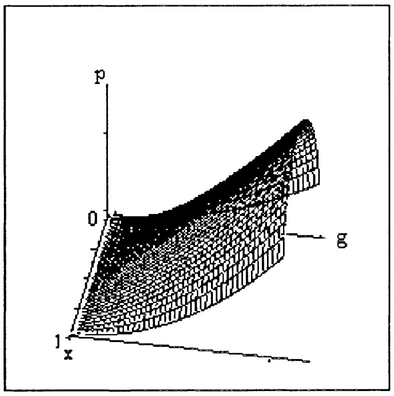

Figure 4. The dependence of the power used in separation on its rate and the composition of the input flux.

Here, η_{Carnot} is the Carnot efficiency and $\eta(p)$ is the maximal efficiency of a heat engine with given power p and given finite heat transfer coefficients, obtained in ref 9,

$$\eta(p) = \frac{2\delta k}{\delta k + 1 - \sqrt{(1-k)(1-k\delta^2)}} \tag{39}$$

Here, $\delta = (\sqrt{T_+} - \sqrt{T_-})/(\sqrt{T_+} + \sqrt{T_-})$, and $k = p/p_{\max}$. For $p \to p_{\max}$, the efficiency $\eta(p)$ tends to the Novikov–Curzon–Ahlborn limit[9]

$$\eta_{\mathrm{NCA}} = 1 - \sqrt{\frac{T_-}{T_+}}$$

If $p \to 0$ (the process is close to reversible), then $\eta(p)$ tends to the Carnot efficiency, η_{Carnot}. This can be easily shown using l'Hopital's rule.

Limiting Productivity of Binary Mixture Separation. The major difference between the mechanical and thermal separation processes is that the productivity of the latter is limited and the productivity of the former is not. Indeed, because $p \le p_{\max}$ and g is a monotonic function of p (which follows from eq 34), the following inequality holds

$$\forall_{p\in[0,\infty]}\, g(p,x,x_1,x_2) \le g(p_{\max},x,x_1,x_2)$$

This inequality holds for any compositions of the input and output fluxes x, x_1, and x_2. $p_{\max}$ depends on the temperatures of the hot and cold reservoirs, T_+ and T_-, and on the heat transfer coefficients on the "hot and cold end", β_+ and β_- in accordance with eq 36.

We will find the limiting productivity of thermal gas separation by solving eq 34 with respect to g and then by substituting p with $p_{\max}(T_+,T_-,\beta_+,\beta_-)$. For $d > 0$, we get

$$g_{\max} = -\frac{a^0_{\mathrm{n}}(x)}{2d(x)b^2(x,x_1,x_2)} + \sqrt{\left(\frac{a^0_{\mathrm{n}}(x)}{2d(x)b^2(x,x_1,x_2)}\right)^2 + \frac{p_{\max}}{d(x)b^2(x,x_1,x_2)}} \tag{40}$$

If mass transfer coefficients α_1 and α_2 are very high ($d \to 0$), then

$$g_{\max} = \frac{p_{\max}(T_+,T_-,\beta_+,\beta_-)}{a^0_{\mathrm{n}}(x,x_1,x_2)}$$

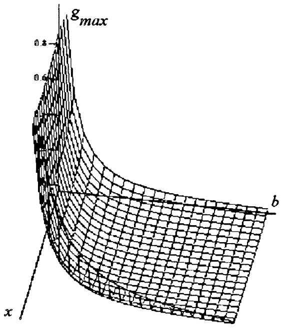

Figure 5. The dependence of the maximal productivity on the concentration of the key component in the initial mixture and on the degree of separation.

The dependence of $g_{\max}$ on the concentration x in the input mixture and the degree of separation b is shown in Figure 5.

In many cases, the productivity of the system as a function of the flux g_1 and concentration x_1 of the key component is given. From the balances, it follows that the fluxes g and g_1 depend on each other as

$$g = g_1 \frac{x_1 - x_2}{x - x_2}$$

Substitution of this equality into eq 34 gives the dependence of the power used in separation and the flux

$$p = g_1[a_n^0(x,x_1,x_2) + g_1 d(x,\alpha_1,\alpha_2) b_1^{\,2}(x,x_1)]$$

Here $a(x)$ and $d(x,\alpha_1,\alpha_2)$ are determined by the same as in eq 34, and

$$b_1(x,x_1) = \frac{x_1 - x}{x(1 - x)}$$

The maximal productivity with respect to the key flux $g_{1\max}$ can be calculated using formula 40, where b is replaced with b_1. When x_1 changes from x to 1, the value of this coefficient changes from 0 to $1/x$.

