## DEVELOPMENT OF A THEORY AND METHODS FOR CALCULATING THE HEAT AND MASS TRANSFER IN DRYING A POROUS BODY WITH MULTICOMPONENT VAPOR AND LIQUID PHASES

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Theoretical fundamentals and a numerical method for calculating the heat and mass transfer and phase transformations in drying porous bodies with multicomponent vapor and liquid phases have been developed. We have obtained expressions for the evaporation intensity and the phase transition heat of liquid mixture components and a formula for the equilibrium partial pressure of vapor phase components, from which, as limiting cases, empirical Raoult and Henry laws follow. The results of comparison between the calculated and experimental data are presented.

**Introduction.** The creation and optimization of modern drying technologies require a further development of the theory and methods for calculating the heat and mass transfer, the phase transformations, and deformations in porous systems.

At present, several approaches to the mathematical description of the drying process are used. The previously proposed mathematical models of the drying dynamics, in particular, the models developed by A. V. Luikov [1], Whi-taker [2], N. N. Grinchik, P. S. Kuts, and P. V. Akulich, were obtained with a number of assumptions narrowing the range of their practical application. They do not take into account the influence of material shrinkage on the dehydration dynamics while the volume of many colloidal capillary-porous bodies in the drying process decreases several times. In describing the drying process, it is commonly assumed that the liquid phase is single-component. In practice, however, the removed moisture often represents a multicomponent solution.

The drying process is strongly influenced by the activation processes associated with it, in particular, evaporation and diffusion. In the above models, the intensity of the activation processes, which sharply increases with increasing temperature, is determined approximately on the basis of the phenomenological approach. For instance, in [1] the intensity of the liquid–vapor phase transition is expressed in terms of the phase transition criterion representing the ratio of the change in the moisture-content of the body as a result of the phase transition to its total change as a result of the moisture transfer and the phase transition. Since in the physical sense moisture transfer and evaporation processes are able to proceed independently, such a technique can be considered as the replacement of one sought function by another.

## Molecular-Radiation Theory of Transfer in Drying Porous Multicomponent Systems.

1. In [4, 5], a new approach to the determination of the intensity of evaporation and diffusion processes was developed. It is based on the molecular-radiation transfer theory [6], in particular, on the law of spectral radiation intensity of particles [6, 7]

$$q_{iv} = \varepsilon_v n_{iv} i h v , \qquad (1)$$

where  $q_{iv}$  is the energy of photons of frequency v emitting per unit time unit-volume particles situated at the *i*th energy level as to frequency v; hv is the photon energy;  $n_{iv}$  is the density of particles situated, as to frequency v, at the

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*i*th energy level. The emissivity of photons is  $\varepsilon \neq f(i)$ . The ratio of  $\varepsilon_{\beta\nu}$  to the effective absorption cross-section  $\sigma_{\beta\nu}$  of the particle is independent of the form of  $\beta$  particles.

From the law of the spectral radiation intensity of particles there follow the Planck formula for the blackbody emissivity and the Maxwell–Boltzmann law on the energy distribution of particles, which have been verified by many experiments.

The elementary law of thermal radiation (1) was formulated on the basis of the concept of energy transfer by material carriers continuously emitted and absorbed by matter particles. This concept is in line with the fact that all macroscopic bodies continuously emit and absorb energy.

The particle radiation law underlies the molecular-radiation theory of heat transfer which, as opposed to the phenomenological theory, also permits obtaining, along with differential transfer equations, both expressions for transfer characteristics of condensed bodies in terms of their thermodynamic parameters, and characteristics of their microparticles. From the viewpoint of this theory we obtained the integrodifferential energy transfer equation [6]

$$\frac{\partial E\left(\mathbf{r},t\right)}{\partial t} = \int_{V} \left[ E\left(\mathbf{r}+\mathbf{\eta},t-\frac{|\mathbf{\eta}|}{c}\right) - E\left(\mathbf{r},t\right) \right] \varepsilon F \Phi\left(\mathbf{\eta}\right) dV, \qquad (2)$$

where F is the effective absorption cross-section of unit volume, particles  $F = \zeta \sum_{\beta} n_{\beta} \sigma_{\beta}, 0 < \zeta < 1; \Phi = \beta$ 

 $\exp\left(-F|\mathbf{\eta}|\right)/(4\pi|\mathbf{\eta}|).$ 

In limiting cases, Eq. (2) goes over into the Fourier heat conduction equation and the hyperbolic transfer equation used to describe intensive nonstationary processes. According to Eq. (2), the heat flow through the interface between two bodies whose temperatures differ by the quantity  $\Delta T$  is [6]  $q = -3F\lambda\Delta T/4$ , i.e., it is bounded. According to the Fourier heat conduction equation, this quantity should be infinitely large, which physically is impossible. From (2) the following expression for the specific internal energy of the multicomponent body follows:

$$E = 9kT^{4} \sum_{\beta=1}^{B} \frac{n_{\beta}^{\vartheta}}{\vartheta_{\beta}^{3}} \int_{0}^{T} \frac{z^{3}dz}{\exp(z) - 1}, \quad \vartheta_{\beta} = \frac{h\nu_{\beta}}{k}, \quad \nu_{\beta} = \left(\frac{9n_{\beta}c^{3}}{8\pi\gamma_{\beta}}\right)^{1/3}.$$
(3)

The quantity  $\gamma_{\beta}$  represents the probable number of degrees of freedom of  $\beta$  component particles ( $\beta = 1, 2, ..., B$ ) exchanging energy with one standing wave. At B = 1 and  $\gamma_{\beta} = 3(c/w_3)^2/2$ , where  $w_3$  is the velocity of sound, the expressions for *E* and for the volume heat capacity  $c_V = \partial E/\partial T$  go over into Debye formulas [6]. The latter are in good agreement with the experiment; however, they have been obtained on the physically unjustified assumption that the change in the particle energy of a solid is due to the propagation throughout its volume of elastic waves each of which is realized by one degree of freedom. According to the present-day notions, the elastic wave is a consequence of the collective oscillation of atoms.

In accordance with (2) the heat conductivity coefficient  $\lambda$  for the multicomponent body is

$$\lambda = \frac{8\pi}{3c^3} \sum_{\beta} \int_{\nu} \frac{\gamma_{\beta} c_{\nu}^* \varepsilon_{\beta\nu} v^2 d\nu}{\zeta_{\beta\nu}^2 F_{\beta\nu}^2}.$$
 (4)

For the amorphous body,  $\zeta = 1$ . Therefore, the heat conductivity coefficient  $\lambda$  is proportional to the heat capacity and this agrees with the experimental data. In crystalline bodies at low temperatures, by virtue of the ordering of the structure,  $\zeta < 1$ , and these bodies, in accordance with (4) and the experiment, have a higher heat conductivity. Expression (4) qualitatively agrees also with the known approximate Debye formula for single-component bodies [6].

