

# Finite-Time Thermodynamics: Limiting Performance of Rectification and Minimal Entropy Production in Mass Transfer

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Rectification and separation processes generally operate far from their thermodynamically optimal conditions. Here, the operating conditions yielding minimal entropy production are obtained for this mass-transfer process. The corresponding optimal concentration profiles are also obtained. The results show that minimal heat consumption corresponds to the minimal entropy production in the rectification process. Estimates are derived of realistic rates of entropy production.

## 1. Introduction

The methods of finite-time thermodynamic have been applied to the analysis of processes of chemical technology in refs 1–6. These analyses take into account the irreversibility due to constraints of nonzero intensity of the processes and to the necessarily finite values of the coefficients of mass and heat transfer. Some of these have dealt primarily with heat transfer<sup>7–12</sup> and others with chemical species and separation processes.<sup>13–17</sup> The estimates of efficiency provided by these methods are more realistic than the reversible estimates. It is even more important that the analyses also give the conditions which show how to adjust the regime of the actual process in order to approach the limiting, maximal effectiveness. In many cases (absorption, desorption, membrane separation, rectification) the major irreversibility factor is the mass-transfer process. If mass transfer operates optimally, it minimizes the energy consumption when its intensity is fixed.

Because the rectification process is one of the most widespread and energy-consuming processes of chemical technology, estimates of its limiting possibilities and the optimal profiles of concentrations that correspond to it are very important. In this article we first find an estimate of the reversible rectification efficiency and the connection of this efficiency with entropy production. Then we derive the conditions on the profiles of concentrations that provide minimal irreversibility for a mass transfer process which has a specified intensity. Finally we determine an estimate of the limiting performance of the rectification process based on the results obtained.

## 2. Efficiency of Rectification and Entropy Production

**2.1. Equations of Thermodynamic Balances.** The rectification process is shown schematically in Figure 1. The feed of mixture  $g_F$  with the (vector of) concentrations  $x_F$  flows into the section  $Z_k$  of rectification column  $K$ . The countercurrent fluxes of vapor  $V$  and liquid (phlegma)  $L$  are established inside the column. The vapor is enriched in the more volatile components and the liquid is enriched in less volatile components in a process of mass transfer. The flux of heat  $q_+$  is added at the lower part of the column (the cube). Similarly, a flux of heat  $q_-$  is removed and the vapor

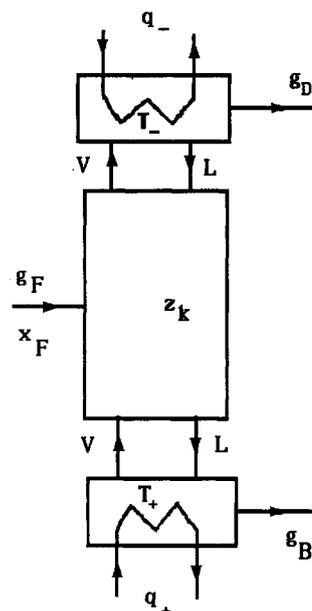


Figure 1. Scheme of the rectification processes.

condenses at the upper part of column (dephlegmator). The temperatures at the cube and dephlegmator are  $T_+$  and  $T_-$ , respectively.  $g_B$  and  $g_D$  flow out of the cube and dephlegmators correspondingly. The first of these consists of the less and the second, of more volatile components of the mixture.

The thermodynamic balances (mass, energy and entropy) for the column with the fluxes shown in the Figure 2 have the form

$$g_F x_{iF} - g_D x_{iD} - g_B x_{iB} = 0, \quad i = 1, \dots, k \quad (1)$$

$$g_F h_{iF} - g_D h_{iD} - g_B h_{iB} + q_+ - q_- = 0 \quad (2)$$

$$g_F s_F - g_D s_D - g_B s_B + \frac{q_+}{T_+} - \frac{q_-}{T_-} + \sigma = 0 \quad (3)$$

where  $h_{ij}$ ,  $s_{ij}$ ,  $i = 1, \dots, k$ , and  $j = F, B, D$  are the molar enthalpies and entropies of the  $i$ th component of the  $j$ th flow;  $k$  is the number of components in the mixture;  $\sigma$  is the rate of entropy production.

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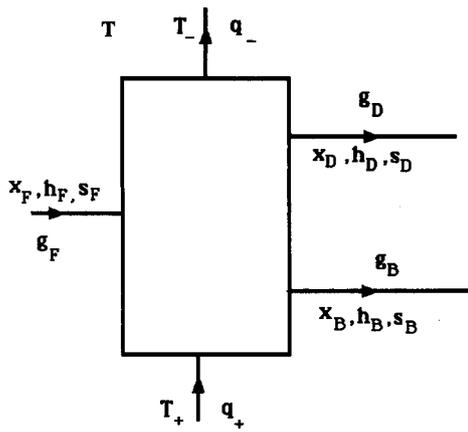


Figure 2. Scheme of the input and output fluxes in the rectification column.

