3. N. A. Izmailov, Solution Electrochemistry [in Russian], Khimiya, Moscow (1966).
4. M. M. Viktorov, Methods of Calculating Physicochemical Quantities and Applied Calculations [in Russian], Khimiya, Leningrad (1977).
5. J. W. Gibbs, Thermodynamic Papers [Russian translation], Goskhimizdat, Moscow (1950), pp. 228-421.
6. J. D. van der Waals, Textbook of Thermostatics [Russian translation], ONTI, Moscow (1936).
7. Yu. D. Yasin and O. V. Degtyarev, "The effects of aqueous salt solutions on cryogenic phase transformations in building materials," Papers from the North Caucasus Scientific Higher School Center: Technical Sciences [in Russian], No. 4, 84-87 (1980).
8. A. I. Ponomarev, Chemical-Analysis Methods for Silicate and Carbonate Rocks [in Russian], Izd. Akad. Nauk SSSR, Moscow (1961).
9. V. M. Moskvin and K. G. Krasil'nikov, Determination of the Corrosiveness of Water as a Medium for Concrete [in Russian], Stroiizdat, Moscow (1950).
10. Chemists Handbook [in Russian], Vol. 3, Khimiya, Moscow—Leningrad (1965).
11. L. Zak, Statistical Estimation [Russian translation], Statistika, Moscow (1976).
12. N. H. Fletcher, "Surface structure of water and ice," Philos. Mag., 7, No. 74, 255-269 (1962).
13. V. I. Kvilidze and A. V. Kurzeav, "The properties of thin layers of water indicated by NMR," in: Surface Forces in Thin Films [in Russian], Nauka, Moscow (1979), pp. 211-215.
14. G. I. Berezin, A. A. Kozlov, and L. V. Kuznetsova, "A calorimetric study of the phase transition in capillary condensate," in: Surface Forces in Thin Films and Disperse Systems [in Russian], Nauka, Moscow (1972), pp. 202-209.
15. A. V. Dumarskii, "Bound water and colloid hydrophilicity," Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 138-147 (1937).
16. V. G. Grigor'eva, "Reduction in the freezing point of water in soil," in: Papers on Laboratory Researches on Frozen Soils, Issue 3 [in Russian], Izd. Akad. Nauk SSSR, Moscow (1957), pp. 93-107.
17. A. W. Adamson, Physical Chemistry of Surfaces, Wiley (1976).
18. J. C. P. Bruckhoff and B. G. Linson, "Studies on texture in adsorbants and catalysts," in: The Structure and Properties of Adsorbants and Catalysts [Russian translation], Mir, Moscow (1973), pp. 23-84.

MODEL OF HEAT AND MASS TRANSFER IN THE DRYING PROCESS WITH THE REMOVAL OF MULTICOMPONENT LIQUID SYSTEMS

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A mathematical model of heat and mass transfer is proposed on the basis of the assumption of thermodynamic equilibrium between the liquid and the vapor removed in the course of drying.

It is often necessary to calculate the drying of a material containing a multicomponent liquid system (MLS), taking account of the change in moisture content of the material for each component, in performing many technological processes. This is a consequence, on the one hand, of stiffening of the requirements on the dried products — the final specific mass contents of each component are specified — and, on the other, of a tendency to optimize drying processes, which requires detailed study of the kinetics of MLS removal from the products.

In [1], under the assumption of thermodynamic equilibrium of the liquid and the vapor removed, the surface mass transfer in convective drying of bodies including MLS was investigated. In [2], it was shown that the values of the transfer coefficients for the MLS differ from their values for the individual liquids, which confirms the urgency of research into the drying process. In [3], a model of the drying process with removal of a binary ideal

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liquid mixture at constant pressure (or constant temperature) in the first period is proposed, on the basis of equilibrium between the liquid and the vapor over the whole volume of the material.

The present work generalizes the idea of [3] to the case of a real liquid mixture of n components with variable pressure and temperature.

Material Balance

In a medium from which MLS is removed, a sufficiently small material volume is isolated, and the parameter U_i, $U = \Sigma U_i$, x_i, y_i, $i = \overline{1, n}$, are introduced. It is assumed that U_i changes only as a result of evaporation, and the vapor content in the material is negligibly small in comparison with the liquid content. It is also assumed that the MLS composition is nonazeotropic (there is a component for which $y_{co} \neq x_{co}$). Then from the material balance of distillation (for example, [4]), it follows that

$$dx_i = (y_i - x_i)\frac{dU}{U}, \quad i = \overline{1, n}. \tag{1}$$

The system in Eq. (1) includes exactly n − 1 independent equations.