2. The intensity of diffusion, evaporation, thermal ionization, dissociation, and chemical reactions sharply increases with increasing temperature. This is explained by the activation of particles as a result of certain fluctuation processes whose nature has until recently been unclear. The diffusion mechanism in view of the radiation law

(1) can be explained as follows. At very low temperatures each atom of the condensed body is at the point of its equilibrium position, e.g., at a lattice site. When an electromagnetic radiation field arises in the body, a particle can absorb a photon of some frequency v' moving along the x axis corresponding to one of the degrees of freedom of the particle. Part of the absorbed photon energy hv' is expended in increasing the particle momentum by a value of  $p = h\overline{v}'/c$  and, accordingly, the kinetic energy by a value of  $E_{kin} = p^2/(2M) = (h\overline{v}')^2/(4Mc^2)$  which is usually referred to as the transfer energy. In so doing, the particle shifts relative to the equilibrium position in the direction of motion of the photon and begins to oscillate with a frequency depending on the crystalline binding forces. The second part of the energy determined from the condition  $h\overline{v}' = hv' - E_{kin}$  is expended in increasing the inert mass necessary for the considered degree of freedom of the particle. However, provided that  $E_{kin} = 0$ , the Mössbauer effect when absorption and radiation of photons by a particle occur "without recoil" and  $h\overline{v}' \approx hv'$  is realized. This takes place when the inert mass of the absorbed photon is much smaller than the particle mass or when the recoil momentum is transferred to the crystal lattice as a whole by the crystalline binding forces. The fact that for condensed bodies the conditions of the absence of recoil are usually satisfied is confirmed by the Kirchhoff radiation law, according to which "atoms absorb the same wavelengths which they radiate." Upon absorption of a photon hv' the particle is able to absorb further photons hv', whose path is parallel to the x axis, as well as photons hv'' moving in the plane normal to the x axis. Further, along with photons hv' and hv'' moving along the x and y axes of Cartesian coordinates, the particle can absorb photons hv''', whose path is normal to the plane x0y. The frequencies v', v", and v" may coincide. As photons are absorbed, the energy of the degree of freedom of the particle increases, taking on values  $E_{iv} = ihv$ , i = 1, 2, .... The same values are taken on by the quantum oscillator energy with respect to the zero level. The representation of each degree of freedom of a condensed body particle by one quantum oscillator enabled Einstein to obtain the temperature dependence of the heat capacity which agrees with experimental data in a fairly wide temperature range. The number of photons of different frequencies, which at each instant of time can be absorbed or emitted, by a particle, coincides with the number of degrees of freedom of the particle. Radiation of photons absorbed by a degree of freedom occurs in accordance with law (1). As a result of the radiation of photons, the degree of freedom of the particle drops to the zero energy level. Staying there, the particle is able to absorb a photon whose frequency is other than the frequency of the radiated photons. Precisely this fact can explain the temperature dependence of the energy distribution function in the radiation spectrum of bodies.

If the energy per degree of freedom exceeds the activation energy  $A_{\beta}$  of the particle, then it breaks the bonds with neighboring particles and executes a diffusion jump. The limiting energy level  $I_{\beta\nu}$  at which a particle of the component  $\beta$  can reside in activation processes is determined from the condition

$$I_{\beta\nu}h\nu < A_{\beta} \le (I_{\beta\nu} + 1) h\nu .$$
<sup>(5)</sup>

The particle residing at the level  $I_{\beta\nu}$  upon absorption of an  $h\nu$  photon is activated and, releasing energy  $(I_{\beta\nu} + 1)/h\nu$ , makes a diffusion transition and finds itself at the zero energy level in the adjacent cell.

The intensity of diffusion processes in a condensed system is characterized by the energy distribution function of particles and the dynamics of their movement from a given energy level to the next higher energy level. The energy distribution function of the component  $\beta$  particles in activation processes, which was found on the basis of the radiation law (1), has the form [4]

$$w_{\beta i\nu} = \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right] \left[1 - \exp\left(-\frac{(I_{\beta\nu} + 1)h\nu}{kT}\right)\right]^{-1} \exp\left(-\frac{E_{i\nu}}{kT}\right).$$
(6)

When  $I_{\beta\nu} \rightarrow \infty$ , formula (6) goes over into the Maxwell–Boltzmann distribution law.

The probable number of particles of a unit volume of the body, which in a unit time attain the activation energy and execute a diffusion jump, is [4]

$$\partial n_{\beta I_{\beta \nu}} / \partial t = \eta_{\beta \nu} w_{\beta I_{\beta \nu}} c \sigma_{\beta \nu} \chi_{\nu} = n_{\beta \nu} \varepsilon_{\beta \nu} s^{I_{\beta \nu} + 1} \left( 1 - s^{I_{\beta \nu} + 1} \right) = n_{\beta \nu} \varepsilon_{\beta \nu} / \left\{ \exp\left[A_{\beta} / (kT)\right] - 1 \right\}, \quad s = \exp\left[-\frac{h\nu}{kT}\right]. \tag{7}$$

Summing this expression over all frequencies v and then multiplying the obtained equation by the particle mass  $m_{\beta}$ , we find the mass of the component  $\beta$  particles from a unit volume attaining in unit time the activation energy:

$$G_{\beta} = \varepsilon_{\beta} \rho_{\beta} \left[ \exp\left(A_{\beta} / kT\right) - 1 \right]^{-1}, \quad \rho_{\beta} = n_{\beta} m_{\beta} = \sum_{\nu} n_{\beta\nu} m_{\beta}.$$
(8)

Since the probable number of diffusion transitions made by an atom of the kind of  $\beta$  in unit time is equal to  $G_{\beta}/\rho_{\beta}$ , and in each transition the atom covers the distance  $l_{\beta}$ , its mean velocity  $w_{\beta} = l_{\beta}G_{\beta}/\rho_{\beta}$ . According to the elementary kinetic transfer theory, the diffusion flow density of atoms of the kind of  $\beta$  through the *z* plane in the positive direction is [4]  $j_{\beta}(z) = l_{\beta}G_{\beta}(z-l_{\beta})/6$ , and in the reverse direction it is  $j_{\beta}(z) = l_{\beta}G_{\beta}(z+l_{\beta})/6$ . The resulting diffusion flow density of atoms in the *z* direction equals

$$j_{\beta} = j_{\beta}^{+} - j_{\beta}^{-} = -l_{\beta}^{2} \left( \partial G_{\beta} / \partial z \right) / 3 .$$
<sup>(9)</sup>

In accordance with (9), the quantity  $G_{\beta}$  is the mass transfer potential for condensed bodies, and for gases the equivalent quantity is the number of collisions in a unit volume per unit time of component  $\beta$  molecules having the mean free path  $l_{g\beta}$  and the mean velocity  $w_{g\beta}$ ,  $G_{g\beta} = \rho_{\beta}w_{g\beta}/l_{g\beta}$ . The expression for the flow density of the  $\beta$ th component of the gaseous mixture  $j_{g\beta} = -l_{g\beta}^2(\partial G_{g\beta}/\partial z)/3 = -l_{g\beta}w_{g\beta}(\partial \rho_{\beta}/\partial z)/3$  coincides thereby with the known formula of the elementary kinetic theory of gases.

Since determination of the  $\varepsilon_{\beta}$  value runs into certain difficulties and its change along the *z* coordinate can be neglected, we use for the mass transfer potential in condensed media the expression

$$\Omega_{\beta} = \rho_{\beta} \left\{ \exp\left[A_{\beta}/(kT)\right] - 1 \right\}^{-1}.$$
(10)

Substituting (9) into the mass equation of the  $\beta$  component [4]  $\partial \rho_{\beta} / \partial t = -\text{div} (J_{\beta})$ , where  $\rho_{\beta} = m_{\beta}n_{\beta}$ ;  $J_{\beta} = m_{\beta}j_{\beta}$ , in view of relations (8), (9) we obtain the mass transfer equation

$$\partial \rho_{\beta} / \partial t = \operatorname{div} \left( D_{\beta} \operatorname{grad} \rho_{\beta} \right) + \operatorname{div} \left[ \left( \kappa_{\beta} / T \right) \operatorname{grad} T \right] ,$$
 (11)

where

$$D_{\beta} = \frac{1}{3} l_{\beta}^{2} \varepsilon_{\beta} \left[ \exp\left(\frac{A_{\beta}}{kT}\right) - 1 \right]^{-1}; \quad \kappa_{\beta} = \frac{1}{3} \rho_{\beta} l_{\beta}^{2} \varepsilon_{\beta} \frac{A_{\beta}}{kT} \exp\left(\frac{A_{\beta}}{kT}\right) \left[ \exp\left(\frac{A_{\beta}}{kT}\right) - 1 \right]^{-2}.$$
(12)

The expression for  $D_{\beta}$  agrees well with the experimental data of [4] and at  $A_{\beta}/RT >> 1$  goes over into the empirical Arrhenius formula for solid media, and at  $A_{\beta}/RT << 1$ , into the Einstein formula for liquid media.