5. Limiting Possibilities of Irreversible Binary Distillation

General Approach. Thermodynamic balances of the distillation column link the amount of heat used for separation with the compositions of the input and output flows and the entropy production in the system. This amount is the sum of the reversible and irreversible terms. Assume that the productivity with respect to the key component (for definiteness, the flow from the condenser) and the compositions of the output and input flows are known. Therefore, the reversible term is fixed. We will derive a lower bound for the irreversible term by calculating the form of operating line that corresponds to the minimal dissipation in a column.

Distillation is based on the conditions of equilibrium between boiling liquid and generated vapor. If the liquid can be described as an ideal solution and vapor as an ideal gas, then the partial pressure of the ith component in the vapor is equal to the product of its concentration on the total pressure:

$$P_i = P y_i = y_i \sum_{\nu} P_{\nu} \tag{41}$$

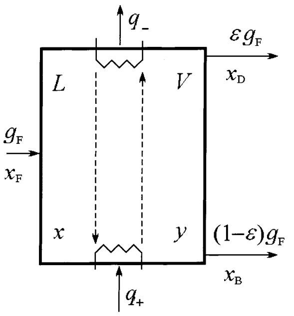

Figure 6. The schema of the distillation column.

On the other hand, in equilibrium, the partial pressure of the ith component in vapor is equal to the pressure of a saturated vapor of pure substance, P_i^0, multiplied on the molar fraction of this substance in the liquid

$$P_i = P_i^0 x_i \tag{42}$$

Here P_i^0 depends on the temperature. If the temperature is fixed, then it is lower for less volatile components than for more volatile components.

For known dependencies $P_i^0(T)$, eqs 41 and 42 allow us to find the equilibrium line, $y_i^0(x_i)$,

$$y_i^0(x_i) = \frac{P_i^0(T) x_i}{\sum_{j=1}^{k} P_j^0(T) x_j} \qquad i = 1, ..., k$$

For a binary mixture, we denote the fraction of the more volatile component in the liquid as x. Then we obtain the equilibrium line for the molar fraction of the more volatile component in vapor,

$$y^0(x) = \frac{P_1}{P} = \frac{P_1^0 x}{P_2^0 + (P_1^0 - P_2^0)x}$$

The coefficient of relative volatility between two components is defined as

$$\alpha(T) = \frac{P_1^0(T)}{P_2^0(T)}$$

and the equilibrium line can be rewritten as

$$y^0(x) = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{43}$$

The relative volatility $\alpha > 1$, because y denotes the concentration of the more volatile component.

Thermodynamic Balances in Distillation: Reversible Estimate of the Amount of Heat Used for Separation. Unlike ref 14, we consider a packed distillation column. The rationale here is that our aim is to obtain a bound on dissipation. But dissipation in a tray column is always higher than dissipation in a packed column because of extra dissipation caused by the hydrodynamics of the tray. Our model of distillation is based on mass transfer and not on heat transfer as in ref 14. We assume that the temperature varies from section to section in a column in accordance with the variations of the corresponding equilibrium composition.

The distillation column is shown schematically in Figure 6. The feed with the rate g_F and vector of concentrations x_F is supplied into the column. The heat flux q_+ is supplied to the bottom liquid in the reboiler, which partially vaporizes it. The resulting flow of vapor V flows upward along the column. This creates contact between this vapor and the liquid L flowing downward. During this contact, more volatile components are transferred from the liquid into the vapor and less volatile components from the vapor into the liquid. The rest of the bottom liquid is removed via the flux g_B.