It is assumed that mainly free moisture is removed, and that diffusion of the liquid from the particle has no significant influence on the process (first period of drying); the state of the removed volume is characterized by temperature T and pressure P. Within the framework of the assumptions introduced, the composition of the vapor phase removed may be regarded as equilibrium.

The pressure is specified as a function of the temperature T

$$P = P(T) \tag{2}$$

(in drying calculations, it is often assumed that P = const over the whole of the material; it is expedient to take some account of the change in P on account of vapor filtration, using theoretical or experimental data).

The values of the parameters U, T, P, $\bar{x}$, $\bar{y}$ — altogether, 2n + 3 unknowns — are of interest here. Suppose that the vapor phase consists only of the MLS components, and that the liquid phase is unique; then, according to the Gibbs phase rule, n + 2 relations may be imposed on the 2n + 2 parameters T, P, $\bar{x}$, $\bar{y}$, so that only n of them are free. If the initial conditions for Eq. (1) are formulated, then a further n − 1 relations result. Finally, taking account of Eq. (2), altogether 2n + 2 independent relations are obtained. Hence, the whole set of 2n + 3 parameters is determined by a single independent variable. It would be natural to take the time as this variable, but then it would be necessary to consider the amount of heat supplied, which falls outside the scope of the material balance. It is assumed that the temperature T increases monotonically with time; then it may be chosen as the independent variable (this is expedient for writing the thermal balance). To find the explicit form of the dependences $\bar{x}(T)$, $\bar{y}(T)$, and U(T), a system consisting of the equations of all the above-noted relations must be written. In the mathematical formulation of the problem, Dalton's law must be written in the form

$$y_i P_e = \gamma_i x_i P_i^0, \quad i = \overline{1, n}. \tag{3}$$

Then the equilibrium pressure

$$P_e = \sum_{i=1}^{n} \gamma_i x_i P_i^0 \tag{4}$$

and

$$y_i = \gamma_i x_i \frac{P_i^0}{P_e}, \quad i = \overline{1, n}. \tag{5}$$

Differentiating the equation $P_e(\bar{x}, T) = P(T)$ with respect to T and using Eq. (1), it is found that

$$I(T)=\frac{1}{U}\frac{dU}{dT}=\frac{\dfrac{dP}{dT}-\dfrac{\partial P_e}{\partial T}}{\sum\limits_{i=1}^{n}(y_i-x_i)\dfrac{\partial P_e}{\partial x_i}}, \tag{6}$$

where I(T) determines the relation between the moisture content and the temperature. To calculate the partial derivatives in Eq. (6), specific form must be given to the dependences $\gamma_i(\bar{x}, T)$. If the Wilson equation is used [4], then

$$\gamma_i=\frac{1}{\sigma_i}\exp\left(1-\sum_{j=1}^{n}\frac{x_jA_{ji}}{\sigma_j}\right) \tag{7}$$

where

$$\sigma_j=\sum_{l=1}^{n}x_lA_{jl}, \tag{8}$$

while $A_{ij}(T)$ is determined by the binary interactions of the components (note that, in the Wilson equation, x_i is the mole fraction of the component i). Now, taking account of Eqs. (4) and (5), the expression for I(T) takes the form

$$I(T)=\frac{P'-\sum\limits_{i=1}^{n}x_i\gamma_i\left[P_i^{0\prime}+P_i^0\left(\sum\limits_{j=1}^{n}x_j\sigma_j'\dfrac{A_{ji}}{\sigma_j^2}-\dfrac{\sigma_i'}{\sigma_i}-\sum\limits_{j=1}^{n}\dfrac{x_j}{\sigma_j}A_{ji}'\right)\right]}{\sum\limits_{i=1}^{n}x_i\left(\gamma_i\dfrac{P_i^0}{P_e}-1\right)\left[\sum\limits_{j=1}^{n}x_j\gamma_jP_j^0\left(\sum\limits_{l=1}^{n}\dfrac{x_lA_{lj}A_{li}}{\sigma_j^2}-\dfrac{A_{ji}}{\sigma_j}-\dfrac{A_{ij}}{\sigma_i}\right)+\gamma_iP_i^0\right]}. \tag{9}$$

Here and below, a prime denotes differentiation with respect to T.

Thus, a closed system of equations is obtained

$$U'=UI,\ x_i'=(y_i-x_i)I,\ i=\overline{1,n}, \tag{10}$$

where the right-hand side is calculated from Eqs. (2), (4), (5), (7), and (9). Together with the initial conditions for the moisture content

$$U_i(T_0)=U_{i0},\ i=\overline{1,n}, \tag{11}$$

this system serves to determine $\bar{x}(T)$, $\bar{y}(T)$, and U(T). It may be solved using methods of integrating systems of first-order ordinary differential equations.