Using these balances, we express the heat used for the process as

$$q_+ = \frac{T_+}{T_+ - T_-} [g_D(h_D - s_D T_-) + g_B(h_B - s_B T_-) - g_F(h_F - s_F T_-)] + \sigma \frac{T_+ T_-}{T_+ - T_-} = q_+^0 + \sigma \frac{T_+ T_-}{T_+ - T_-} \quad (4)$$

Because the entropy production  $\sigma \geq 0$  the reversible estimate of the heat consumption of the column is  $q_+ \geq q_+^0$ . Any estimate of  $\sigma^* \leq \sigma$  caused by the given intensities of the processes and finite values of mass- and heat-transfer coefficients gives, after substitution into expression 4, a value of minimal heat consumption more realistic than  $q_+^0$ . It gives not only its dependence on the parameters of the external fluxes but on the kinetics of the processes inside the column as well.

**2.2. Estimate of the Reversible Efficiency.** Let us give a more detailed form of the reversible estimate just obtained. Assume that (1) the pressures in the fluxes  $g_F$ ,  $g_D$ , and  $g_B$  are the same and equal to  $P$ ; (2) the mixtures can be described as ideal solutions. Thus their enthalpies and entropies depend on parameters as

$$h(T, P, x) = \sum_{i=1}^k x_i h_i(T, P)$$

$$s(T, P, x) = \sum_{i=1}^k x_i s_i(T, P) - R \sum_{i=1}^k x_i \ln x_i$$

here  $R$  is the universal gas constant. The increments of the enthalpy and entropy due to the change of the flux temperatures can be expressed in terms of the heat capacities  $C_{Pi}(T)$  at the constant pressure  $P$ . Thus

$$\Delta h_i = h_i(T_2, P) - h_i(T_1, P) = \int_{T_1}^{T_2} c_{Pi}(T) dT$$

$$\Delta s_i = s_i(T_2, P) - s_i(T_1, P) = \int_{T_1}^{T_2} (c_{Pi}/T)(T) dT \quad (5)$$

If the temperature of the phase transition  $T_{i0}$  lies in the interval  $[T_1, T_2]$ , then the terms

$$\delta h_{i0} = Q_{i0}, \quad \delta s_{i0} = Q_{i0}/T_{i0}$$

should be added to the right-hand sides of eqs 5. Here  $Q_{i0}$  is the latent heat of phase transition of 1 mol of  $i$ th component.

Taking all this into account and expressing  $g_F$  in terms of  $g_D$  and  $g_B$ , we get the following reversible estimate for heat consumption in the rectification process

$$q_+^0 = \frac{T_+}{T_+ - T_-} \sum_{i=1}^k \left[ g_D x_{iD} \left( \int_{T_D}^{T_F} c_{Pi}(T) \left( \frac{T_-}{T} - 1 \right) dT + Q_{i0} \left( \frac{T_-}{T_{i0}} - 1 \right) u_{iD}(T_{i0}) \right) + RT_- (g_B x_{iB} \ln x_{iB} + g_D x_{iD} \ln x_{iD} - g_F x_{iF} \ln x_{iF}) + g_B x_{iB} \left( \int_{T_F}^{T_B} c_{Pi} \left( 1 - \frac{T_-}{T} \right) dT + Q_{i0} \left( 1 - \frac{T_-}{T_{i0}} u_{iB}(T_{i0}) \right) \right) \right] \quad (6)$$

If the component  $i$  is transferred from the vapor into the liquid then the heat of evaporation  $Q_{i0} > 0$ . If it is transferred from liquid to vapor, then  $Q_{i0} < 0$ . The functions  $u_D$  and  $u_B$  are equal zero if the temperature of the phase transition does not fall in either of the intervals  $[T_D, T_F]$  and  $[T_B, T_F]$  correspondingly. Otherwise it is equal to 1.

### 3. Minimal Irreversibility of Mass Transfer

**3.1. One-Way Mass Transfer.** Assume that the system consists of two fluxes (Figure 3) and the objective (desired) component is transferred from one flux to the other. We also assume that the temperatures of both fluxes are the same in every section of the system. The problem of finding the regime of this process with minimal irreversibilities takes the form

$$\sigma = \int_0^L \frac{g(c_1, c_2)}{T(c_1, c_2)} (\mu_1(c_1, T) - \mu_2(c_2, T)) dl \rightarrow \min \quad (7)$$

subject to constraints

$$\int_0^L g(c_1, c_2) dl = N \quad (8)$$

$$dG_1/dl = -g(c_1, c_2), \quad G_1(0) = G_{10} \quad (9)$$

$$d(G_1 c_1)/dl = dG_1/dl \quad (10)$$

where  $G_1(l)$  is the total rate of the first flux;  $c_i(l)$ ,  $\mu_i(c_i, T)$   $i = 1, 2$  are concentrations of the objective component and its chemical potential in the  $i$ th flux;  $T(c_1, c_2)$  is the temperature of the fluxes;  $N$  is the total amount of transferred material,  $L$  is the length of the contact surface,  $l$  is the coordinate along this surface, and  $g(c_1, c_2)$  is the flux density of the mass flow from the first flux to the second (per unit length).

