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GENERAL PROBLEMS OF TRANSPORT THEORY

STEPWISE APPROXIMATION OF FUNCTIONS AND INTERMEDIATE EQUILIBRIA IN THERMODYNAMICS

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An analogy has been considered between the problems of approximation of functions by piecewise constant functions and the problems arising in thermodynamics when intermediate equilibrium states in irreversible processes are used. Conditions have been obtained for the optimum selection of boundaries of constancy portions for different statements of such problems. A solution has been obtained to the problem of cooling with intermediate equilibria and it has been shown that the problem on selection of the number and arrangement of plates in a rectifying column is also the problem on intermediate equilibria.

Keywords: *entropy-production minimum, piecewise constant functions, intermediate equilibrium states, energy dissipation.*

Introduction. The problem of approximation of functions by polynomials of various types, harmonic functions, and splines has been the focus of a vast literature [1, 2]. This is one of the most important branches of mathematical analysis. The problem of approximation of functions by piecewise constant (step) functions has attracted much less interest of the researchers. Meanwhile, approximation involves many interesting problems part of which has been considered in the present work. A special class of these problems are problems on conducting irreversible thermodynamic processes "from stage to stage" with the introduction of intermediate equilibrium states [3]. The approximating function $x_s(t)$ is entirely defined by the function $x(t)$ that is approximated by it and by t_i values in which it changes its value abruptly from $x(t_i)$ to $x(t_{i+1})$. The values of "discontinuity points" t_i are the sought variables in such problems (Fig. 1).

Criteria from which these variables are sought may be different. In approximation problems, this can be the distance between $x(t)$ and $x_s(t)$ in one metric or another or a uniform approximation. Since the selection of t_i influences the function $x_s(t)$ only on the interval preceding it or following it, this selection should minimize the total difference between $x(t)$ and $x_s(t)$ on just the interval t_{i-1}, t_{i+1}, so that with introducing each new point of the t_i jump, the decrease in the criterion on this interval is maximum.

In thermodynamics, there arise two classes of problems in which the criterion is the entropy-production minimum. For one class of problems, the duration of the process τ is limited and the mean value of the flux of energy or substance is prescribed. It is necessary to find such a law of variation in intense variables of subsystems participating in the exchange that the entropy production is minimum. These are the problems on minimum-dissipation processes [4].

Another class of problems is that of problems on step processes with intermediate equilibria. For spontaneous processes, the intense variables of contacting systems are equalized by virtue of the equations of state due to the fluxes of energy or substance that arise between them and change their extensive variables. In such processes, the total entropy also grows in the case where their duration is not limited. The entropy increment can be decreased by introducing intermediate equilibrium states so as to equalize the system′s parameters with each of them "from stage to stage." The sought variables are intermediate-equilibrium levels, when the process goes through several states, with its intense variables being equalized with variables characterizing the environmental state in each. It is desirable to select these states at such a level that the entropy decrease turns out to be maximum.

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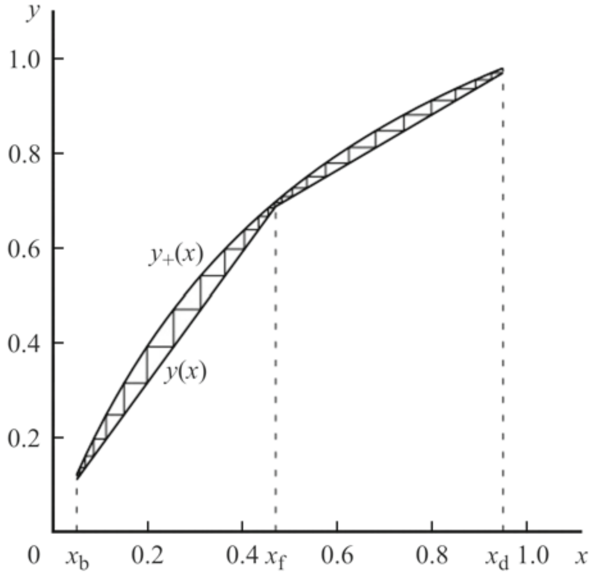

Fig. 1. Approximation of the monotonic step function.