Thermal Balance

To find U(τ) and $\bar{x}(\tau)$ in the material volume, as shown, it is sufficient to know T(τ). However, ultimately, what is of interest is the distribution of U, $\bar{x}$, and T over the whole material — mean values are insufficient. Therefore, the given material balance is used only for small volumes in deriving the heat-conduction equation.

It is assumed that the heat is transmitted in the material only by heat conduction — heat transfer with vapor may also be taken into account by the thermal conductivity λ(T) — and only in the positive direction of the Ox axis (one-dimensional problem). Suppose that the material is motionless (there is no settling in the drying process) and the material volume coincides with the coordinate volume. Writing the heat-balance equation for the coordinate parallelepiped, and passing to the limit as Δx → 0, Δτ → 0, the ordinary heat-conduction equation is obtained

$$\frac{\partial}{\partial x}\left[\lambda(T)\frac{\partial T}{\partial x}\right]=\rho\left[c+U(T)\sum_{i=1}^{n}x_i(T)c_i(T)-U'(T)\sum_{i=1}^{n}y_i(T)r_i(T)\right]\frac{\partial T}{\partial\tau}. \tag{12}$$

The Kirchhoff substitution reduces Eq. (12) to the form

$$\frac{\partial^2 T}{\partial x^2} = \varphi(T)\frac{\partial T}{\partial \tau}, \tag{13}$$

where

$$\varphi(T) = \frac{\rho}{\lambda(T)}\left[c + U(T)\sum_{i=1}^{n} x_i(T)c_i(T) - U'(T)\sum_{i=1}^{n} y_i(T)r_i(T)\right]. \tag{14}$$

Thus, the heat-propagation process in the material being dried is described by Eq. (13) with a coefficient of the special form in Eq. (14). The quantity in square brackets may be understood to be the specific heat in a generalized sense. Calculations of $\varphi(T)$ for a series of ideal binary liquid systems [5] show that, in the temperature range presently of interest, φ changes very strongly but monotonically. Low efficiency of numerical methods of solving boundary problems for Eq. (13) would be expected, because, as shown in [6], the differential properties of the coefficients play a determining role in the numerical solution of any problem.

In the case of the first boundary problem

$$\frac{\partial^2 T}{\partial x^2} = \varphi(T)\frac{\partial T}{\partial \tau}, \quad \begin{array}{l} T(x,\ 0) = T_0,\ 0 \leqslant x < \infty, \\ T(0,\ \tau) = T_c,\ 0 < \tau < \infty, \end{array} \tag{15}$$

with a monotonically nonincreasing coefficient $\varphi(T) > 0$, a method giving the solution in the form of a smooth function with an error specified in advance is proposed below. Note that the problem in Eq. (15) is posed, for example, in calculating brief contact of the material with a heating wall.

The Boltzmann substitution transforms Eq. (15) to the equivalent two-point boundary problem for an ordinary differential equation

$$T'' + 2\xi\varphi(T)T' = 0,\ T(0) = T_c,\ T(\infty) = T_0,\ 0 < \xi = \frac{x}{2\sqrt{\tau}} < \infty, \tag{16}$$

where the prime in this case denotes differentiation with respect to ξ; the method of reduction to a Cauchy problem leads to a series of problems of the form

$$T'' + 2\xi\varphi(T)T' = 0, \quad T(0) = T_c, \quad T'(0) = z, \quad 0 < \xi < \infty. \tag{17}$$

Integration of Eq. (17) is taken in stages, in each of which an approximate solution of the Cauchy problem is constructed

$$T'' + 2\xi\varphi(T)T' = 0,\ T(\xi_i) = T_i.\ T'(\xi_i) = T'_i,\ \xi_i \leqslant \xi \leqslant \xi_{i+1}, \tag{18}$$

in the form

$$T'(z,\ \xi) = T'_i E_i(\xi,\ \varphi_m),\ T(z,\ \xi) = T_i + T'_i\int_{\xi_i}^{\xi} E_i(t,\ \varphi_m)\,dt, \tag{19}$$

where $E_i(\xi,\ \varphi_m) = \exp[(\xi_i^2 - \xi^2)\ \varphi_m]$; $\varphi_m = 1/2(\varphi_{min} + \varphi_{max})$; $\varphi_{min} = \varphi(T_i)$; $\varphi_{max} = \varphi[T_i + T'_i\ (\xi_{i+1} - \xi_i)]$. The step $(\xi_{i+1} - \xi_i)$ is chosen so as to satisfy the condition