The overhead vapor, saturated with more volatile components, enters the condenser where the heat flux q_- is removed from it by the cooling liquid and it is condensed to obtain distillate. The fraction of distillate, $g_D = \epsilon g_F$, is removed from the column as overhead product, and the rest of it, $L = V - g_D$, is refluxed into the column. The fraction that is removed, ϵ, is one of the controls. T_- denotes the temperature in the condenser. Index j corresponds to the jth component of the mixture. h_F, h_D, and h_B denote molar enthalpies of the corresponding fluxes; s_F, s_D, and s_B are their entropies. σ denotes the entropy production.

From thermodynamic balances, it follows that (similar to eq 7) the amount of heat used in distillation depends on the entropy production in it:

$$q_+ = \frac{T_+}{T_+ - T_-}[g_F(s_F T_- - h_F) - g_D(s_D T_- - h_D) - g_B(s_B T_- - h_B)] + \sigma\frac{T_+ T_-}{T_+ - T_-} = q_+^0 + \sigma\frac{T_+ T_-}{T_+ - T_-} \quad (44)$$

The first term, q_+^0, in this expression represents the heat consumed in a reversible process. It depends only on the parameters of the input and output flows. The second term is nonnegative and corresponds to the dissipative energy losses.

Assume that the mixtures can be described as ideal solutions; then the expressions of eqs 9 and 10 for entropy and enthalpy hold. The increments of the molar enthalpy and molar entropy when the temperature is changed are expressed via the heat capacity, $c_{pj}(T)$, as

$$\Delta h_j = h_j(T_2,P) - h_j(T_1,P) = \int_{T_1}^{T_2} c_{pj}(T)\,\mathrm{d}T$$

$$\Delta s_j^0 = s_j^0(T_2,P) - s_j^0(T_1,P) = \int_{T_1}^{T_2} \frac{c_{pj}(T)}{T}\,\mathrm{d}T$$

We consider the flow of distillate, removed from condenser, as the objective flow. It represents ϵ, fraction of the feed. Then the reversible estimate for the heat consumption in distillation can be rewritten in the following form

$$q_+^0 = \frac{RT_- g_D}{\eta_{\mathrm{Carnot}}\epsilon}\sum_{j=1}^{k}\Big[\epsilon x_{jD}\ln x_{jD} + (1-\epsilon)x_{jB}\ln x_{jB} - x_{jF}\ln x_{jF} - \frac{\epsilon x_{jD}}{RT_-}\int_{T_-}^{T_F}\Big(1 - \frac{T_-}{T}\Big)c_{pj}(T)\,\mathrm{d}T + \frac{(1-\epsilon)x_{jB}}{RT_-}\int_{T_F}^{T_+}\Big(1 - \frac{T_-}{T}\Big)c_{pj}(T)\,\mathrm{d}T\Big] \quad (45)$$

The value

$$p^0 = \frac{g_D}{\epsilon}RT_-\sum_{j=1}^{k}[\epsilon x_{jD}\ln x_{jD} + (1-\epsilon)x_{jB}\ln x_{jB} - x_{jF}\ln x_{jF}] \quad (46)$$

represents the reversible isothermal work of separation of the flow g_F with the concentration x_F into two flows with concentrations x_B and x_D at the temperature T_-.

Nonisothermal character of the separation yields an additional term,

$$\Delta p^0 = \frac{g_D}{\epsilon}\sum_{j=1}^{k}\Big[(1-\epsilon)x_{jB}\int_{T_F}^{T_+}\Big(1 - \frac{T_-}{T}\Big)c_{pj}(T)\,\mathrm{d}T - \epsilon x_{jD}\int_{T_-}^{T_F}\Big(1 - \frac{T_-}{T}\Big)c_{pj}(T)\,\mathrm{d}T\Big] \quad (47)$$

If we assume that the heat capacity does not depend on the temperature and denote the constant heat capacities over the intervals (T_-, T_F) and (T_F, T_+) as c_{pi}^- and c_{pi}^+, correspondingly, then this additional reversible work can be rewritten

$$\Delta p^0 = \frac{g_D}{\epsilon}\sum_{j=1}^{k}\Big[(1-\epsilon)x_{jB}c_{pj}^+\Big(T_+ - T_F - T_-\ln\frac{T_+}{T_F}\Big) - \epsilon x_{jD}c_{pj}^-\Big(T_F - T_- - T_-\ln\frac{T_F}{T_-}\Big)\Big]$$