The two mentioned classes of problems are the reverse of each other to a degree. In the problems on minimum dissipation, the time of the process is limited. In the problems on intermediate equilibria, each process of equalization of the system′s parameters with the parameters of the intermediate reservoir lasts indefinitely, so that the total duration of the process grows as many times as the number of intermediate equilibria grows. Dissipation tends to zero only when the number of intermediate equilibria tends to infinity.

In a number of cases, sought is the dependence of the number of stages k on the required degree of approximation or of the number of intermediate equilibria on the entropy increment in the process "from stage to stage."

Problems of Stepwise Approximation. Let the $x(t)$ function be prescribed such that the integral $X = \int_0^{t_k} x(t)\,dt$ exists. The derivative is $\frac{dx}{dt} < 0$. It is necessary to find such "discontinuity points" t_i, $i = 1, 2, \ldots, k$ that

$$I = \int_0^{t_k} (x(t) - x_s(t))\,dt \quad \to \quad \min/x_s(t) = x(t_i) \quad \text{at} \quad t_{i-1} < t \le t_i \ , \quad t_k - \text{fix} \ . \tag{1}$$

The value of the function I may be written as

$$I = X - X_s = X - \int_0^{t_k} x_s(t)\,dt = X - \sum_{i=1}^{k} x(t_i)(t_i - t_{i-1}) \ , \quad t_0 = 0 \ .$$

The minimum condition of this expression for t_i leads to the boundary-value problem

$$\left(\frac{dx}{dt}\right)_{t_i} (t_i - t_{i-1}) + x(t_i) - x(t_{i+1}) = 0 \ , \quad t_0 = 0 \ , \quad t_k,\, x(t_k) - \text{fix} \ . \tag{2}$$

Since the function $x(t)$ and its derivative have been prescribed, Eq. (2) determines the dependence $t_i^* = \Phi(t_{i-1}, t_{i+1})$, i.e., the optimization relation.

Optimization relation. A relationship between the abscissas of the jumps may also be obtained in explicit form: $\Phi(t_{i-1}, t_i, t_{i+1}) = 0$, but in the case where this equality is solvable for t_i^* and conforms to the following conditions:

1) $t_{i-1} < \Phi(t_{i-1}, t_{i+1}) < t_{i+1}$;

2) $\Phi(t_{i-1}, t_{i+1}) = \Phi(t_{i+1}, t_{i-1})$ (symmetric function);

3) $\Phi(t_{i-1}, t_{i+1}) = \Phi[\Phi(t_{i-1}, t_i^*), \Phi(t_i, t_{i+1})]$.

The last equality corresponds to the statement that the value of t_i^* should be optimum not only for t_{i-1}, t_{i+1}, but also for t values computed by the same formula and lying between t_{i-1}, t_i and between t_i, t_{i+1}. To these conditions, there conform the functions realizing the averaging of t_{i-1}, t_{i+1}, such as the arithmetic mean or geometric mean of these values.

Example 1. Let

$$x(t) = x_0 - \alpha t \ , \quad t_k = \frac{x_0}{\alpha} \ , \quad x(t_k) = 0 \ .$$

Condition (2) will take the form

$$\frac{\alpha(t_i - t_{i+1})}{t_i - t_{i-1}} = \alpha \quad \to \quad t_i = 0.5(t_{i-1} + t_{i+1}) \ , \quad t_i = \frac{t_k}{k} i \ . \tag{3}$$

All the intervals between the "discontinuity points" must be the same and equal to t_k/k, the function Φ is the arithmetic mean, and the minimum difference between the function $x(t)$ and its step approximation is $I^* = \frac{x_0^2}{2\alpha k}$.

Example 2. Let

$$x(t) = e^{-\alpha t} \ , \quad t_k = \frac{2}{\alpha} \ , \quad x(t_k) = e^{-2} \ .$$

Condition (2) will take the form

$$t_{i-1} = t_i - \frac{1 - e^{-\alpha(t_{i+1} - t_i)}}{\alpha} \ , \quad i = 1, 2, \dots , k - 1 \ , \quad t_0 = 0 \ . \tag{4}$$

To solve the similar boundary-value problem (4), one usually employs the "shooting" method. Here, t_{k-1} is prescribed and all the remaining "discontinuity points" up to t_0 are calculated from condition (4). If it turns out that $t_0 = 0$, the problem is solved. If not, another value of t_{k+1} is prescribed and the calculation is repeated.