3. In evaporation and sublimation processes, the probable number of activated particles is determined, as in diffusion processes, by expression (8). Activated particles, losing the accumulated energy, move with equal probability in all directions. Those situated near the free surface and whose path to this surface does not exceed  $\delta^*$ , break loose from the body. The value of  $\delta^* \approx A/(\xi \rho_{\text{liq}})$ , where  $\xi = \text{const}$ , and can be considered as the thickness of the boundary layer adjoining the free surface of a rather massive condensed body in which the evaporation process proceeds. The probability of evaporation of an activated particle located at a distance  $\eta \leq \delta^*$  from the outer surface is equal [5] to  $w_e(\eta) = \frac{1}{2} \left( 1 - \frac{\eta}{\delta^*} \right)$  and the mass of particles evaporating in the elementary layer  $d\eta$  of the unit area is  $dI_e = w_e(\eta)G_\beta d\eta$ . The specific evaporation intensity of a layer of thickness  $\delta$  is determined by integrating  $dI_e$  with respect to the evaporating layer thickness [5]:

$$I_{\rm e} = \epsilon \rho_{\rm liq} \delta^* \overline{\delta} (2 - \overline{\delta}) / \left\{ 4 \left[ \exp \left( A / kT \right) - 1 \right] \right\}, \tag{13}$$



Fig. 1. Comparison of the dependences of saturated vapor pressure  $P_{\text{sat}}$  on temperature *T* for water (1) and ammonia (2) calculated by Eq. (32) to the tabulated data of [8] indicated by dots.  $P_{\text{sat}}$ , MPa; *T*, K.

where  $\overline{\delta} = \delta/\delta^*$  at  $0 < \delta < \delta^*$  and  $\overline{\delta} = 1$  at  $\delta > \delta^*$ .

The specific mass flow of condensing vapor molecules, which is determined in accordance with the Maxwell law of velocity distribution of molecules, equals

$$I_{\rm c} = f_{\rm c} m P_{\rm v} / (\sqrt{2\pi kmT}) . \tag{14}$$

At thermal equilibrium of the condensed body-gas phase system the phase temperatures and the mass flows of evaporating and condensing molecules coincide, and the vapor pressure  $P_v$  takes on the value of the equilibrium pressure of vapor  $P_{eq}$ . Under these conditions, from (13) and (14) we find

$$P_{\rm eq} = N\rho_{\rm liq}\delta^*\overline{\delta} \left(2 - \overline{\delta}\right)\sqrt{T} / \left\{ f_{\rm c} \left[\exp\left(A/kT\right) - 1\right] \right\}, \quad N = \varepsilon\sqrt{2\pi k/m}/4.$$
<sup>(15)</sup>

For massive bodies,  $\overline{\delta} = 1$ , and (15) goes over into the formula for the saturated vapor pressure

$$P_{\text{sat}} = N\rho_{\text{liq,sat}}\delta^* \sqrt{T} / \{f_c \left[\exp\left(\frac{A}{kT}\right) - 1\right]\}.$$
(16)

As is seen from Fig. 1, expression (16) under the condition that  $N\rho_{\text{liq,sat}}\delta^* = \text{const}$  agrees well with the experimental data presented in the literature [8] in the form of tables of saturated vapor and liquid on the saturation line. To find the parameters *A* and *N*, it suffices to dispose of *P*<sub>sat</sub> for two values of *T*.

From formulas (15) and (16) it follows that

$$P_{\rm eq}/P_{\rm sat} = \delta \left(2 - \delta\right) = \varphi \,. \tag{17}$$

In accordance with this expression, the condensate layer thickness  $\delta$  on the surface of a nonevaporating body in a medium with moisture  $\phi$  is equal to [5]

$$\delta = \delta^* \overline{\delta} = \delta^* \left( 1 - \sqrt{1 - P_v / P_{\text{sat}}} \right) = \delta^* \left( 1 - \sqrt{1 - \varphi} \right).$$
<sup>(18)</sup>

According to (18), as the mass of the liquid introduced into a closed isothermal cavity increases, the equilibrium condensate layer thickness on the cavity surface increases monotonically until the vapor pressure reaches the saturation pressure. A further increase in the introduced liquid mass does not lead to a change in  $\delta$ .

From formula (16) and the Clausius-Clapeyron equation the expression for the phase transition heat follows:



Fig. 2. Comparison of the dependences of partial pressures of water vapors (1 and 1'), ethyl alcohol vapors (2 and 2'), and the total pressure (3 and 3') on the molar fraction of alcohol  $x_{alc}$  in the mixture obtained as a result of the calculation (solid curves), experiments [10] (dots), and by the Raoult law (dashed curves) for the temperature of 293 K. *P*, Pa.

$$L = N \left( v_{\text{liq}} - v_{\text{g}} \right) \Phi \left( T \right), \quad \Phi \left( T \right) = \frac{\sqrt{T}}{2} \left[ \exp \left( \frac{A}{RT} - 1 \right) \right]^{-1} + \frac{A}{R\sqrt{T}} \exp \left( \frac{A}{RT} \right) \left[ \exp \left( \frac{A}{RT} - 1 \right) \right]^{-2}. \tag{19}$$

The resulting evaporation flow (sorption or desorption intensity) I on the surface of a single-component body when its temperature T is other than the temperature of the vapor-gaseous environment temperature  $T_{env}$ , is defined by the formula [5]

$$I = n\varepsilon\delta^* \left\{ \overline{\delta} \left(2 - \overline{\delta}\right) \left[ \exp\left(\frac{A}{RT}\right) - 1 \right] - \varphi_{\text{env}} \left[ \exp\left(\frac{A}{RT}_{\text{env}}\right) - 1 \right] \right\} / 4, \quad \varphi_{\text{env}} = P_{\text{env}} / P_{\text{sat}}. \tag{20}$$

In this expression, the first term between braces characterizes the evaporation intensity and the second one, the condensation (sorption) intensity. If the first term is larger than the second one, then desorption and otherwise sorption occurs.