The reversible estimate for the heat consumption in distillation can be rewritten in the following form

$$q_+^0 = \frac{p^0 + \Delta p^0}{\eta_{\mathrm{Carnot}}} \quad (48)$$

The removed fraction ϵ in formulas 45−47 depends on the compositions of the input and output flows via the conditions of mass balance

$$\epsilon = \frac{x_F - x_B}{x_D - x_B}$$

Only if the composition of distillate x_D is fixed, then such removed fraction ϵ should be chosen that minimizes q_+^0 on ϵ. ϵ here uniquely determines the composition of bottom flow x_B.

Minimal Entropy Production in Distillation. From eq 44, it follows that the energy consumption in the distillation column consists of the reversible term q_+^0 and an irreversible term proportional to the entropy production in a column, σ. We will now consider the problem of minimal entropy production in binary distillation. We assume that this is a packed column: the mass transfer between the flows of vapor and liquid is equimolar (that is, the condition of constant molar overflow holds); the mixtures are close to ideal; the temperature in each section of the column l is constant and the same for both liquid and vapor; the heat of mixture is zero and there are no heat leaks into the environment; the compositions of the vapor and liquid are the same in both overhead condenser and bottom reboiler. We also assume that the feed g_F enters in the section of the column where the temperature is the same as its temperature and the composition of the liquid is the same as its composition and that there is no excess entropy production due to the mixing of the flows. We do not take into account the entropy production caused by heat exchange in reboiler and condenser because the heat transfer coefficients there are very high.

The concentrations of the more volatile component in vapor and liquid are denoted as $y(l)$ and $x(l)$, correspondingly. The distribution of the driving force of the mass transfer process is determined by the form of the equilibrium line and the form of the operating line. We will derive the ideal (the least dissipative) concentration profile (distribution of concentrations) in the column and the corresponding value of σ_{min}. This profile can be then approximated by supplying/removing heat along the column. The ideal profile of concentrations allows us to evaluate various new designs of distillation column.[11,12]

Because in the binary distillation the concentrations of the less volatile component in the liquid and vapor flows are $(1 - x)$ and $(1 - y)$, correspondingly, and the driving force of the process is determined by the difference between y and the equilibrium concentration $y^0(x)$, the entropy production can be expressed in terms of the flows and the chemical potentials as

$$\sigma(x) = \frac{1}{T}\{g_1(y,y^0)(\mu_1(T,y^0) - \mu_1(T,y)) + g_2(1-y,1-y^0)(\mu_2(T,1-y) - \mu_2(T,1-y^0))\} \quad (49)$$

Because each chemical potential has the form

$$\mu_i(T,P,z_i) = \mu_{i0}(P,T) + RT \ln z_i, \quad i = 1, 2 \quad (50)$$

we get

$$\mu_1(T,y^0) - \mu_1(T,y) = RT \ln \frac{y^0}{y}$$

$$\mu_2(T,1-y) - \mu_2(T,1-y^0) = RT \ln \frac{1-y}{1-y^0}$$

After taking into account the condition of constant molar overflow

$$g_1(y,y^0) = g_2(1-y,1-y^0) = g(y,y^0)$$

expression 49 takes the form

$$\sigma(x) = Rg(y,y^0) \ln \frac{y^0(1-y)}{y(1-y^0)} \quad (51)$$

Functions y and y^0 depend on x, but σ does not explicitly depend on x. Because y^0 is a unique and monotone function of x and x changes from x_B to x_D in the column, the entropy production here can be written as

$$\sigma = R\int_{y^0(x_B)}^{y^0(x_D)} g(y,y^0) \ln \frac{y^0(1-y)}{y(1-y^0)}\, dy^0 \quad (52)$$

The mass flow of more volatile component from liquid to vapor g depends on the concentration $y(x)$, equilibrium concentration $y^0(x)$, and mass transfer coefficient per unit of column length k. If the independent variable l is replaced with another variable that monotonically depends on l, then the new mass transfer coefficient $\bar{k}$ should be used by multiplying k on H and dividing it on the range of the new independent variable. For example, if x replaces l,

$$\bar{k} = \frac{kH}{x(H) - x(0)} \quad (53)$$

H is the height of the column. If y^0 is used, then the denominator here is $y^0(H) - y^0(0)$.