Uniform Approximation and Its Generalization. A uniform approximation of $x(t)$ and $x_s(t)$ (maximum-deviation minimum) may serve as another criterion for selecting "discontinuity points." The maximum deviation is obtained at the points t_i and is equal to $\Delta_i = x(t_i) - x(t_{i-1})$. In uniform approximation, these deviations are the same, so that the condition

$$\Delta_i = x(t_i) - x(t_{i+1}) = x(t_k) \quad \to \quad x(t_i) = x(t_{i+1}) + x(t_k) \ , \quad i = k - 1, k - 2, \dots \tag{5}$$

is observed. If the number of stages k is prescribed, then $x(t_k) = \frac{x_0}{k}$.

A generalization of the uniform-approximation problem is the problem of approximation of the function $x(t)$ by the step function $x_s(t)$, so that the difference between $x(t)$ and $x_s(t) < x(t)$ does not exceed the difference between $x(t)$ and a certain prescribed monotonic function $x_-(t) < x(t)$ on the interval $[0, \tau]$ at the minimum number of stages k. The requirement of minimum for k and the condition of monotony of the functions $x_-(t)$ and $x(t)$ lead to the fact that the boundaries of the $x_s(t)$ stages must lie on the plots of these functions. In this case, between the discontinuity points, there is the relationship

$$x\_ - (t\_\{i - 1\}) = x(t\_i) \ , \quad i = k, k - 1, \dots , 1 \ , \tag{6}$$

which allows finding successively, from $i = k - 1$ to $i = 1$, the boundaries of portions function $x_s(t)$ constancy at prescribed values of t_k, $x(t_k)$, and $x_-(t_k)$.

The number of stages depends on the form of $x(t)$ and $x_-(t)$ and in some problems, this number should be found as a function of their parameters. Let the variable t vary from zero to τ. We introduce the notation $\Delta x(t) = x(t) - x_-(t)$ for the difference of boundary functions.

The average height of the stage is equal to

$$h = \frac{1}{\tau} \int_0^{\tau} \Delta x(t)\, dt \,. \tag{7}$$

For the minimum and maximum number of stages, we obtain the estimates:

$$k^{\min} = \frac{x_-(0) - x(\tau)}{h}\,, \quad k^{\max} = \frac{x(0) - x_-(\tau)}{h}\,. \tag{8}$$

These estimates are not necessarily integers. If at $t = 0$ and at $t = \tau$, the values of the boundary functions are the same, the estimates of the number of stages coincide with each other. If the boundary functions depend on certain parameters, the estimates obtained from formulas (7) and (8) for the number of stages depend on these parameters, too.

For a uniform approximation, the quantity h is equal to δ, and from formulas (8) for the function $x(t) = x_0 - at$, $x_-(t) = x_0 - at - \delta$, and $x_-(t) - = 0$ at $t > \frac{x_0 -}{\delta}\, a$ and $\tau = x(0)/a$, we have $k^{\min} + 1 = k^{\max} = \frac{x_0}{\delta}$.

The boundary functions may also be monotonically increasing.

Proximity criterion of general form. Let there be prescribed the function $\eta(x, x_s)$ determining the "distance" between the functions $x(t)$ and $x_s(t) < x(t)$ and the discontinuity points t_{i-1} and t_{i+1}; the functions $\eta(x, x_s) \geq 0$, $\eta(x, x_s) = 0$. On the interval $[t_{i-1}, t_i]$, the function $x_s = x(t_i)$, and on the interval $[t_i, t_{i+1}]$, $x_s = x(t_{i+1})$. It is necessary to find t_i so that the value of the criterion of proximity of the functions $x(t)$ and $x_s(t) < x(t)$ on the interval between these points is minimum for t_i. The optimality condition is of the form

$$\frac{\partial \left(\int_{t_{i-1}}^{t_i} \eta(x, x(t_i))\, dt + \int_{t_i}^{t_{i+1}} \eta(x, x(t_{i+1}))\, dt \right)}{\partial t_i} = 0 \,. \tag{9}$$