4. The equilibrium partial pressure of the  $\beta$  component of vapor  $P_{eq\beta}$  ( $\beta = 1, 2, ..., B$ ) over the liquid mixture is found from the equality condition of the flows  $I_{e\beta} = I_{c\beta}$  of evaporating and condensing molecules:

$$P_{\rm eq\beta} = n_{\beta} \varepsilon_{\beta} \delta_{\beta}^* \overline{\delta}_{\beta} \left(2 - \overline{\delta}_{\beta}\right) \left[ \exp\left(A_{\beta}/RT\right) - 1 \right]^{-1} \sqrt{2\pi k m_{\beta} T} / (4f_{\beta}) .$$
<sup>(21)</sup>

If the thickness of the condensed mixture layer  $\delta_{\beta} \ge \delta_{\beta}^*$ , then  $\overline{\delta}_{\beta} = 1$  and  $P_{eq\beta} = P_{sat\beta}$ . The condensation coefficient  $f_{\beta}$  of the particle of the  $\beta$ th component of the vapor phase on the surface of a multicomponent liquid is expressed in terms of the condensation coefficients  $f_{\beta\gamma}$  of this particle on the pure component  $\gamma$  by means of the additive formula

$$f_{\beta} = \sum_{\gamma} f_{\beta\gamma} \Psi_{\gamma} = \sum_{\gamma} f_{\beta\gamma} U_{\gamma} / \rho_{\gamma} = f_{\beta\beta} \sum_{\gamma} (f_{\beta\gamma} U_{\gamma} / f_{\beta\beta} \rho_{\gamma}) , \quad \gamma = 1, 2, ..., B .$$
<sup>(22)</sup>

As a result of dividing (21) by Eq. (15) written for the pure  $\beta$ th component when  $P_{eq} = P_{eq\beta}^0$ ,  $\overline{\delta} = \overline{\delta}_{\beta}^0 = A_{\beta}/(n_0/\xi)$  and  $f = f_{\beta}$ , we arrive at the formula

$$P_{\rm eq\beta} = \frac{U_{\beta}}{\sum_{\beta} U_{\beta}} \frac{\delta_{\beta}^{*} \overline{\delta}_{\beta} (2 - \overline{\delta}_{\beta}) f_{\beta}^{0}}{\delta_{\beta}^{*0} \overline{\delta}_{\beta}^{0} (2 - \overline{\delta}_{\beta}^{0}) f_{\beta}} P_{\rm eq\beta}^{0} .$$
<sup>(23)</sup>

When  $\delta_{\beta} \ge \delta_{\beta}^*$ ,  $m_{\beta} = m = \text{const}$  and  $f_{\beta} = f_{\beta}^0$ , from (23) the empirical Raoult law



Fig. 3. Temperature dependences of partial pressures of water (solid curves) and ethyl alcohol (dashed lines) vapors and their comparison to the tabulated data of [10] (dots) at various molar fractions of water  $x_w$  and  $x_{alc}$  in the solution: 1)  $x_{alc} = 1$ ; 2)  $x_w = 1$ ; 3, 3')  $x_w = 0.2$ ;  $x_{alc} = 0.8$ ; 4, 4')  $x_w = 0.5$ ,  $x_{alc} = 0.5$ ; 5, 5')  $x_w = 0.7$ ,  $x_{alc} = 0.3$ . *P*, Pa; *T*, K.

$$P_{\rm eq\beta} = P_{\rm eq\beta}^0 n_{\beta} / \sum_{\beta} n_{\beta} = P_{\rm eq\beta}^0 x_{\rm liq\beta}$$
(24)

follows for the ideal solution of liquids, whose mixing occurs without a change in the volume, with molecules having similar properties when  $U_{\beta} / \sum_{\beta} U_{\beta} = n_{\beta} m_{\beta} / \sum_{\beta} (n_{\beta} m_{\beta}) \approx n_{\beta} / \sum_{\beta} n_{\beta} = x_{\text{liq}\beta}$ . Let us write (23) for the massive layer of a binary ultimately diluted solution of the component  $\beta = 2$  in solvent  $\beta = 1$  in the form  $P_{\text{eq}2} = K_2 x_{\text{liq}2}$ , where  $K_2 = k_2 x_{\text{liq}2}$ .

 $m_2 f_2^0 P_{eq2}/(m_1 f_2) \neq P_{eq2}^0$ . The formula for  $P_{eq2}$  represents the empirical Henry law, and the expression for  $K_2$  discloses the physical meaning of the Henry constant.

Figure 2 presents the dependences of partial pressures of water and ethyl alcohol vapors and the total pressure on the molar fraction of alcohol  $x_{alc}$  in the mixture obtained experimentally [9] and as a result of calculations by formulas (23) and (24). The calculation by formula (23) agrees with the experimental data, while the error in the calculations made on the basis of the Raoult law (24) is rather high. The temperature dependences of partial pressures of water and ethyl alcohol vapors (Fig. 3) plotted on the basis of formula (23) and tabular data are in good agreement.

The phase transition heat of the volatile  $\beta$  component ( $\beta = 1, 2, ..., B$ ) of a solution containing B nonvolatile components and  $\hat{B}$  inert gases at temperature *T* is equal to

$$L_{\beta} = (v_{g\beta} - v_{liq\beta}) n_{\beta} \varepsilon_{\beta} \delta_{\beta}^{*} \overline{\delta}_{\beta} (2 - \overline{\delta}_{\beta}) \sqrt{2\pi k m_{\beta}} \Phi (T, A_{\beta}) / (4f_{\beta})$$
$$- v_{liq\beta} \left\{ \left[ \left( 1 - \sum_{\beta}^{B} (1/v_{liq\beta}) / \sum_{\beta}^{B} (1/v_{g\beta}) \right) T \sum_{\beta}^{\hat{B}} (\hat{R}_{\beta} \hat{U}_{\beta}) \right] / \left[ 1 - \widetilde{\Psi} - U / \sum_{\beta}^{B} (1/v_{liq\beta}) \right] + P_{cap} \right\}.$$
(25)

Here U and  $\hat{U}_{\beta}$  are the volume concentrations of all volatile components and the inert component;  $\tilde{\Psi}$  is the volume fraction of all nonvolatile components.

Disposing of the functions  $I_{e\beta}$ ,  $I_{c\beta}$ , and  $P_{eq\beta}$ , we write the expression for the resulting specific evaporation flow of the *i*th component in the mixture in the form

$$I_{\beta} = \frac{1}{4} \frac{U_{\beta}}{\mu_{\beta}} N_{\beta} \delta^* \left\{ \overline{\delta}_{\beta} \left(2 - \overline{\delta}_{\beta}\right) \left[ \exp\left(\frac{A_{\beta}}{RT}\right) - 1 \right]^{-1} - \varphi_{\text{env}\beta} \left[ \exp\left(\frac{A_{\beta}}{RT_{\text{env}}}\right) - 1 \right]^{-1} \right\},$$
(26)

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where  $N_{\beta} = \varepsilon_{\beta} \sqrt{2\pi k/m_{\beta}}/4$ . The condensed layer thickness of the mixture on a nonevaporating surface is

$$\delta_{\text{mix}} = \max\left\{\delta_{\beta}^{*} \left(1 - \sqrt{1 - \varphi_{\beta}}\right)\right\}.$$
(27)

In the second period of drying when  $U_{\beta}|_{\nu=0}$  approaches the corresponding equilibrium value, the evaporation intensity of the component is determined from the equation

$$I_{\beta} = -D_{\beta} \left( \partial U_{\beta} / \partial x \right)_{\nu=0}.$$
<sup>(28)</sup>

5. The intensity of the liquid-vapor phase transition  $I_{V\beta}$  in the capillaries of a unit volume of a porous body is proportional to the product of  $I_{\beta}$  by the contact area S of the liquid and gas phases. The value of S can be determined through the differential size distribution function of pores F(r) = dV/dr, where dV is the total volume of pores with a radius from r to r + dr in a unit volume of the body. The total length of capillaries with a radius from r to r + dr is equal to  $F(r)dr/(\pi r^2)$ . We assume that a liquid-gas contact can arise only in open capillaries of radius  $r > \delta_{\text{mix}}$ . According to (27), it is assumed that at each instant of time t on the surface of a capillary of radius  $r > \delta_{\text{mix}}$  a condensate layer of thickness  $\delta_{\text{mix}}(T, \varphi_{\text{mix}})$  is formed, and capillaries of radius  $r \le \delta_{\text{mix}}$  are completely filled with the liquid. Then the contact area of the liquid and gas phases in capillaries of a unit volume of the body with radii from r to r + dr at  $r > \delta_{\text{mix}}$  will equal  $dS = F(r)2\pi(r - \delta_{\text{mix}})dr/(\pi r^2)$ . The total contact area of the phases is

$$S = \int_{r_{\min}+\delta_{\min}}^{r_{\max}} dS = 2 \int_{r_{\min}+\delta_{\min}}^{r_{\max}} \frac{F(r)}{r} dr - 2\delta^* \left(1 - \sqrt{1 - \varphi_{\min}}\right) \int_{r_{\min}+\delta_{\min}}^{r_{\max}} \frac{F(r)}{r} dr .$$
(29)