Let us calculate now the operating line, which minimizes σ, subject to the given equivalent mass transfer load

$$\int_{y^0(0)}^{y^0(H)} g(y,y^0)\, dy^0 = C \quad (54)$$

The constant C characterizes the rate of mass transfer. It depends on the concentrations of the input and output fluxes.

For the majority of laws of mass transfer, the problem of eqs 52 and 54 is concave on y and its solution is determined by the condition of stationarity of the Lagrange function

$$L = g(y,y^0)\left(\ln \frac{y^0(1-y)}{y(1-y^0)} - \gamma\right)$$

where γ is a Lagrange multiplier. This condition determines the ideal operating line—the optimal dependence $y(y^0,\gamma)$.

For a binary distillation column with a variable (not necessarily constant) vapor flow V along the column, we obtain

$$\ln \frac{y^0(1-y)}{y(1-y^0)} - \frac{g(y,y^0)}{\partial g/\partial y(1-y)y} = \gamma \quad (55)$$

The expression in the left-hand side of eq 55 must be constant in each column's section. In particular, for the linear law of mass transfer,

$$g(y,y^0) = \bar{k}(y^0 - y) \quad (56)$$

the condition of eq 55 takes the form

$$\ln \frac{y^0(1-y)}{y(1-y^0)} + \frac{y^0 - y}{y(1-y)} = \gamma \quad (57)$$

If the distillation process is close to equilibrium and the equivalent flux is proportional to the driving force,

$$g(y,y^0) = \bar{k} \ln \frac{y^0(1-y)}{y(1-y^0)} \quad (58)$$

and the condition of eq 55 can be resolved with respect to y. Then eq 55 takes the form

$$\frac{y^0(1-y)}{y(1-y^0)} = \gamma = \text{const} \quad (59)$$

Therefore,

$$y(y^0) = \frac{y^0}{\gamma - (\gamma - 1)y^0} \quad (60)$$

For $y^0(x)$ given by eq 43, we get

$$y(x) = \frac{\alpha x}{\gamma + (\alpha - \gamma)x} \quad (61)$$

Because $y(x) > x$,

$$1 < \gamma < \alpha \quad (62)$$

After taking into account that $\bar{k} = kH/(y^0(x_D) - y^0(x_B))$ and substituting eqs 58 and 59 into eq 52, we obtain the expression for minimal dissipation caused by mass transfer in a column that operates not far from equilibrium,

$$\sigma_{\min} = RkH(\ln \gamma)^2 \quad (63)$$

Dependence of Mass Transfer Rate in a Column on the Parameters of External Fluxes: Thermodynamic Limit of the Column's Productivity. If γ is known, then the condition of eq 55 and the dependencies of eqs 58 and 60 completely determine $y(y^0)$. To find this constant, we need to express C in eq 54 in terms of the productivity of the column and the concentrations of the external fluxes.

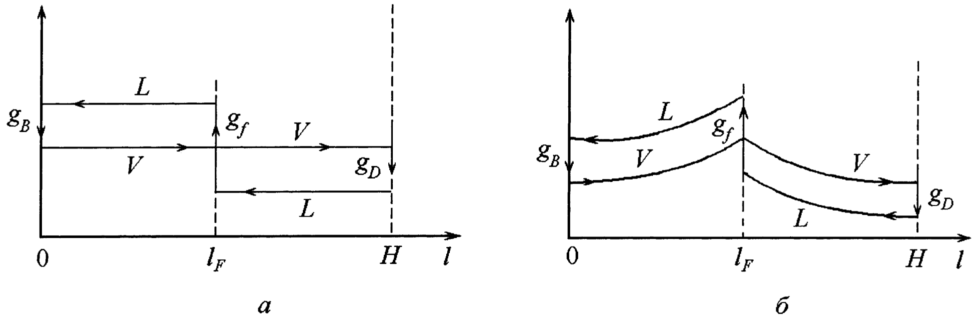

Figure 7. Characteristic dependencies of the rates of vapor and liquid along the height of a column (a) without intermediate heat supply/removal and (b) with it.