$$|T'_i|\,\frac{\xi_{i+1}(\xi_{i+1} - \xi_i)^2(\varphi_{max} - \varphi_{min}) + (\xi_k - \xi_{i+1})\,\psi_i(\xi_{i+1})}{\xi_{i+1} - \xi_i} \leqslant \frac{\delta}{3\xi_k}. \tag{20}$$

where $\psi_i(t) = \begin{cases} E_i(t,\ \varphi_{min}) - E_i(t,\ \varphi_{max}) \text{ when } t^2 < \alpha^2 = \xi_i^2 + \dfrac{\ln\varphi_{max} - \ln\varphi_{min}}{\varphi_{max} - \varphi_{min}}, \\ \left(\dfrac{\varphi_{max}}{\varphi_{min}} - 1\right)E_i(\alpha,\ \varphi_{max}) \text{ when } t^2 \geqslant \alpha^2, \end{cases}$

δ is specified, and ξ_k is the solution of the inequality

$$|z|\sqrt{\frac{\pi}{\varphi(T_c)}}\operatorname{erfc}[\xi_k\sqrt{\varphi(T_c)}] \leqslant \frac{2}{3}\delta. \tag{21}$$

In the next step, it is assumed that $T_{i+1} = T(z,\ \xi_{i+1})$, $T'_{i+1} = T'(z,\ \xi_{i+1})$, ξ_{i+2} are chosen, and so on. The process begins with $\xi_0 = 0$ and continues until ξ_N is such that

$$\sqrt{\pi}\,|T_N' + zE_0(\xi_N, \varphi_0)|\frac{E_0(\xi_N, -\varphi_0)}{2\sqrt{\varphi_0}}\operatorname{erfc}(\xi_N\sqrt{\varphi_0}) \leqslant \left(1 - \frac{\xi_N}{3\xi_k}\right)\delta, \tag{22}$$

where

$$\varphi_0 = \varphi\left(\max\left\{T_c, T_N + \frac{\xi_N}{3\xi_h}\delta\right\}\right).$$

This ξ_N is found, and does not exceed ξ_k. For all $\xi > \xi_N$, $T(z, \xi)$ is constructed from Eq. (19) with $i = N$ and $\varphi_m = \varphi_0$. Selecting δ, z_1, and z_2 such that

$$\sup_{\xi\geqslant 0}|T(z_2, \xi) - T(z_1, \xi)| \leqslant \varepsilon - \delta, \tag{23}$$

$$T(z_1, \infty) < T_0 - \delta < T_0 < T_0 + \delta < T(z_2, \infty) \tag{24}$$

where $T(z_m, \infty)$, $m = 1, 2$, is understood to denote the asymptote of the solution, any of the functions $T(z_1, \xi)$ or $T(z_2, \xi)$ may be taken as the solution of Eq. (16); the error is no higher than ε.

The essence of the above method is the actual replacement of $\varphi(T)$ by piecewise-constant functions. Estimates of the error of the method follow from the mathematical basis, which entails significant use of analytical solutions of Cauchy problems in Eq. (18) with the constant coefficient φ.

For comparison with the method proposed, the test problem is solved using: the difference method for Eq. (15), the iterative method, for Eq. (16), and the Runge–Kutta method and the predictor–corrector method of fourth-order accuracy for Eq. (17). In all cases, one of the principal properties of the solution was disrupted: its monotonicity; the methods for Eq. (17) are unstable at large ξ, and the methods for Eqs. (15) and (16) require much machine time and converge slowly. The method proposed here automatically satisfies many physical conditions ($T' \leq 0$, $T'' \geq 0$, asymptotic behavior), gives guarenteed accuracy, and requires much less time than the difference method in machine realization.

Comparison with Experimental Data

The basic assumption of equilibrium composition of the vapor has been tested for a series of experiments on removal of the MLS acetone–methanol–water from oxyethylcellulose in vacuum–rake drying apparatus [5]. The initial data for the tests were the pressure in the apparatus (maintained constant in the course of each experiment) and the values of $U_i^E(\tau_k)$, $i = \overline{1, 3}$, $k = \overline{0, N}$.