In accordance with expression (26) and the condition that the temperatures of the phases at each point of the body coincide, the volume evaporation intensity is

$$I_{V\beta} = \gamma_{V\beta} \frac{U_{\beta}}{\mu_{\beta}} N_{\beta} \delta^* \left[ \exp\left(\frac{A_{\beta}}{RT}\right) - 1 \right]^{-1} \left[ \overline{\delta}_{\beta} \left(2 - \overline{\delta}_{\beta}\right) - \varphi_{\beta} \right].$$
(30)

Here  $\varphi_{\beta} = P_{\beta}/P_{\text{sat}\beta}(T)$ ;  $\gamma_{V\beta} = \gamma_{V0\beta}S$ ,  $0 < \gamma_{V0\beta} \le 1$ .

The pressures of the vapor-gas mixture  $P_g$  and the liquid mixture in the body pores are expressed in terms of the temperature *T*. The volume concentrations of liquid  $U_\beta$  ( $\beta = 1, 2, ..., B$ ) and vapor  $U''_\beta$  ( $\beta = 1, 2, ..., B$ ) volatile

components and inert gas  $\hat{U}_{\beta}$  ( $\beta = 1, 2, ..., \hat{B}$ ) and nonvolatile liquid  $\tilde{U}_{\beta}$  ( $\beta = 1, 2, ..., \tilde{B}$ ) components are expressed as follows. The volume fraction of liquid components in a porous body  $\Psi = \sum_{\beta}^{B} (U_{\beta}/\rho_{\beta}) + \sum_{\beta}^{B} (\tilde{U}_{\beta}/\tilde{\rho}_{\beta})$ , where  $\rho_{\beta}$ 

and  $\tilde{\rho}_{\beta}$  are the true densities of these components. The volume fraction of the vapor-gas mixture  $\Psi_g$  is determined through the volume fractions of components of the liquid  $\Psi$  and the solid skeleton  $\Psi_s$ :  $\Psi_g = 1 - \Psi_s - \Psi$ . The partial densities of vapor and inert gas components in the vapor-gas mixture are equal to  $\rho_{\beta}'' = U_{\beta}'/\Psi_g$ ,  $\hat{\rho}_{\beta} = \hat{U}_{\beta}/\Psi_{\beta}$ , and their partial pressures  $P_{\beta}$  and  $\hat{P}_{\beta}$  are found from the equation of state for the gas. The pressure in the liquid phase is determined by the sum

$$P_{\rm liq} = \sum_{\beta}^{\rm B} P_{\beta}'' + \sum_{\beta}^{\rm B''} \hat{P}_{\beta} + P_{\rm cap} , \qquad (31)$$

where  $P_{cap}$  [10] is found as the mean capillary pressure of the liquid in the porous body capillaries whose walls are covered with a liquid layer:

$$P_{\rm cap} = \sigma_{\rm mix} \left(T\right) \int_{r_{\rm min}+\delta_{\rm mix}}^{r_{\rm max}} F dr \bigwedge_{r_{\rm min}+\delta_{\rm mix}}^{r_{\rm max}} \Theta F dr = \frac{\sigma_{\rm mix} \left(T\right)}{r^{*}}.$$
(32)

The volume fraction  $\theta$  of the liquid in a capillary of radius r is determined from the expressions

$$\theta(T, \phi, r) = \pi \frac{[r^2 - (r - \delta_{\min})^2]}{\pi r^2} = \frac{2\delta_{\min}}{r} - \frac{\delta_{\min}^2}{r^2}, \quad r > \delta_{\min}; \quad \theta(T, \phi, r) = 1, \quad r \le \delta_{\min}.$$
(33)

The characteristic radius of pores  $r^*$  lies in the range  $r_{\min} + \delta_{\min} < r^* < r_{\max}$ . The surface tension of the mixture  $\delta_{\min}$  can be determined approximately through the surface tensions of the pure components by the expression  $\delta_{\min}^{1/4} = \sum_{\beta} x_{\text{liq}\beta} \sigma_{\beta}^{1/4}$  obtained on the basis of the McLeod–Sugden formula.

From the expressions for  $\theta(T, \varphi, r)$  and F(r) the following formula for the volume concentration of the liquid in a porous body which is at equilibrium with humid air follows:

$$U(T, \varphi) = \rho_{\min} \int_{r_{\min}}^{r_{\max}} \theta(T, \varphi, r) F(r) dr.$$
(34)

For a given temperature formula (34) represents a desorption isotherm.

6. In constructing the system of equations of heat transfer in drying capillary-porous bodies with a multicomponent liquid phase, we use the differential equation of substance (energy, mass, momentum) transfer in a deformable body presented in [11]

$$\frac{\partial W}{\partial t} = -\nabla J_W + I_W - \frac{W}{1 + \varepsilon_V} \frac{\partial \varepsilon_V}{\partial t}.$$
(35)

In the case where the relative volume deformation  $\varepsilon_V = 0$ , expression (35) goes over into the known Umov equation.

The flux density  $J_W$  of substance W in the general case is composed of the diffusion  $J_W^d$  and filtration  $J_W^f$  components:  $J_W = J_W^d + J_W^f$ . Component  $\beta$  ( $W = U_\beta$ ) mass transfer is realized under the action of the volume concentration and temperature gradients  $J_\beta^d = -D_\beta(\nabla U_\beta + \kappa_\beta \nabla T)$ . The diffusion energy flux density  $J_q^d$  is composed of the heat fluxes arising as a result of the heat conduction and diffusion of the mass of the components:  $J_q^d = -\lambda \nabla T + \sum E_\beta J_\beta^d$ .

The filtration flux densities of liquid and gas components are defined by the expressions  $J_{\beta}^{f} = Uw_{\text{liq}}$ ,  $\hat{J}_{\beta}^{f} = \hat{U}_{\beta}w_{\text{liq}}$ ,  $J_{\beta}^{\prime\prime f} = U_{\beta}^{\prime\prime}w_{g}$ ,  $\tilde{J}_{\beta}^{f} = \tilde{U}_{\beta}w_{g}$ . The filtration flow velocities of the liquid  $w_{\text{liq}}$  and gas  $w_{g}$  phases according to the Darcy law are proportional to their pressure gradients  $\nabla P_{\text{liq}}$  and  $\nabla P_{g}$  [1]:  $w_{\zeta} = -K_{0}K_{\zeta}\nabla P_{\zeta}/\eta_{\zeta}$ ,  $\zeta = \text{lig}$ , g.