Upon taking the integrals with allowance for the properties of the function η, we obtain the expression to calculate t_i

$$\int_{t_{i-1}}^{t_i} \left(\frac{\partial \eta}{\partial x_s} \right)_{x(t_i)} \left(\frac{dx}{dt} \right)_{t_i} dt = \eta(x(t_i), x(t_{i+1})) \,. \tag{10}$$

Intermediate Equilibria in Irreversible Thermodynamics. ***Cooling of a cup of coffee and the entropy of the universe.*** We consider the problem on how much the entropy of the Universe on cooling of a 100-gram cup of coffee from a boiling point of 373 K to a temperature of 300 K will grow. It is convenient to take the quantity of heat Q, instead of time, given up by the coffee to the ambient air at the instant t as the argument. This quantity monotonically grows with time and when the coffee temperature T becomes equal to the air temperature T^0, the quantity Q turns out to be equal to $\overline{Q} = 0.42$ $(373 - 300) = 30.7$ J. Here 0.42 is the heat capacity of 100 g of coffee in J/K. The entropy increment of the Universe is equal to

$$\Delta S = \int_0^{\overline{Q}} \left(\frac{1}{300} - \frac{1}{373 - \dfrac{Q}{0.42}} \right) dQ \,. \tag{11}$$

Evaluation of the integral leads to the expression

$$\Delta S = \frac{30.7}{300} - 0.42 \ln \frac{3000.42}{3000.42 - 30.7} = 0.0105 \text{ J/K} \,,$$

i.e., approximately a hundredth fraction of J/K. This is, certainly, not much, but many millions of such cups of coffee cool down daily.

Can we decrease ΔS with the same boundary conditions? It turns out we can, if we initially place coffee in a vacuum bottle with temperature T_1 that conforms to the inequality $T_0 > T_1 > T^0$ and wait until the coffee cools down to this intermediate temperature. After which we cool this warm coffee down to the air temperature. This two-stage process is called the process with intermediate equilibrium. The duration of such a process is twice as long as that on contact of the coffee with just air (two infinities), but the entropy growth of the Universe will decrease. This decrease depends on selection of the intermediate-equilibrium temperature.

Next, we consider the problem on how the values of intermediate equilibrium states of a thermodynamic system are selected so as to have a minimum entropy increment.

Thermodynamic process of general form. We consider a thermodynamic system of two subsystems the second of which is a reservoir. At the instant $t = 0$, the subsystems came in contact with each other, after which the intense variable of the first subsystem x (scalar, for simplicity) began to change approaching the value y_0 of the intense variable of the reservoir. This change is associated with the occurrence of the flux $g(x, y_0)$ which is positive when $x > y_0$. The flux changes the value of the intensive variable of the first subsystem, and this, by virtue of the equation of state, also changes x. So that

$$\frac{dx}{dt} = -\frac{g(x, y_0)}{C}, \quad x(0) = x_0 , \tag{12}$$

where C is the capacity of the subsystem contacting the reservoir. The dependence $g(x, y_0)$ is called the kinetic function.

In this exchange, the system′s entropy grows

$$\frac{dS}{dt} = \sigma = g(x, y_0)F(x, y_0) , \tag{13}$$

where $F(x, y_0)$ is the motive force of the process of exchange, which is equal to zero at $x = y_0$ and has the same sign, as $g(x, y_0)$, when these variables are dissimilar.

We introduce the auxiliary variable $G(t)$, i.e., the quantity of the energy or substance, transferred from the subsystem to the reservoir, at the instant t. It grows monotonically with time in accordance with the equation

$$\frac{dG}{dt} = g(x, y_0) , \quad G(0) = 0 , \quad G(\tau) = \bar{G} . \tag{14}$$

We replace the independent variable t by G. The problem on selection of intermediate equilibrium states of the reservoir will take the form

$$\Delta S = \int_0^{\bar{G}} F(x, y)\, dG \quad \rightarrow \quad \min{}_y / y(G) = y_s(G) , \quad x(G) = x_0 - \frac{G}{C} , \quad x(0) = x_0 . \tag{15}$$

Here $y_s(G)$ is the step function taking on $x(G_i)$ values at $G_{i-1} \le G \le G_i$.