Condition 10 expresses the fact that there is transfer of the objective component only between two fluxes. From (9) and (10) it follows that

$$\frac{dc_1}{dl} = -\frac{1 - c_1}{G_1} g(c_1, c_2), \quad c_1(0) = c_{10} \quad (11)$$

If  $c_2(l)$  is given, then eqs 9 and 11 and the boundary conditions (for instance,  $c_1(0)$  and  $G_1(0)$ ) define  $c_1(l)$  and  $G_1(l)$ . Thus we can consider the concentration  $c_2(l)$  as a control variable of the problem.

Such one-way mass transfer occurs in the processes of absorption, adsorption, membrane separation, and drying. But the temperatures of the fluxes are not always the same at every section of the system and mass transfer does not occur simultaneously with heat transfer.

Let us use the concentration  $c_1$  as a new independent variable instead of the distance  $l$ . From (11) we get

$$dl = -dc_1 \frac{G_1}{(1 - c_1)g(c_1, c_2)} \quad (12)$$

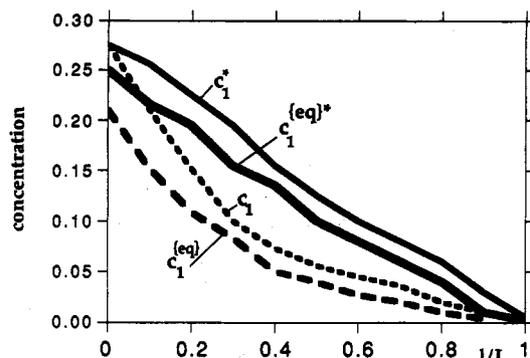


Figure 3. Optimal (solid line) and real (dashed line) concentration's profiles in the lower part of the rectification column.

Condition 8 can be rewritten as

$$\int_{c_1(L)}^{c_{10}} \frac{G_1(c_1)}{1-c_1} dc_1 = N \quad (8a)$$

and eq 9 as

$$\frac{dG_1}{dc_1} = \frac{G_1}{1-c_1} \quad (13)$$

$$G_1(c_1) = G_{10} \frac{1-c_{10}}{1-c_1} = \frac{\tilde{G}_1}{1-c_1} \quad (13a)$$

where  $\tilde{G}_1 = G_{10}(1-c_{10})$  is the flux of inert components in the stream. The mass balance constraint on the objective component gives

$$G_{10}c_{10} - \tilde{g} = G_1(L) c_1(L)$$

and taking into account the dependence of  $G_1$  on  $c_1$ , we get

$$c_1(L) = \frac{G_{10}c_{10}}{G_{10} - N} \quad (14)$$

Substitution of (12) into (7) leads to the transformed problem

$$\sigma = \int_{c_1(L)}^{c_{10}} \frac{\tilde{G}_1}{T(c_1, c_2)(1-c_1)^2} [\mu_1(c_1, T) - \mu_2(c_2, T)] dc_1 \rightarrow \min \quad (15)$$

subject to the condition

$$\int_{c_1(L)}^{c_{10}} \frac{\tilde{G}_1}{T(c_1, c_2)(1-c_1)^2} dc_1 = L \quad (16)$$

The Lagrange function of this problem takes the form

$$M = \frac{\tilde{G}_1}{(1-c_1)^2} \left[ \frac{1}{g(c_1, c_2)} (\mu_1(c_1, T) - \mu_2(c_2, T)) + \frac{m}{g(c_1, c_2)} \right]$$

Here  $m$  is a Lagrange multiplier. The stationarity condition of  $M$  with respect to  $c_2$  gives the condition of minimal entropy production of one-way mass transfer

$$\frac{\partial T}{\partial c_2} \frac{1}{T} \left( \frac{\partial(\mu_1 - \mu_2)}{\partial T} - \frac{\mu_1 - \mu_2}{T} \right) - \frac{1}{T} \frac{\partial \mu_2}{\partial c_2} = m \left( \frac{\partial g}{\partial c_2} \right) \frac{1}{g^2} \quad (17)$$

If the chemical potential is

$$\mu_i(c_i) = \mu_0(P, T) + RT \ln c_i, \quad i = 1, 2 \quad (18)$$

then  $\partial \mu_2 / \partial c_2 = RT/c_2$  and condition 17 takes the form

$$-\frac{R}{c_2} = m \left( \frac{\partial g}{\partial c_2} \right) \frac{1}{g^2} \quad (17a)$$

This expression defines the optimal dependence  $c_2^*(m, c_1)$  up to constant  $m$ . Substitution of  $c_2^*$  into (16) gives the equation which defines  $m = m^*$ . Finally, substitution of  $c_2^*(m^*, c_1)$  into (15) gives the minimal entropy production  $\sigma^*$  and into (11) gives the differential equation for  $c_1(l)$

$$\frac{dc_1}{dl} = -\frac{(1-c_1)^2}{\tilde{G}} g(c_1, c_2^*(c_1)), \quad c_1(0) = c_{10} \quad (19)$$

The solution of (19) gives the optimal profile of concentrations  $c_1^*(l)$  and  $c_2^*(l) = c_2^*(m^*, c_1^*(l))$ .