The rate of change with time in the relative volume of the body element is [9]

$$\frac{1}{\Delta V(t)} \frac{\partial \Delta V(t)}{\partial t} = \frac{1}{1 + \varepsilon_V(t)} \frac{\partial \varepsilon_V(t)}{\partial t} = \frac{1}{1 + \varepsilon_{11}} \frac{\partial \varepsilon_{11}}{\partial t} + \frac{1}{1 + \varepsilon_{22}} \frac{\partial \varepsilon_{22}}{\partial t} + \frac{1}{1 + \varepsilon_{33}} \frac{\partial \varepsilon_{33}}{\partial t}.$$
(36)

The normal deformation tensor components  $\varepsilon_{kk}$  (k = 1, 2, 3) are related to the displacement vector components  $u_k$  in Cartesian coordinates by the relations [6]  $\varepsilon_{kk} = \frac{\partial u_k}{\partial x_k}$ . Expressions for the displacement vector components  $u_k$  can be obtained on the basis of the solution of thermoconcentration deformation equation [6], which for the case of elastic deformation where the dynamic effects can be neglected has the form

$$\mu_1 \nabla^2 \mathbf{u} + (\mu_2 + \mu_1) \operatorname{grad} \left(\operatorname{div} \mathbf{u}\right) - \operatorname{grad} \left[N\left(2\mu_1 + 3\mu_2\right)\right] + \rho F = 0.$$
(37)

Here N =  $\alpha_T(T - T_0) + \sum_{\beta} \alpha_{x\beta}(\omega_{\beta} - \omega_{\beta 0}), \ \alpha_T = (\partial x / \partial T) / x, \ \alpha_{x\beta} = (\partial x / \partial \omega_{\beta}) / x.$ 

In individual cases, the solution of the problem of deformation in drying bodies of elementary form can be obtained analytically. In particular, for a flat plate  $0 < x_1 < H$ , whose deformation is due to the inhomogeneity of the component concentration and temperature fields, which is symmetric about its midplane, the following expressions for the deformation tensor components  $\varepsilon_{kk}$  have been obtained [10]:

$$\varepsilon_{22} = \varepsilon_{33} = \frac{1}{H} \int_{0}^{H} N dx_{1} , \quad \varepsilon_{11} = \frac{1 + v_{P}}{1 - v_{P}} N - \frac{2v_{P}}{1 - v_{P}} \varepsilon_{22} .$$
(38)

As a result of the substitution into the substance transfer equation (35) of the above expressions for the diffusion coefficient and volume evaporation intensity, as well as of the relationships between the pressures, velocities, and mass flux densities of components and their volume concentrations, we have constructed a system of equations describing the interrelated processes of heat and mass transfer, phase transformations, and shrinkage in drying colloidal capillary-porous bodies with a multicomponent liquid phase:

$$\frac{\partial U_{\beta}}{\partial t} + \nabla \left( w_{\text{liq}} U_{\beta} \right) = \nabla \left[ D_{\beta} \left( \nabla U_{\beta} + \kappa_{\beta} \nabla T \right) \right] - I_{V\beta} - \frac{U_{\beta}}{1 + \varepsilon_{V}} \frac{\partial \varepsilon_{V}}{\partial t}, \quad \beta = 1, 2, ..., B ;$$
<sup>(39)</sup>

$$\frac{\partial U_{\beta}''}{\partial t} + \nabla \left( w_{g} U_{\beta}'' \right) = \nabla \left[ D_{\beta}'' \left( \nabla U_{\beta}'' + \kappa_{\beta}'' \nabla T \right) \right] + I_{V\beta} - \frac{U_{\beta}''}{1 + \varepsilon_{V}} \frac{\partial \varepsilon_{V}}{\partial t}, \quad \beta = 1, 2, ..., B ;$$

$$\tag{40}$$

$$\frac{\partial \hat{U}_{\beta}}{\partial t} + \nabla \left( w_{\text{liq}} \hat{U}_{\beta} \right) = \nabla \left[ \hat{D}_{\beta} \left( \nabla \hat{U}_{\beta} + \hat{\kappa}_{\beta} \nabla T \right) \right] - \frac{\hat{U}_{\beta}}{1 + \varepsilon_{V}} \frac{\partial \varepsilon_{V}}{\partial t}, \quad \beta = 1, 2, ..., \hat{B};$$
(41)

$$\frac{\partial \tilde{U}_{\beta}}{\partial t} + \nabla \left( w_{g} \tilde{U}_{\beta} \right) = \nabla \left[ \tilde{D}_{\beta} \left( \nabla \tilde{U}_{\beta} + \tilde{\kappa}_{\beta} \nabla T \right) \right] - \frac{\tilde{U}_{\beta}}{1 + \varepsilon_{V}} \frac{\partial \varepsilon_{V}}{\partial t}, \quad \beta = 1, 2, ..., \tilde{B} ;$$

$$(42)$$

$$c_{\rm eff}\left(\frac{\partial T}{\partial t} + w_{\rm eff}\,\nabla T\right) = \nabla \left[\lambda_{\rm eff}\nabla T + \sum_{\beta} h_{\beta}D_{\beta}\,(\nabla U_{\beta} + \kappa_{\beta}\nabla T)\right],\tag{43}$$

where

$$\begin{split} c_{\rm eff} &= c_{\rm s} U_{\rm s} + \sum_{\beta} (c_{\beta} U_{\beta}) + \sum_{\beta} (c_{\beta}^{\prime \prime} U_{\beta}^{\prime \prime}) + \sum_{\beta} (\hat{c}_{\beta} \hat{U}_{\beta}) + \sum_{\beta} (\tilde{c}_{\beta} \tilde{U}_{\beta}); \\ \lambda_{\rm eff} &= \lambda_{\rm s} U_{\rm s}^{\prime} / \rho_{\rm s} + \sum_{\beta} (\lambda_{\beta} U_{\beta}^{\prime} \rho_{\beta}) + \sum_{\beta} (\lambda_{\beta}^{\prime \prime} U_{\beta}^{\prime \prime} \rho_{\beta}^{\prime \prime}) + \sum_{\beta} (\hat{\lambda}_{\beta} \hat{U}_{\beta}^{\prime} \hat{\rho}_{\beta}) + \sum_{\beta} (\tilde{\lambda}_{\beta} \tilde{U}_{\beta}^{\prime} \hat{\rho}_{\beta}); \\ w_{\rm eff} &= \left[ w_{\rm liq} \left( \sum_{\beta} U_{\beta} + \sum_{\beta} \tilde{U}_{\beta} \right) + w_{\rm g} \left( \sum_{\beta} U_{\beta}^{\prime \prime} + \sum_{\beta} \hat{U}_{\beta} \right) \right] \Big/ \left( \sum_{\beta} U_{\beta} + \sum_{\beta} \tilde{U}_{\beta} + \sum_{\beta} U_{\beta}^{\prime \prime} + \sum_{\beta} \hat{U}_{\beta} \right). \end{split}$$

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The given additive expression of the effective heat conductivity  $\lambda_{eff}$  can only be used in the first approximation. The quantity  $\lambda_{eff}$  for capillary-porous and disperse systems depends on many factors, in particular, on the volume concentration of the phases and their components, the structure of the material, the sizes of particles and pores, the character of contacts between particles, and the influence of the convective and radiation components of the heat flow. There is a large number of calculation relations taking into account the influence of the temperature, the gas pressure, the material porosity, and the radiative energy transfer on the  $\lambda_{eff}$  value for relatively simple systems. For multicomponent and multiphase systems, the following approach to the determination of  $\lambda_{eff}$  can be used. In a system consisting of *B* parallel multicomponent layers of solid, liquid, and gas phases, the maximum value of the effective heat conductivity  $\lambda_{eff}^+$  is attained provided that the heat flow is directed along the layers, and it is equal to

$$\lambda_{\rm eff}^{+} = \sum_{b=1}^{B} \lambda_b \Psi_b \,. \tag{44}$$

For this same system, the minimum value of the effective heat conductivity  $\lambda_{eff}^-$  is attained when the heat flow is directed across the layers and fibers. It is determined in the same manner as the thermal resistance of a multilayer wall:

$$\lambda_{\text{eff}}^{-} = 1 / \sum_{b=1}^{B} (\Psi_b / \lambda_b).$$
(45)