Not only has the above replacement of the variable simplified the problem, but it also shows that the solution to the problem on selection of intermediate equilibrium states is not influenced by the kinetics of change. The solution only depends on the form of the motive force.

On the interval $[G_{i-1}, G_{i+1}]$, the entropy increment depends on the selection of G_i; it is equal to

$$\Delta S_i = \int_{G_{i-1}}^{G_i} F\left(x_0 - \frac{G}{C}, x_0 - \frac{G_i}{C}\right) dG + \int_{G_i}^{G_{i+1}} F\left(x_0 - \frac{G}{C}, x_0 - \frac{G_{i+1}}{C}\right) dG . \tag{16}$$

The extremum condition of this expression for G_i determines the optimum value of G_i by the interval boundaries. It is of the form

$$\frac{\partial \Delta S_i}{\partial G_i} = 0 \quad \rightarrow \quad -\frac{1}{C}\int\limits_{G_{i-1}}^{G_i} \frac{\partial F\left(x_0 - \dfrac{G}{C},\, x_0 - \dfrac{G_i}{C}\right)}{\partial\left(x_0 - \dfrac{G_i}{C}\right)}\, dG - F\left(x_0 - \frac{G_i}{C},\, x_0 - \frac{G_{i+1}}{C}\right) = 0\,. \tag{17}$$

The optimum position of intermediate equilibrium should not change, when the G_{i-1} and G_{i+1} values change places. Therefore, the solution of Eq. (17) must be a symmetric function of these two variables.

Process of cooling. The process of cooling is simpler than the thermodynamic process of general form, and the result here can be brought to an analytical expression. We consider the process of cooling of a body on contact with a reservoir whose temperature may take on step values T_i^0 that are lower than the body′s initial temperature.

The temperature of the body having the heat capacity C and the initial temperature T_0 on contact with the reservoir having the temperature $T^0 < T_0$ changes in accordance with the equation

$$\frac{dT}{dt} = -\frac{q(T, T^0)}{C}\,, \quad T(0) = T_0\,, \quad q(T, T^0) > 0\,. \tag{18}$$

The entropy of the system consisting of the body to be cooled and the reservoir increases as

$$\frac{dS}{dt} = q(T, T^0)(1/T^0 - 1/T)\,, \quad S(0) = 0\,. \tag{19}$$

We introduce a new variable Q corresponding to the equation $dQ/dt = q(T, T^0)$. This is the quantity of heat transferred by the cooled body to the reservoir to the current instant of time. The quantity Q varies from zero to $\bar{Q} = C(T_0 - T^0)$.

By virtue of the invariability of the sign of the heat flux, Q depends monotonically on t. Therefore, this quantity can be made a new independent variable. On such a replacement, Eqs. (18) and (19) will take a simpler form:

$$\frac{dT}{dQ} = -\frac{Q}{C}\,, \quad T(Q) = T_0 - \frac{Q}{C}\,, \quad \frac{dS}{dQ} = (1/T^0 - 1/T(Q))\,, \quad S(0) = 0\,. \tag{20}$$

Note that upon this replacement, Eqs. (20) contain no $q(T, T^0)$ function, hence, all the implications obtained from these equations hold true for any heat-exchange kinetics. Furthermore, the process as a function of time tended to equilibrium asymptotically, and a variation in the new argument is limited by the interval $[0, \bar{Q}\,]$.

The entropy increment as a function of Q is of the form

$$\Delta S(Q) = \frac{Q}{T^0} - C \ln \frac{T_0 C}{T_0 C - Q}\,. \tag{21}$$

With account taken of the relationship between Q and T, this increment may be expressed as a function of T

$$\Delta S(T) = C\left(\frac{T_0 - T}{T^0} - \ln \frac{T_0}{T}\right). \tag{22}$$