Mass transfer and (intermediate) heat supply/removal change the flow rates of vapor and liquid along the column. Because we assume that the condition of constant molar overflow holds for mass transfer and because all of the liquid that is vaporized is transferred to vapor, the following condition holds for $l \neq l_F$:

$$\frac{dV}{dL} = 1 \tag{64}$$

Therefore, for the stripping and enriching section of the column,

$$L_B = V_B + g_B, \quad L_D = V_D - g_D \tag{65}$$

Characteristic dependencies of the vapor and liquid flow rates on the height of the column without and with intermediate heat supply are shown in Figure 7.

If L and V depend on l and on any other variable that changes monotonically along the height of the column $\{x, y^0, y, ...\}$, then the equalities of eq 65 hold. The vapor flow in any section of the column (consequently for any value of x that corresponds to this section) can be found from material balance on the more volatile component for the part of the column between the current section and its upper/lower end. For the enriching section, we have

$$V_D(x)y(x) - g_D x_D - xL_D(x) = 0$$

If we take into account that for any x $L = V - g_D$, we obtain

$$V_D(x) = g_D\frac{x_D - x}{y(x) - x} \tag{66}$$

Similarly, for the stripping section,

$$V_B(x) = g_B\frac{x - x_B}{y(x) - x} \tag{67}$$

Let us estimate the range of the variable x for which the equalities of eqs 66 and 67 hold. We assumed that all vapor is condensed in dephlegmator ($l = H$). From the material balance for the dephlegmator,

$$V(H) - L(H) - g_D = 0, \quad V(H)y(H) - (L(H) + g_D)x_D = 0$$

it follows that $y(H) = x_D$. Therefore, $x(H) = x_d$, where x_d is the root of the equation

$$y(x_d) = x_D \tag{68}$$

We denote the concentration of the more volatile component in the liquid, which enters reboiler as x_b, $x(0) = x_b$. From the material balance,

$$L(0) - V(0) - g_B = 0, \quad L(0)x_b - g_B x_B - V(0)y^0(0) = 0$$

it follows that

$$x_b = \frac{g_B x_B + V(x_b)y^0(x_B)}{g_B + V(x_b)}$$

This equation jointly with eq 67 yields the following equation for x_b:

$$y(x_b) = y^0(x_B) \tag{69}$$

Thus, when l changes from 0 to H, x changes from x_b to x_d.

The flow of the more volatile component from liquid to vapor consists of the flow of mass transfer $g(y,y^0)$ and the flow, caused by vaporization or condensation, that occurs when heat is supplied/removed. From the condition of constant molar overflow, it follows that the latter flow is proportional to the change of vapor rate. When liquid is vaporized, the flow of more volatile component, which is added to the vapor, is

$$g_q(y,x) = y\frac{dV}{dx}$$

The flow of the less volatile component, which is transferred to the liquid, here is

$$g_q(y,x) = -(1 - x)\frac{dV}{dx}$$

From eqs 67 and 68, we obtain

$$g_q^D(y,x) = -g_D(1 - x)\left[\frac{(1 - dy/dx)(x_D - x)}{(y - x)^2} - \frac{1}{y - x}\right] = g_D f_D(x,\gamma), \quad x_F \le x \le x_d \tag{70}$$

$$g_q^B(y,x) = g_D y\frac{x_D - x_F}{x_F - x_B}\left[\frac{(1 - dy/dx)(x - x_B)}{(y - x)^2} - \frac{1}{y - x}\right] = g_D f_B(x,\gamma), \quad x_b \le x \le x_F \tag{71}$$

Here, γ is the above-defined parameter, which describes the rate of mass transfer in the dependence $y(x,\gamma)$.