*Example 1.* Consider a system obeying the linear law of mass transfer:

$$g(c_1, c_2) = k[\mu_1(c_1) - \mu_2(c_2)] \quad (20)$$

Substitution of  $g(c_1, c_2)$  into (17) gives

$$g^*(c_1, c_2) = \text{constant} = N/L$$

From (9) we get

$$G_1(l) = G_1(0) - \frac{N}{L}l$$

Let us rewrite eqs 11 as

$$\frac{dc_1}{dl} = -\frac{N(1-c_1)}{L \left( G_{10} - \frac{N}{L}l \right)} \quad (11a)$$

Its solution is

$$c_1^*(l) = 1 - (1-c_{10}) \frac{G_{10}L}{G_{10}L - lN}$$

The difference between the two chemical potentials is constant. Thus if  $\mu_i(c_i)$ ,  $i = 1, 2$ , have form 18 and  $c_i$  are molar concentrations, we get

$$RT(c_1^*, c_2^*) \ln \frac{c_1^*}{c_2^*} = \frac{N}{Lk} \quad (21)$$

If the process is isothermal,  $T = T_A$ , then

$$c_1^*(l)/c_2^*(l) = \text{constant} = \exp(N/LRkT_A)$$

and the minimal entropy production is

$$\sigma^* = \int_{c_1(L)}^{c_{10}} \frac{\tilde{G}_1 N}{(1-c_1)^2 T_A L k} dc_1$$

Taking into account (13a), we obtain

$$\sigma^* = N^2 / LkT_A \quad (22)$$

Thus, to achieve this minimal entropy production, the concentration ratio  $c_1^*(l)/c_2^*(l)$  must be kept constant along the reactor, either by addition of more key component to flux 1 or withdrawal of it from flux 2, continuously from  $l = 0$  to  $l = L$ .

In many problems the constrained quantity is not the total amount of transferred material but the concentration at the output,  $c_1(L)$ . Then usually the rate  $G_{10}$  is controlled in such a way that  $c_1(L)$  has its required value. The other rate  $G_{20}$  is used to establish equality of the concentration ratio at the input and output of the

system  $c_1(L)/c_2(L) = c_1(0)/c_2(0)$ . As a rule, the ratios of concentrations in intermediate sections are approximately constant.

The mass-transfer coefficient  $k$  in (20) can depend on  $l$ . One can show that in this case the driving force should be constant with respect to  $l$  and equal to

$$\Delta^*(c_1, c_2) = \mu_1(c_1) - \mu_2(c_2) = N / \int_0^L k(l) dl$$

the flux is

$$g^* = \frac{N}{\int_0^L k(l) dl} k(l)$$

and the minimal entropy production is

$$\sigma^* = N^2 / T \int_0^L k(l) dl$$

**Example 2.** Consider the isothermal linear mass-transfer process

$$g = k(c_1 - c_2) \quad (23)$$

Condition 17 takes form  $k(c_1 - c_2)^2 = c_2/mR$  or

$$c_1 = c_2 + \sqrt{\tilde{m}c_2} \quad (24)$$

where  $m$  and  $\tilde{m}$  are constants. The optimal concentration is

$$c_2^*(\tilde{m}, c_1) = c_1 + \frac{\tilde{m}}{2} - \sqrt{c_1\tilde{m} + \frac{\tilde{m}^2}{4}} \quad (25)$$

Its substitution into (16) gives the condition

$$\int_{c_1(L)}^{c_1(0)} \frac{\tilde{G}_1 dc_1}{(1-c_1)^2 k(\sqrt{c_1\tilde{m} + \frac{\tilde{m}^2}{4}} - \tilde{m}/2)} = L$$

which defines the constant  $\tilde{m}$ . Equation 19 takes the form

$$\frac{dc_1}{dl} = -\frac{k}{\tilde{G}_1} \left[ \frac{\tilde{m}}{2} - \sqrt{c_1\tilde{m} + \frac{\tilde{m}^2}{4}} \right] (1-c_1)^2$$

Together with the initial condition  $c_1(0) = c_{10}$  it defines the optimal concentration profile  $c_1^*(l)$ . And the minimal entropy production is

$$\sigma^* = \int_{c_1(L)}^{c_{10}} \frac{R\tilde{G}_1}{(1-c_1)^2} \ln \frac{c_1}{c_1 + \tilde{m}/2 - \sqrt{c_1\tilde{m} + \frac{\tilde{m}^2}{4}}} dc_1$$

In many cases the driving force of the mass transfer process is the difference of the concentration of redistributed component in one of phase  $c_1$  and its equilibrium concentration  $c_1^{eq}(c_2)$  which depends on  $c_2$ . Thus

$$g = k(c_1 - c_1^{eq}(c_2)) \quad (26)$$

The chemical potential  $\mu_2(c_2)$  in the liquid phase can be found from the conditions of equilibrium  $\mu_2(c_2) = \mu_1[c_1^{eq}(c_2)]$ . If (18) defines  $\mu_1$ , then

$$\frac{\partial \mu_2}{\partial c_2} = \frac{RT}{c_1^{eq}(c_2)} \frac{dc_1^{eq}}{dc_2}$$