Let the "stage temperatures" T_{i-1} and T_{i+1} be fixed. We find conditions with which the entropy increment on this interval of variation in the temperatures is minimum for T_i. This increment consists of two terms, with each following from (22)

$$\Delta S(T_i) = C\left[\left(\frac{T_{i-1} - T_i}{T_{i-1}} - \ln \frac{T_{i-1}}{T_i}\right) + \left(\frac{T_i - T_{i+1}}{T_i} - \ln \frac{T_i}{T_{i+1}}\right)\right]. \tag{23}$$

The condition of steadiness of this expression in T_i yields the optimization relation satisfying all the above-given conditions:

$$T_i^* = \sqrt{T_{i-1}T_{i+1}} \quad \rightarrow \quad \ln T_i^* = 1/2(\ln T_{i-1} + \ln T_{i+1}) \,, \tag{24}$$

so that with the optimum selection of the temperature of intermediate equilibria on a logarithmic temperature scale must be equally spaced by $\Delta = \dfrac{\ln T_0 - \ln T^0}{k}$, and

$$\ln T_i^* = \ln T_0 - i\Delta = (1 - i/k) \ln T_0 + i/k \ln T^0 \quad \rightarrow \quad T_i^* = T_0^{(1-i/k)}(T^0)^{i/k} \,. \tag{25}$$

Conditions (25) are true for any kinetics of heat exchange.

For the example with a cup of coffee, the optimum intermediate-equilibrium temperature of one vacuum bottle is $T_1 = \sqrt{373{,}300} = 334.5$ K = 61.5°C, which is two degrees lower than the average one between the initial and final temperatures.

Since the geometric mean is smaller than the arithmetic mean, the distances between the optimum equilibrium temperatures grow with i. From the values of intermediate-equilibrium temperatures, we easily determine the optimum values of heat taken from the cooled body with each such equilibrium.

Intermediate equilibria in the process of rectification. Number of column plates and their arrangement. The process of rectification is intended to separate liquid mixtures consisting of components that have different boiling points. If there are two such components, rectification is called binary. We consider below binary rectification. The component with a low boiling point is called highly volatile, and with a high one, high-boiling. The composition of the mixture is characterized by the fraction x of the highly volatile component in it [5].

The process is implemented in a column in whose lower part there is a boiler (cube), in which the temperature is close to the boiling point of the high-boiling component, and the concentration of the highly volatile component x_{b} is nearly zero. The vapor from the cube rises upward along the column and contacts the liquid (reflux) flowing down out of the condenser (dephlegmator) located above. On contact of the vapor and the reflux, the highly volatile component goes from the liquid into the vapor, and the high-boiling one, from the vapor into the liquid. This exchange is such that exchange counterflows are the same (equimolar), so that the vapor flow remains constant with height, and the liquid flow changes only due to the fact that the flow of liquid raw material at a point, where its composition is close to the composition of the reflux, enters the column and mixes with it. The concentration of the highly volatile component x_{d} in the dephlegmator is nearly 1. The column's lower part to the point of injection of raw material is called the exhausting section, and the upper part, the supporting section. In most cases, contact between the vapor and the reflux is implemented on plates (vessels in which the vapor bubbles through the liquid and the concentration of the highly volatile component in the liquid is equalized with its equilibrium concentration in the vapor), i.e., the principle of intermediate equilibrium states is implemented. Therefore, the problems on the necessary number of plates and on the concentrations with which an equilibrium should be implemented are directly related to the problems on approximation of functions by step ones.

The ratio of the condensate flow to be returned to the column in the form of a reflux to the flow removed from the column is called the reflux ratio R, and the difference in boiling points of the components is characterized by the relative-volatility coefficient $\alpha > 1$. The larger the coefficient, the easier the separation of the mixture and the smaller the number of required plates with intermediate equilibria. Therefore, it is important to find the dependence of the number of plates on α.