If the layers of the system are multicomponent, then the value of  $\lambda_b$  can be determined from the additive expression  $\lambda_b = \sum_{\beta} (\lambda_{\beta} U_{\beta} / \rho_{\beta}).$ 

Since  $\lambda_{eff}^+ \ge \lambda_{eff} \ge \lambda_{eff}$ , the effective heat conductivity  $\lambda_{eff}$  in an arbitrary direction at any point of a heterogeneous layer system can be given by the following one-parameter formula:

$$\lambda_{\rm eff} \approx \Omega \lambda_{\rm eff}^+ + (1 - \Omega) \lambda_{\rm eff}^-, \quad 0 \le \Omega \le 1.$$
<sup>(46)</sup>

The weight parameter  $\Omega$  can be determined experimentally or on the basis of the data on the structure of the system. In particular, if the body can be considered as a system of fibers whose direction is equiprobable, then for it  $\lambda_{eff} = \lambda_{eff}^+/3 + 2\lambda_{eff}^-/3$ .

The specific evaporation heat  $L_{\beta}$  of the liquid component  $\beta$  inside a porous material depends on its moisture content and is composed of the specific evaporation heat of the free liquid and the specific moisture desorption energy. Equation (43) has been obtained by combining the energy equation in the form (35) and the mass transfer equation of substances (39)–(42). The second term of the right-hand side of Eq. (43), which is due to the diffusion energy transfer, can usually be neglected [1].

For the system of equations (39)-(43), the heat and mass transfer boundary conditions have the form

$$\lambda \frac{\partial T}{\partial \nu} \bigg|_{\nu=0} = \alpha \left( T_{\text{env}} - T \big|_{\nu=0} \right) - \sum_{\beta=1}^{B} \left( L_{\beta} I_{\nu\beta} \right), \qquad (47)$$

$$D_{\beta} \frac{\partial U_{\beta}}{\partial \nu} \bigg|_{\nu=0} + K_{\beta} \frac{\partial T}{\partial \nu} \bigg|_{\nu=0} = I_{\beta}, \quad \frac{\partial \tilde{U}_{\beta}}{\partial \nu} \bigg|_{\nu=0} = 0, \qquad (48)$$

$$-D_{\beta}^{\prime\prime}\frac{\partial U_{\beta}^{\prime\prime}}{\partial \nu}\bigg|_{\nu=0} + K_{\beta}^{\prime\prime}\frac{\partial T}{\partial \nu}\bigg|_{\nu=0} = \gamma_{\beta}^{\prime\prime}\bigg[\bigg(U_{\beta}^{\prime\prime}\big|_{\nu=0} - \rho_{en\nu\beta}^{\prime\prime}\Psi_{\beta}^{\prime\prime}\bigg) + \kappa_{\beta}^{\prime\prime}\Psi_{\beta}^{\prime\prime}\bigg(T\big|_{\nu=0} - T_{en\nu}\bigg)\bigg].$$
(49)

For inert gases, the mass transfer boundary conditions are written analogously to (49). Note that the latter satisfies the conditions under which the body reaches equilibrium [9].

Mesh Computing Method and Results of Numerical Experiments. The equations of system (39)–(43) are nonlinear. Their solution is possible on the basis of numerical methods. For the general case of diffusion-filtration transfer in a deformable system ( $\varepsilon \neq 0$ ), a mesh method based on the explicit three-layer scaling finite-difference scheme [12] and the procedure of breaking down the algorithm into physical factors [13] has been developed. To approximate Eq. (39) in Cartesian coordinates  $x_1$ ,  $x_2$ ,  $x_3$  on a uniform computing mesh  $x_{k,m_k} = m_k h_k$  ( $m_k = 0, 1, ..., h_k$ = const, k = 1, 2, 3),  $t_n = nl$  (n = 0, 1, ..., l > 0) the following difference equations are used:

$$\delta_t \overline{U}_{\beta} = \sum_{k=1}^3 \delta_k \left( D_{\beta} \delta_k U_{\beta} \right), \tag{50}$$

$$(1+\Omega_{\beta})\,\delta_{t}\widetilde{U}_{\beta}-\Omega_{\beta}\delta_{t}U_{\beta}^{n-1}=-\sum_{k=1}^{3}\delta_{k}\,(w_{\mathrm{lig}k}\overline{U}_{\beta})+\sum_{k=1}^{3}\left[\delta_{k}\,(D_{\beta}\delta_{k}\overline{U}_{\beta})+\delta_{k}\,(\kappa_{\beta}\delta_{k}T)\right]-I_{V\beta}\,,\tag{51}$$

$$\delta_t \widetilde{U}_{\beta} = \frac{\widehat{U}_{\beta}}{1 + \varepsilon_V} \delta_t \varepsilon_V, \tag{52}$$

where  $\delta_t \overline{W}^n = (\overline{W}_{m_1 m_2 m_3}^n - W_{m_1 m_2 m_3}^n)/l$ ;  $\delta_t \widehat{W}^n = (\widehat{W}_{m_1 m_2 m_3}^n - W_{m_1 m_2 m_3}^n)/l$ ;  $\delta_t W^{n-1} = (W_{m_1 m_2 m_3}^n - W_{m_1 m_2 m_3}^{n-1})/l$ ;  $\delta_1 (D\delta_1 W) = [(D_{m_1+1,m_2 m_3} + D_{m_1 m_2 m_3})(W_{m_1+1,m_2 m_3}^n - W_{m_1 m_2 m_3}^n) - (D_{m_1 m_2 m_3} - D_{m_1-1,m_2 m_3})(W_{m_1 m_2 m_3}^n - W_{m_1 m_2 m_3}^n)]/(2h_1^2)$ ;  $\delta_t \widetilde{W}^n = (W_{m_1 m_2 m_3}^{n+1} - \widehat{W}_{m_1 m_2 m_3}^n)/l$ .

The error of approximation of the differential equation (39) by the difference equations (50)–(52) has the order  $l + h_1^2 + h_2^2 + h_3^2$ . The necessary stability conditions for solving the system of difference equations (50–(52), which were determined on the basis of the method of conditional definition of certain sought functions of the system [6], can be written as follows:

$$l_{\beta} \le \min\left[\left(\sum_{k=1}^{3} \frac{w_{k}}{h_{k}}\right)^{-1}, \quad (1+2\Omega_{\beta})\left(2D_{\beta}\sum_{k=1}^{3} \frac{1}{h_{k}^{2}}\right)^{-1}\right].$$
(53)

The difference approximations of their stability conditions for the other equations of system (39)–(43) are written in much the same manner as for (50)–(52). The computing time step l is determined in accordance with the condition

$$l \le \min\left\{l_{\beta}, l_{\beta}^{"}, \hat{l}_{\beta}, \tilde{l}_{\beta}, l_{T}\right\},\tag{54}$$

where  $L''_{\beta}$ ,  $\hat{l}_{\beta}$ ,  $\hat{l}_{\beta}$ ,  $l_{T}$  are admissible time steps for the difference equations approximating, respectively, Eqs. (40), (41), (42), and (43). The shrinkage of capillary-porous materials can usually be neglected. In this case, in system (50)–(52) one has to assume  $\hat{U}_{\beta} = U^{n+1}_{\beta}$  and reject Eq. (52). In the absence of filtration, it is necessary to assume  $\overline{U}_{\beta} = U^{n+1}_{\beta}$  and reject Eq. (52).