Its substitution into (17) gives the result that for the linear mass-transfer process with minimal irreversibility, the following condition is fulfilled in any section of system  $l$ :

$$(c_1 - c_1^{eq}(c_2))^2 / c_1^{eq}(c_2) = \tilde{m}$$

If the law of mass transfer has the form 20, then  $c_2$  should be replaced with  $c_1^{eq}(c_2)$  but the condition of constant flux still holds:  $g = N/L$ , which gives

$$k[\mu_1(c_1) - \mu_1(c_1^{eq})] = RT \ln(c_1/c_1^{eq}(c_2)) = N/L$$

or

$$c_1(l)/c_1^{eq}(l) = \exp(N/LkR) \quad (27)$$

This condition defines the optimal equilibrium concentration

$$c_1^{eq}(c_2^*(l)) = \left( 1 - (1 - c_{10}) \frac{G_{10}L}{G_{10}L - Nl} \right) \exp\left(\frac{N}{LkR}\right)$$

If the dependence  $c_1^{eq}(c_2)$  is known, then this expression gives  $c_2^*(l)$ .

**3.2. Two-Way Mass Transfer.** In a two-way mass transfer, one component is transferred from the first flux to the second with intensity  $g_1$  and the other component is transferred from the second flux to the first with intensity  $g_2$ . We assume for simplicity that both fluxes consist of two components only. In this case the entropy production takes form

$$\sigma = \int_0^L \frac{1}{T(c_1, c_2)} (g_1(c_1, c_2) [\mu_1(c_1) - \mu_2(c_2)] + g_2(1 - c_1, 1 - c_2) [\mu_2(1 - c_1) - \mu_1(1 - c_2)]) dl \quad (28)$$

First we consider the equimolar mass transfer

$$g_1(c_1, c_2) = -g_2(1 - c_1, 1 - c_2) = g(c_1, c_2)$$

Taking into account (18), we get

$$\sigma = R \int_0^L g(c_1, c_2) \ln \frac{c_1(1 - c_2)}{c_2(1 - c_1)} dl \rightarrow \min \quad (29)$$

Because the flux  $G_1$  is constant, the differential equation for  $c_1(l)$  takes the form

$$\frac{dc_1}{dl} = -\frac{g(c_1, c_2)}{G_1}, \quad c_1(0) = c_{10} \quad (30)$$

After replacement of the independent variable  $l$  with  $c_1$

$$dl = \frac{G_1}{g(c_1, c_2)} dc_1$$

we get the problem

$$\sigma = RG_1 \int_{c_1(L)}^{c_{10}} \ln \frac{c_1(1 - c_2)}{c_2(1 - c_1)} dc_1 \rightarrow \min, \quad \int_{c_1(L)}^{c_{10}} \frac{G_1}{g(c_1, c_2)} dc_1 = L \quad (31)$$

The stationarity condition of the Lagrange function  $M$  of this problem with respect to  $c_2$  is

$$\frac{\partial M}{\partial c_2} = G_1 \frac{\partial}{\partial c_2} \left[ R \ln \frac{c_1(1 - c_2)}{c_2(1 - c_1)} + \lambda \frac{1}{g(c_1, c_2)} \right] = 0$$

It leads to the condition of equimolar mass transfer with minimal

entropy production

$$\frac{\partial g(c_1, c_2)}{\partial c_2} = -mR \frac{g^2(c_1, c_2)}{c_2(1-c_1)} \quad (32)$$

where  $\lambda$  and  $m$  are constants. The concentration  $c_1(L) = c_{10} - N/G_1$ .

In the more general case of nonequimolar mass transfer, one has to use expression 28 to calculate the entropy production and

$$dG_1/dl = -g_1(c_1, c_2) + g_2(1 - c_2, 1 - c_2), \quad G_1(0) = G_{10} \quad (33)$$

$$dc_1/dl = -\frac{1}{G_1} [g_1(c_1, c_2)(1 - c_1) + g_2(1 - c_2, 1 - c_1)c_1], \quad c_1(0) = c_{10} \quad (34)$$

It is convenient to set the intensity of the process by fixing the value of concentration in the output section  $c_1(L) = c_{1L}$ . The problem of minimization 28 subject to constraints 33 and 34 and  $0 \leq c_2 \leq 1$  is the general control problem, which can be solved only numerically.

**Example 3.** Let us find the optimal profile of concentrations and estimate the thermodynamic efficiency of the lower part of the rectification column for water-methanol separation. We take the input to be a mixture that contains 40% methanol and 60% water. We suppose the cube bottom should contain only 1.5% methanol.