Let x be the concentration of the highly volatile component in the liquid, and $y(x) > x$ be the equilibrium concentration of the highly volatile component in the vapor. This dependence is of the form [6, 7]

$$y(x) = \frac{\alpha x}{1 + (\alpha - 1)x} \,. \tag{26}$$

The actual (working) concentration depends linearly on x: $y\_(x) = ax + c$, with the coefficients a and c being equal for the exhausting, lower, section:

$$a^{\mathrm{b}} = \frac{R + F}{R + 1} \,, \quad c^{\mathrm{b}} = -\frac{F - 1}{R + 1} x_{\mathrm{b}} \,, \tag{27}$$

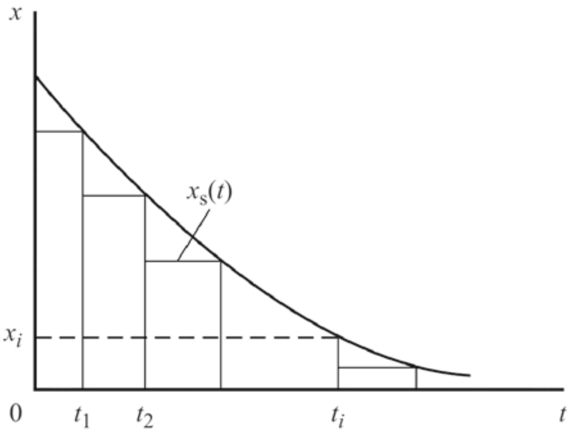

Fig. 2. Equilibrium and working concentrations and the intermediate equilibria on the plates of the rectification column.

where $F = \dfrac{x_d - x_b}{x_f - x_b}$ is the feed flow rate referred to the flow rate of distillate extracted in the column′s upper part. For the supporting, upper, section, we have

$$a^d = \frac{R}{R+1}, \quad c^d = \frac{x_d}{R+1}. \tag{28}$$

The motive force of the process of mass transfer is the difference between the working and equilibrium concentrations; it is precisely this concentration that determines the entropy production. Passage to intermediate equilibria corresponds to constructing the step function $y_s(x)$ between the lines of working and equilibrium concentrations. This function is closer to $y(x)$, which reduces the entropy production (Fig. 2).

We calculate the average height of the stage as the area of the difference of the equilibrium and working concentrations, that is referred to the change in x:

$$\bar{\Delta}_y = \frac{1}{x_d - x_b}\left[\int_{x_b}^{x_d} \frac{\alpha x}{1+(\alpha-1)x}\,dx - \int_{x_b}^{x_f}(a^b x + c^b)\,dx - \int_{x_f}^{x_d}(a^d x + c^d)\,dx\right]. \tag{29}$$

Boundary values of the equilibrium and working lines are determined as

$$y(x_d) = \frac{\alpha x_d}{1+(\alpha-1)x_d}, \quad y(x_b) = \frac{\alpha x_b}{1+(\alpha-1)x_b}, \quad y_-(x_d) = x_d, \quad y_-(x_b) = x_b. \tag{30}$$

Upon evaluating the integrals in (29), we obtain

$$\begin{aligned}\bar{\Delta}_y(\alpha) = {} & \frac{\alpha}{(x_d - x_b)(\alpha-1)}\left[x_d - x_b - \frac{\alpha}{\alpha-1}\ln\frac{1+(\alpha-1)x_d}{1+(\alpha-1)x_b}\right] - 0.5(x_d - x_b)^2 \\ & - \frac{1}{x_d - x_b}\left[c^b(x_f - x_b) + c^d(x_d - x_f) + 0.5a^b(x_f - x_b)^2 + 0.5a^d(x_d - x_f)^2\right].\end{aligned} \tag{31}$$

The number of plates k required for separation satisfies the inequalities

$$\frac{y(x_d,\alpha) - x_b}{\bar{\Delta}_y(\alpha)} \ge k \ge \frac{x_d - y(x_b,\alpha)}{\bar{\Delta}_y(\alpha)}. \tag{32}$$

The intermediate equilibrium concentrations are calculated iteratively from the formulas

$$\frac{R+F}{R+1}x_i - \frac{F-1}{R+1}x_\mathrm{b} = \frac{\alpha x_{i-1}}{1+(\alpha-1)x_{i-1}}, \quad x_0 = x_\mathrm{b} \tag{33}$$

for the exhausting ($x_i < x_\mathrm{f}$) section and

$$\frac{R}{R+1}x_i + \frac{x_\mathrm{d}}{R+1} = \frac{\alpha x_{i-1}}{1+(\alpha-1)x_{i-1}} \tag{34}$$

for the supporting ($x_i > x_\mathrm{f}$) section.