The overall mass transfer from liquid to vapor in the stripping section is equal to the difference between the amount of the more volatile component that enters with phlegma and with feed and the amount that is removed with the bottom flux,

$$\int_{x_b}^{x_F}[g(y,y^0) + g_q^B(y,x)]\,dx = L(x_F)x_F + (g_B + g_D)x_F - g_Bx_B$$

$L(x_F)$ in the feed section, l_F, can be expressed in terms of the vapor flow $V(x_F)$ using eq 65. Then eq 65 can be rewritten as

$$\int_{x_b}^{x_F}g(y,y^0)\,dx = g_B(x_F - x_B) + V(x_F)x_F - \int_{x_b}^{x_F}g_q^B(y,x)\,dx \tag{72}$$

Similarly, for the enriching section, the flow of the less volatile component from vapor to liquid is equal to the difference between the amount of the less volatile component that enters with the vapor into the section l_F and the amount that is removed with the product flow

$$\int_{x_F}^{x_d}[g(y,y^0) + g_q^D(y,x)]\,dx = V(x_F)(1 - y(x_F)) - g_D(1 - x_D)$$

Thus,

$$\int_{x_F}^{x_d}g(y,y^0)\,dx = V(x_F)(1 - y(x_F)) - g_D(1 - x_D) - \int_{x_F}^{x_d}g_q^D(y,x)\,dx$$

Finally, the combined total flow of mass transfer is

$$\int_{x_b}^{x_d}g(y,y^0)\,dx = g_D\left\{\frac{x_D - x_F}{y(x_F) - x_F} - (1 - x_D) - \int_{x_b}^{x_F}f_B(x,\gamma)\,dx - \int_{x_b}^{x_d}f_D(x,\gamma)\,dx\right\} \tag{73}$$

Because y, x_b, x_d, and $y(x_F)$ depend on the unknown constant γ, this equation determines γ as a function of the given productivity, g_D, and the compositions of the input and output flows.

If the ideal operating line has the form of eq 61, then

$$x_d = \frac{\gamma x_D}{\gamma x_D + \alpha(1 - x_D)}$$

$$x_b = \frac{\gamma y^0(x_B)}{\gamma y^0(x_B) + \alpha(1 - y^0(x_B))}$$

$$\frac{dy}{dx} = \frac{\alpha\gamma}{[\alpha x + \gamma(1 - x)]^2}$$

Example. Consider a column with the following parameters: $k = 10$ mol/(s M)], $x_D = 0.95$, $x_F = 0.5$, $x_B = 0.05$, and $g_D = 53$ mol/s and $H = 10$ m; the dependence $y^0(x)$ has the form of eq 43, $\alpha = 4$, and the dependence $y(y^0)$ has the form of eq 60. The numerical solution of the eq 73 yields $\gamma = 1.5$. Figure 8 shows the ideal operating line for this column.

Note, that eq 73 allows us also to find the thermodynamic limit for maximal productivity, g_D^{max}, of a column. This is achieved by finding the function $g_D(\gamma)$ as a solution of eq 73 and then by maximizing it with respect to γ

$$g_D^{max} = \max_{\gamma} g_D(\gamma)$$

The dependence of the productivity of the column on the parameter γ is shown in Figure 9 for the same column as in the example above. Two values of γ correspond to every g_D except $g_D^{max} = 576.8$ mol/s. The lowest of these two values corresponds to the minimum of the entropy production σ and the highest to its maximum. For example, $\gamma = 1.5$ and $\gamma = 2.25$ correspond to $g_D = 530$ mol/s.

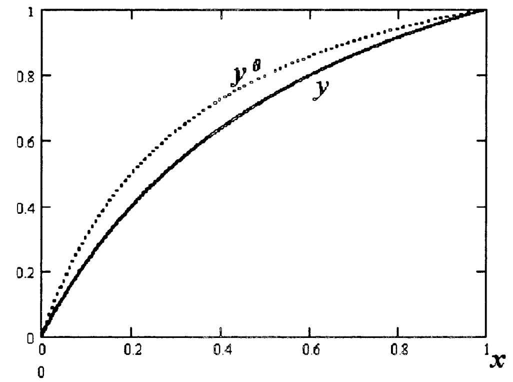

Figure 8. The ideal operating line for the distillation column in the example.