The following parameters of the actual column are taken<sup>6</sup> in units of kilograms, kilomoles, hours, and meters: the rate of liquid which flows down the column  $G_1 = 7480$  kg/h or  $G_1 = 344$  kmol/h; the rate of vapor that goes up the column  $G_2 = 4470$  kg/h or  $G_2 = 170$  kmol/h; the molar concentrations of methanol in liquid and vapor are  $c_{10} = 0.27$ ,  $c_{1L} = 0.0085$ ,  $c_{20} = 0.58$ , and  $c_{2L} = 0.022$  correspondingly. The height of the column is  $L = 1.3$  m.

We assume that the law of mass transfer has the form 26 and that the equilibrium methanol concentration in the liquid depends linearly on its concentration in the gas phase:

$$c_1^{eq}(c_2) = ac_2, \quad \text{or} \quad c_2^{eq} = c_1/a \quad (35)$$

The expression for mass balance of the column between the sections 0 and  $l$  is

$$G_1(c_{10} - c_1(l)) = G_2(c_{20} - c_2(l)) \Rightarrow c_2(l) = c_{20} - \frac{G_1}{G_2}(c_{10} - c_1(l)) \quad (36)$$

Substitution of (36), (26), and (35) into (30) gives the differential equation for  $c_1(l)$ . Its solution is

$$c_1(l) = A + (c_{10} - A) \exp\left[-\frac{k(G_1 - aG_2)l}{G_1G_2}\right] \quad (37)$$

where  $A = a(c_{20} - (G_1/G_2)c_{10})$ . Using the actual values of the flux's concentrations we obtain the values of the coefficients:  $k = 3680$  kmol/(h m) and  $a = 0.35$ .

We denote the chemical potential of methanol and water as  $\mu_1$  and  $\mu_2$  correspondingly. In the vapor they are  $\mu_1(c_2)$  and  $\mu_2(1 - c_2)$  and have the form (18). The condition of equality of the chemical potentials of the phases gives

$$\tilde{\mu}_1(c_2) = \mu_1\left(\frac{c_1}{a}\right) = \mu_1^0 + RT \ln \frac{c_1}{a} \quad (38)$$

$$\tilde{\mu}_2(1 - c_2) = \mu_2\left(1 - \frac{c_1}{a}\right) = \mu_2^0 + RT \ln\left(1 - \frac{c_1}{a}\right) \quad (39)$$

Taking into account these formulas, we transform the problem of minimal entropy production into the form

$$\sigma = R \int_0^L g(c_1, c_2) \ln \frac{(1 - c_2)c_1}{c_2(a - c_1)} dl \rightarrow \min \quad (40)$$

The optimality conditions of the problem (40) and (30) can be derived in a way similar to what we used for problem (29) and (30). They are the same as condition 32. Because, under our given law of mass transfer,  $\partial g/\partial c_2 = -ka = \text{constant}$ , the optimality condition takes the form

$$\frac{(c_1 - ac_2)^2}{c_2(1 - c_2)} = m = \text{constant} \quad (41)$$

where  $m$  is some constant. From (41) it follows that

$$c_2^*(c_1, m) = \frac{ac_1 + \frac{m}{2} - \sqrt{mc_1(a - c_1)}}{a^2 + m} \quad (42)$$

The value of  $m$  should be found from the equation

$$\int_{c_1(L)}^{c_{10}} \frac{G_1 dc_1}{c_1 g(c_1, c_2^*(c_1, m))} = L \quad (43)$$

The result is that  $m^* = 0.0027$ .

Substitution of  $m^*$  into (42) and (30) gives the equation for  $c_1^*(l)$ . The resulting optimal profiles  $c_1^*(l)$  and  $c_2^{eq}(c_1^*(l))$  and the concentrations  $c_1(l)$  and  $c_2^{eq}(c_2(l))$  in the real process are shown in Figure 3.

The entropy production in the optimal process is

$$\sigma^* = 281 \text{ kJ/(h K)}$$

The same value in a real column (not optimized) is<sup>6</sup>

$$\sigma = 442 \text{ kJ/(h K)}$$

#### 4. Minimal Entropy Production under Linear Heat and Mass Transfer

In this paragraph we consider the contact of two fluxes that have different composition and temperatures. They exchange both mass and heat. We denote the rate, the concentration of the objective component, its chemical potential, and the temperature of the  $i$ th flux as  $G_i$ ,  $c_i$ ,  $\mu_i(T_i, c_i)$ , and  $T_i$ ,  $i = 1, 2$ , respectively. We assume that

$$T_2(l) > T_1(l), \quad \mu_1(l) > \mu_2(l) \quad \forall l$$

Therefore the heat flux  $q$  is directed from the second flux to the first and the mass flux  $g$  has opposite direction. The rate  $G_1$ , the concentration  $c_1$ , and the temperature  $T_1$  obey the following equations:

$$\frac{dG_1}{dl} = \frac{d(G_1 c_1)}{dl} = -g, \quad G_1(0) = G_{10}, \quad c_1(0) = c_{10} \quad (44)$$

$$\frac{d(T_1 G_1)}{dl} = \frac{q}{r_1}, \quad T_1(0) = T_{10} \quad (45)$$

where  $r_1$  is the heat capacity of the first flux. From (44) we obtain

$$\frac{dc_1}{dl} = \frac{g(1 - c_1)}{G_1} \quad (46)$$

We choose the temperature  $T_2$  and the concentration  $c_2(l)$  of the

second flux as control variables. The problem of minimal entropy production of the heat and mass-transfer process takes the form