Since the vapor flow is constant over the height, the assumption can be made that the distance between the plates is proportional to the difference in concentrations of the highly volatile component in the vapor: $\delta_i = y(x_i) - y(x_{i-1})$. In this case, the distance between the plates is equal to $h_i = \frac{H\delta_i}{x_\mathrm{d} - x_\mathrm{b}}$, where H is the column height. Here, the height should be such that the minimum distance between the plates satisfies the requirement of absence of the removal of a liquid with the vapor flow. This distance is nearly 0.5 m. Plates in the vicinity of the point of injection of the feed should be arranged closer to each other. The distance between them grows as the cube and the dephlegmator are approached.

Entropy Production in the Plate Column. The entropy production in a plate column consists of two terms:

(1) the entropy production σ_q by heat exchange in the cube and the dephlegmator;

(2) the entropy production σ_g by mass transfer on the plates.

Let the flows in the cube and the dephlegmator be close to a mixing regime, the medium′s temperatures be close to the boiling points of high-boiling (HBCs) T_b and low-boiling (LBCs) T_d components, the heat-transfer coefficients be equal to β_b and β_d, and the temperature head $\Delta T = \frac{q}{\beta}$ be prescribed (usually, it is about 4 K). In this case, we have

$$\sigma_q = q\left(\frac{1}{T_\mathrm{b}} - \frac{1}{T_\mathrm{b}+\Delta T} + \frac{1}{T_\mathrm{d}-\Delta T} - \frac{1}{T_\mathrm{d}}\right). \tag{35}$$

In turn, the flux of supplied (and removed) heat can be expressed by the vapor flow from the cube and the heat of vaporization of HBCs $q = r_\mathrm{b}V_u$, and the vapor flow, by the extraction of the product from the dephlegmator and the reflux ratio R: $V_u = g_\mathrm{f}x_\mathrm{f}(R^\mathrm{f} + 1)$. Here, the separation is considered to be sharp and the entire LBC is removed from the dephlegmator.

The entropy production on the ith plate is equal to the sum of the difference in entropies on the flows going out of this plate and entering it. The vapor flow rate V_u is constant in equimolar mass exchange, and the flow rate of the reflux L depends on its composition

$$L_\mathrm{d}(x) = g_\mathrm{f}x_\mathrm{f}R \quad \text{at } x > x_\mathrm{f}\ , \ L_\mathrm{b}(x) = g_\mathrm{f}(x_\mathrm{f}R+1) \quad \text{at } x \le x_\mathrm{f}\ , \tag{36}$$

so that for the supporting section, the reflux flow rate is lower than for the exhausting one.

We will number the plates from the bottom upward and will write the entropy-production expression for the ith plate:

a) for the vapor

$$\begin{aligned}\sigma_{gi}^\mathrm{p} = V_\mathrm{u}R^0(&-[(y^0(x_i)\ln y^0(x_i)) + (1-y^0(x_i))\ln(1-y^0(x_i))] \\ &+ [(y^0(x_{i-1})\ln y^0(x_{i-1})) + (1-y^0(x_{i-1}))\ln(1-y^0(x_{i-1}))]);\end{aligned} \tag{37}$$

b) for the liquid

$$\sigma_{gi}^\mathrm{f} = L(x_i)R^0(-[x_i \ln x_i + (1-x_i)\ln(1-x_i)] + [x_{i+1}\ln x_{i+1} + (1-x_{i+1})\ln(1-x_{i+1})])\,. \tag{38}$$

Here R^0 is the universal gas constant.

The entropy production in the plate column is

$$\sigma = \sigma_q + \sum_i \sigma_{gi}^{\mathrm{p}} + \sum_i \sigma_{gi}^{\mathrm{f}} .$$

It may be smaller than in a packed column due to intermediate equilibria.

Conclusions. We have shown the relationship between the problems on approximation of monotonic functions by step functions and the problems on intermediate equilibria in thermodynamic processes. The optimum intermediate equilibrium temperatures in the process of cooling have been found. We have obtained formulas relating the number of plates in a binary-rectification column to the relative-volatility coefficients and the reflux ratio and determining equilibrium concentrations for each plate. Expressions to calculate the entropy production in a plate column have been given.

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