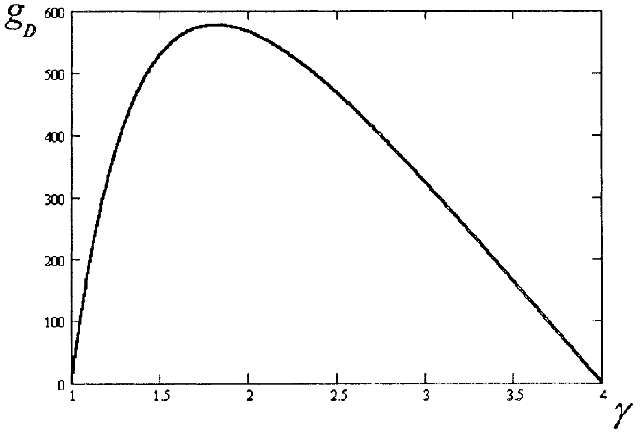

Figure 9. The dependence of the productivity of the column on the parameter γ of the ideal operating line.

Realization of the Ideal Operating Line. The following equality holds in each column section

$$V(x)\frac{dy}{dl} = g(y,y^0)$$

Because $dy/dl = (dy/dx)(dx/dl)$, the concentration of the more volatile component in liquid along the column is governed by the following differential equation

$$\frac{dx}{dl} = \frac{g(y,y^0)}{V(x)\dfrac{dy}{dx}}, \quad x(0) = x_b, \quad x(H) = x_d \tag{74}$$

The optimal (from the viewpoint of minimization of dissipation of the column) location of the feed point, l_F, is determined by the condition $x(l_F) = x_F$. Equations 66, 67, and 74 allow us to find the concentration profiles $x(l)$, $y(l) = y(x(l))$, and the vapor and liquid flows $V(l) = V(x(l))$ and $L(l)$, for which the conditions of eq 65 hold.

The rate of the corresponding heat supply/removal for the ideal operating line is

$$q(l) = \beta\frac{dV}{dx}\frac{dx}{dl}$$

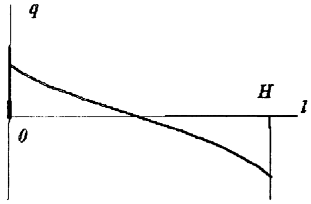

Figure 10. Characteristic optimal profile of heat supply/removal.

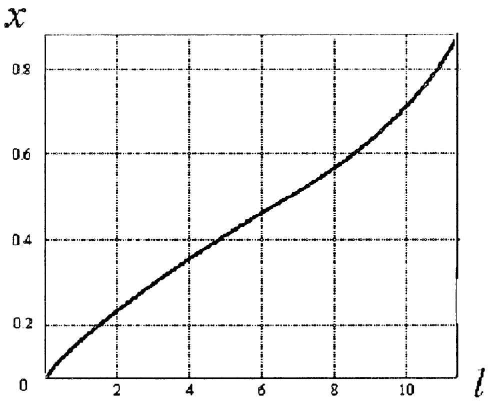

Figure 11. The optimal concentration profile of the more volatile component in liquid along the height of the column.

where β is the heat of evaporation. For the enriching and stripping sections of the column, these rates are

$$q_D(l) = \beta \frac{\left[V_D(x)\left(1 - \frac{dy}{dx}\right) - g_D\right]}{y(x) - x} \frac{g(y,y^0)}{V_D(x)\frac{dy}{dx}}$$

$$q_B(l) = \beta \frac{\left[V_B(x)\left(1 - \frac{dy}{dx}\right) + g_B\right]}{y(x) - x} \frac{g(y,y^0)}{V_B(x)\frac{dy}{dx}} \tag{75}$$

Characteristic optimal profile of heat supply/removal is shown in Figure 10.

Example. The optimal profile of concentration of the more volatile component in liquid along the height of the column, used in example, is shown in Figure 11. $x_F = 0.5$ corresponds to the feed location $l_F = 6.76$ m.

6. Conclusion

The minimal power required for separation of a gas mixture is derived in this paper. It is also proven that heat-driven separation has limited productivity (analogue of the maximal power of heat engine), and this limit is found. The expressions for the minimal entropy production and energy consumption in an irreversible binary distillation column are derived. The ideal operating line of irreversible binary distillation, for which dissipative losses are minimal, is found. The ideal regime of intermediate heat supply/removal, which is determined by this ideal operating line, is constructed.

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