$$\sigma = \int_0^L \left[ \left( \frac{1}{T_1} - \frac{1}{T_2} \right) q + \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) g \right] dl \rightarrow \min \quad (47)$$

subject to constraints (44) and (45) and the given rates of heat and mass transfer:

$$\int_0^L q \, dl = Q \quad (48)$$

$$\int_0^L g \, dl = N \quad (49)$$

We assume that the transfer process occurs near equilibrium, so that we can suppose that the laws of heat and mass transfer have Onsanger's form:

$$q = \lambda \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \alpha \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \quad (50)$$

$$g = \alpha \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + k \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \quad (51)$$

or in vector form

$$\mathbf{y} = \mathbf{A}\mathbf{x} \quad (52)$$

where  $\mathbf{y} = (q, g)$  is vector of fluxes,  $\mathbf{x} = ((1/T_1 - 1/T_2), (\mu_1/T_1 - \mu_2/T_2))$  is a vector of the driving forces, and

$$\mathbf{A} = \begin{bmatrix} \lambda & \alpha \\ \alpha & k \end{bmatrix}$$

is a matrix of the phenomenological coefficients;  $\lambda$  and  $k$  are the coefficients of heat and mass transfer, and  $\alpha$  is the diffusion coefficient.

After substitution of these expressions into (47), it takes the form

$$\sigma = \int_0^L (\mathbf{y}^T \mathbf{A}^{-1} \mathbf{y}) \, dl \rightarrow \min \quad (53)$$

subject to constraints (44), (48), and (49). Here the superscript  $T$  denotes transposition. This is an averaged problem which can be written in the standard form<sup>8</sup>

$$\sigma = \overline{L(\mathbf{y}^T \mathbf{A}^{-1} \mathbf{y})} \rightarrow \min, \quad \bar{y}_1 = Q/L, \bar{y}_2 = N/L \quad (54)$$

where the overbar denotes averaging  $\bar{f} = (1/L) \int_0^L f(l) \, dl$ . Because the matrix  $\mathbf{A}$  is positive definite the inverse matrix  $\mathbf{A}^{-1}$  is also positive definite. Thus the integrand of the functional (53) is convex and<sup>8</sup> its solution is constant with respect to  $l$ :

$$\begin{aligned} \sigma &= L(\mathbf{y}^* \mathbf{A}^{-1} \mathbf{y}^*), & \mathbf{x}^* &= \mathbf{A}^{-1} \mathbf{y}^* \\ q^* &= y^*_1 = Q/L, & g^* &= y^*_2 = N/L \end{aligned} \quad (55)$$

Equations 44 and 46 become

$$\frac{dG_1}{dl} = -\frac{N}{L} \Rightarrow G^*_1(l) = G_{10} - \frac{N}{L}l \quad (56)$$

$$\frac{dT_1}{dl} = \frac{1}{G_{10}L - Nl} \left( \frac{Q}{r_1} + T_1 N \right), \quad T_1(0) = T_{10} \quad (57)$$

$$\frac{dc_1}{dl} = -\frac{N(1-c_1)}{L(G_{10} - \frac{N}{L}l)}, \quad c_1(0) = c_{10} \quad (58)$$

The solutions of the last two equations give the optimal dependencies on  $l$  of the temperature and the concentrations for the first flux

$$T^*_1(l) = \frac{G_{10} \left( T_{10} + \frac{Q}{r_1} \right)}{G_{10} - \frac{N}{L}l} - \frac{Q}{r_1 N} \quad (59)$$

$$c^*_1(l) = 1 - (1 - c_{10}) \frac{G_{10}L}{G_{10}L - Nl} \quad (60)$$

The concentration  $c^*_1(l)$  coincides with the optimal profile of concentration obtained in the previous section. The optimal vector of the driving forces  $\mathbf{x}^* = \mathbf{A}^{-1}\mathbf{y}$ . After substitution of (59) into  $\mathbf{x}$ , the first of these condition defines  $T^*_2(l)$ . The second gives  $c^*_2(l)$  if the dependencies  $\mu_1(c_1, T_1)$  and  $\mu^*_2(c_2, T_2)$  are known. If the chemical potentials have the form

$$\mu_i = \mu_0(P, T_i) + RT_i \ln c_i, \quad i = 1, 2$$

the temperature changes are small and the ratio of  $\mu_0(P, T_i)/T_i$  is approximately constant, then

$$\frac{\mu_1}{T^*_1} - \frac{\mu^*_2}{T^*_2} \approx R \ln \frac{c^*_1}{c^*_2}$$

and the optimal values of  $T^*_2(l)$  and  $c^*_2(l)$  become

$$T^*_2(l) = \frac{T^*_1(l)}{1 - \beta_T T^*_1(l)}$$

$$c^*_2(l) = c^*_1(l) \exp(-\beta_c/R) \quad (61)$$

The optimal profiles that have been obtained in this and previous paragraphs and the correspondent minimal values of entropy production give not only the estimate of the limiting efficiency  $\eta = \sigma^*/\sigma$  of the real system but also show how to choose its regime's parameters (like phlegma number in rectification, the velocity of circulation in the adsorption-desorption, etc.) in order to approach the best possible performance, defined by (59), (60), and (61).