These data are used to determine $U_k = \sum_{i=1}^{3} U_i^E(\tau_k)$, $k = \overline{0, N}$; $x_i^E(\tau_k) = \frac{U_i^E(\tau_k)}{U_k}$, $i = \overline{1, 3}$ $k = \overline{0, N}$, and then Eq. (1) is integrated by the broken-curve method according to the formulas

$$x_i^e(\tau_{k+1}) = x_i^c(\tau_k) + 2\,[y_i^c(\tau_k) - x_i^c(\tau_k)]\frac{U_{k+1} - U_k}{U_{k+1} + U_k}, \quad i = \overline{1, 3},\ k = \overline{0, N-1},$$

where $x_i^c(\tau_0) = x_i^E(\tau_0)$, $i = \overline{1, 3}$, and $y_i^c(\tau_k)$, $i = \overline{1, 3}$, is the equilibrium composition of the volume, and $U_i^c(\tau_k) = x_i^c(\tau_k)U_k$ are calculated.

A typical picture of the agreement between the calculation and experiment for the whole series of experiments is shown in Fig. 1. In the initial period, the agreement is very good; then (beginning at $\tau \approx 50$ min), marked discrepancy between calculation and experiment is observed. This difference is explained in that, in the final period, little acetone remains — $U_1^e(50) \approx 0.03$ — and its rate of diffusion from the particle plays a determining role; the vapor becomes nonequilibrium. In the initial (first) period of drying, for which the mathematical model is constructed, the assumption of equilibrium composition of the vapor removed is satisfied.

The corresponding equilibrium temperature, calculated simultaneously with $y_i^c(\tau_k)$, is an increasing function of the time, which confirms the possibility of choosing this quantity as the independent variable in the material balance.

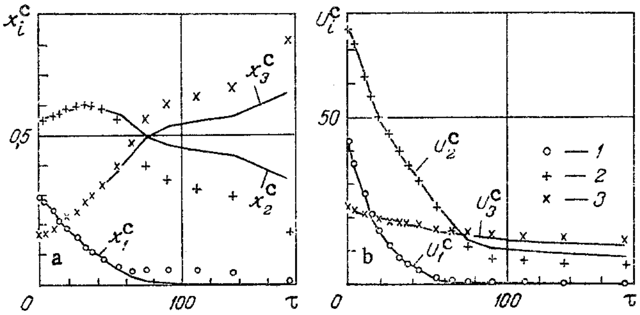

Fig. 1. Comparison of theoretical (continuous curves) and experimental (points) values of the concentration (a) and specific mass content (b): 1) acetone; 2) methanol; 3) water; time, min.

NOTATION

n, number of components in MLS (multicomponent liquid system): U, specific mass content in dry mass of material; T, temperature; P, pressure; I(T), logarithmic derivative of the specific mass content with respect to the temperature; λ(T), thermal conductivity; ρ, c, bulk density and specific heat of the dry material; $c_i(T)$, $r_i(T)$, specific heat and of vaporization of component i; $\bar{x}$, $\bar{y}$, n-dimensional concentration vectors in the liquid and vapor phases, respectively; x_i, y_i, components of the vectors $\bar{x}$, $\bar{y}$; P_e, equilibrium pressure; P^o, saturation pressure; γ, activity coefficients; $A_{ij}(T)$, coefficient in Wilson equation; x, τ, space and time variables; Δx, Δτ, increments in x and τ; ξ, variable in Boltzmann substitution; z, initial condition when ξ = 0; ε, positive constant. Subscripts: i, j, k, l, m, N, numbers; superscripts: E, c, experiment, calculation.

LITERATURE CITED

1. B. Palancz and M. Parti, "Digital simulation of multicomponent drying," Acta Tech. Acad. Sci. Hung., 81, No. 1-2, 65-74 (1975).
2. B. Palancz, "The determination of transport coefficients in three-component systems," Acta Tech., Acad. Sci. Hung., 83, No. 3-4, 229-246 (1976).
3. L. G. Golubev, V. A. Labutin, R. A. Sadykov, and E. K. Voronin, "Heat and mass transfer in the first period of drying of disperse materials, with the removal of binary liquid systems," in: Abstracts of the Proceedings of the Sixth All-Union Scientific–Technical Conference on Heat and Mass Transfer [in Russian], ITMO im. A. V. Lykov, Minsk (1980), pp. 60-61.
4. V. B. Kogan, Theoretical Principles of Typical Processes of Chemical Technology [in Russian], Khimiya, Leningrad (1977).
5. R. A. Sadykov, "Kinetics of vacuum drying of disperse materials with the removal of multicomponent liquid systems," Candidate's Dissertation, Kazan (1978).
6. K. I. Babenko (ed.), Theoretical Principles and Construction of Numerical Algorithms for Mathematical-Physics Problems [in Russian], Nauka, Moscow (1979).