## 5. Entropy Production in Irreversible Rectification

We assume that the feed flux  $g_F$  enters the rectification column in a section where the liquid composition and its temperature in the column are the same as those of the feed. The same is assumed for the fluxes  $L$  and  $g_B$ . Thus our model here supposes no excess entropy production due to mixture of the fluxes. We assume also that the amounts of mass  $N_i$  and heat  $Q$  transferred inside the column are fixed:

$$N_i = \int_0^{z_k} n_i \, dz = L(z_k) x_i(z_k) - L(0) x_i(0) + g_{F_x} x_{F_i}, \quad i = 1, \dots, k \quad (62)$$

$$Q = \int_0^{z_k} q \, dz = L(z_k) h_x(z_k) - L(0) h_x(0) + g_{F_x} h_{F_x}, \quad i = 1, \dots, k \quad (63)$$

where  $L$  is the flux of liquid inside column,  $h_x$  is the enthalpy of this flux,  $h_{F_x}$  is the enthalpy of the feed, and  $g_{F_x}$  is the flux of liquid feed.

It is assumed that the kinetics of the heat and mass transfer is described by Onsanger's equations 50 and 51 with constant

coefficients. If the processes occur near equilibrium this is valid. As has been shown above, the minimum of  $\sigma$  corresponds to constant heat and mass fluxes along the length of column

$$n_i^* = N_i/z_k, \quad q_i^* = Q/z_k, \quad i = 1, \dots, k \quad (64)$$

The corresponding estimate of  $\sigma$  is

$$\sigma^* = y^{*T} A^{-1} y^*, \quad y^{*T} = (n_1^*, \dots, n_k^*, q^*) \quad (65)$$

The mass and energy balances for the column are

$$L(0) - V(0) = g_B, \quad V(z_k) - L(z_k) = g_D \quad (66)$$

$$L(z_k) h_x(z_k) + V(0) h_v(0) - V(z_k) h_v(z_k) - L(0) h_x(0) = -g_F h_F \quad (67)$$

where subscript  $x$  corresponds to the enthalpy of the liquid flux and  $v$  to the vapor flux:

$$h_F = h_{Fx} + h_{Fv}, \quad g_F = g_{Fx} + g_{Fv}$$

Let us express the  $L(z_k)$  in terms of  $L(0)$  and substitute it into (66). We get

$$\sigma^* = (c'L(0) + c'')^T A^{-1} (c'L(0) + c'') \quad (68)$$

where  $c'$  and  $c''$  are vectors that depend on the parameters of feed and the fluxes of liquid and vapor in the lower and upper sections of column:

$$c'^T = \left( \frac{h_v(0) - h_x(0)}{h_v(z_x) - h_x(z_k)} x_1(z_k) - x_1(0), \dots, \frac{h_v(0) - h_x(0)}{h_v(z_x) - h_x(z_k)} h_x(z_k) - h_x(0) \right)$$

$$c''^T = \left( \frac{g_F h_F - g_B h_v(0) - g_D h_v(z_k)}{h_v(z_x) - h_x(z_k)} x_1(z_k) + g_{Fx} x_{F1}, \dots, \frac{g_F h_F - g_B h_v(0) - g_D h_v(z_k)}{h_v(z_x) - h_x(z_k)} h_x(z_k) + g_{Fx} h_{Fx} \right)$$

After minimization of  $\sigma^*$  with respect to  $L(0)$ , we get

$$\sigma^* = \frac{1}{z_k} \left[ c''^T A^{-1} c'' - \frac{(c'^T A^{-1} c'')^2}{c'^T A^{-1} c'} \right] \quad (69)$$

Thus if the coefficients of the Onsager's kinetics are obtained using the experimental data then we can calculate vectors  $c'$  and  $c''$  using the parameters of fluxes in the sections  $o$  and  $z_k$  and get the  $\sigma^*$ . We can also obtain the estimation of the minimal heat consumption  $q_+$  using (4).

## 6. Conclusions

Beginning with the reversible limit of rectification, we have analyzed the conditions for minimal entropy production for rectifying systems constrained to operate at fixed rates or to yield fixed fluxes of product. The cases of one-way mass transfer, two-way equimolar mass transfer and linear heat and mass transfer are analyzed to obtain the minimal entropy production itself and optimal concentration profiles. Examples of special cases to which this analysis has been applied are (1) a system obeying the linear law of mass transfer (such as Fick's law, in case of diffusion), (2) isothermal linear mass transfer, and (3) the water-methanol separation in the lower part of rectification column. The next step in this line of study would naturally be the application of these analyses to the design and optimization of new rectification processes, for purposes of making them as efficient as is practically possible.

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