On the basis of the proposed method, we have calculated the drying dynamics and kinetics of a flat layer  $0 < x_1 < H$  of a capillary-porous body with a two-component liquid phase blown symmetrically by heated air. The drying conditions were chosen so that the influence of the filtration and deformation of the material could be neglected.



Fig. 4. Distribution of the relative volume concentrations of the liquid-phase components — water  $\overline{U} = U(x)/U_0$  (solid curves) and ethyl ether  $\overline{U}_{alc} = U_{alc}(x)/U_{alc0}$  (dashed lines) — over the silicate plate thickness at a drying agent temperature  $T_{env} = 393$  K at different instants of time: 1, 1') t = 5 min; 2, 2') 10; 3, 3') 20; 4, 4') 40; 5, 5') 56.3; 6, 6') 90; 7, 7') 120.



Fig. 5. Change with time in the specific moisture content of the capillary-porous body — a silicate plate of thickness 12 mm symmetrically blown by the drying agent: a) for the case of the single-component liquid phase (1 and 1' for water; 2 and 2' for alcohol); b) for the ethyl alcohol solution (40 vol. %) in water (1 and 1' for the solution; 2 and 3 for the solution components — water and alcohol).  $T_{env} = 323$  K, w = 3.5 m/sec, d = 8 g/kg of dry air.  $\omega$ , %; t, min.

Figure 4 presents the results of the calculation of the dynamics of drying a capillary-porous layer (lime-andsand brick) of thickness 12 mm, in which the liquid phase is a mixture of water (60 vol. %) and ethyl alcohol (40 vol. %), by means of a coolant with a temperature  $T_{env} = 323$  K, velocity w = 3.5 m/sec, and moisture content d =8 g/kg of dry air. The initial value of the layer temperature was  $T_0 = 293$  K and that of the volume fraction of the liquid phase was 0.35. It is seen from the figure that as the moment of completion of the first period of drying is approached, at the outer boundary of the layer x = H the volume concentrations of both components of the liquid phase simultaneously tend to equilibrium values. The results of the numerical and physical experiments on the drying kinetics of the same system presented in Fig. 5 are in good agreement.

**Conclusions.** A mathematical model of the heat and mass transfer, phase transformations, and deformation in drying porous bodies with multicomponent vapor and liquid phases has been constructed. We have obtained expressions for the evaporation intensity and heat of the phase transition of the liquid phase components, as well as a for-

mula for the equilibrium partial pressure of the vapor phase components, from which the empirical Raoult and Henry laws follow. A mesh computing method based on the explicit three-layer scaling finite-difference scheme and the procedure of breaking down the algorithm into physical parameters has been developed. The results of the numerical and physical experiments point to the possibility of using the theoretical results presented for calculating and optimizing the drying conditions for capillary-porous and colloidal capillary-porous materials.

## NOTATION

A, activation energy, J; b, ordinal number of the substance layer in a flat heterogeneous system; B, number of layers in the system; c, velocity of light, m/sec;  $c_{\beta}$ , mass isobaric heat capacity of the  $\beta$  component, J/(kg·K);  $c_V$ , heat capacity per unit volume, J/(m<sup>3</sup> K);  $c_V^*$ , heat capacity referred to one degree of freedom of the component  $\beta$  particle, J/(kg·K); d, moisture content, g/kg of dry air; D, diffusion coefficient, m<sup>2</sup>/sec; E, specific internal energy, J/m<sup>3</sup>;  $E_{kin}$ , kinetic energy of the particle, J; f, condensation coefficient;  $f_{\beta\gamma}$ , vapor condensation coefficient of the component  $\beta$  on the surface of the pure liquid component  $\gamma$ , F(r), differential size distribution function of pores; G, mass of unit-volume particles attaining in a unit time the activation energy, kg/( $m^3$ -sec); h, Planck constant, J/sec;  $h_k$ , size of the computational mesh width on the space coordinate  $x_k$  (k = 1, 2, 3), m;  $h_{\beta}$ , specific enthalpy of the component  $\beta$ , J/kg; H, plate thickness, m; i, ordinal number of the particle energy level;  $I_{\beta\nu}$ , limiting energy level at which a component  $\beta$  particle oscillating with frequency v can reside in activation processes;  $I_W$ , specific source power of substance,  $W/m^3$ ;  $j^+$ ,  $j^-$ , densities of diffusion flows of atoms through the z plane in the positive and negative directions of the z axis, kg/(m<sup>2</sup>·sec);  $J_W$ , flow density of substance; k, Boltzmann constant, J/K;  $K_0$ , total permeability of the medium;  $K_{\zeta}$ , relative permeability of the phase; l, time step of the computational mesh, sec;  $l_{\beta}$ , diffusion mean free path of the component  $\beta$  particle, m;  $l_{g}$ , mean free path of the atom, m; L, specific heat of the liquid-vapor phase transition, J/kg; m, n, ordinaly numbers of computational mesh widths on the space coordinate and in time;  $m_{\rm B}$ , mass of the  $\beta$  component particle, kg; M, mass of a photon-absorbing particle or crystal, kg;  $n_{\beta}$ , density of  $\beta$  component particles, m<sup>-3</sup>; P, density, Pa;  $P_{\beta}$ , partial pressure of the  $\beta$  component, Pa; r, radius, m;  $r^*$ , characteristic dispersion parameter of pore sizes, m; R, universal gas constant, J/(mole K); r, radius vector; S, specific liquid-gas contact area in a unit volume  $m^{-1}$ ; t, time, sec; T, temperature, K;  $u_k$ , displacement vector component along the coordinate axis  $x_k$ , m; U, volume concentration, kg/m<sup>3</sup>; v, specific volume, m<sup>3</sup>/kg; V, volume,  $m^3$ ; w, velocity, m/sec; W, transferred substance;  $\overline{W}$ , value of the grid function determined numerically in the first approximation, W = U, T;  $x_{\beta}$ , molar fraction of the component; x, y, z, Cartesian coordinates, m;  $\alpha$ , heat transfer coefficient, W/(m<sup>2</sup>·K);  $\alpha_T$ , linear thermal expansion coefficient, K<sup>-1</sup>;  $\alpha_r$ , linear shrinkage coefficient; B, number of volatile components in the mixture; B, number of nonvolatile components in the liquid mixture; B, number of inert components in the gaseous mixture;  $\gamma_V$ , volume evaporation coefficient, kg/(m<sup>3</sup>·sec);  $\delta$ , evaporated layer thickness, m;  $\delta^*$ , boundary layer thickness of a massive body in which the evaporation process is proceeding, m;  $\delta$ , relative thickness of the condensate layer;  $\delta_t$ , operator of the difference time derivative t;  $\epsilon$ , radiation coefficient of particles,  $\sec^{-1}$ ;  $\varepsilon_{\beta}$ , frequency-averaged radiation coefficient,  $\sec^{-1}$ ;  $\varepsilon_{V}$ , relative volume deformation;  $\eta$ , dynamic viscosity coefficient, Pa sec;  $\eta$ , radius vector;  $\zeta$ , overlap coefficient of particles;  $\theta$ , volume fraction of the liquid in a capillary;  $\kappa$ , thermal diffusion coefficient, kg/(m<sup>3</sup>·sec);  $\lambda$ , heat conductivity coefficient, W/(m·K);  $\lambda_{eff}^{-}$ ,  $\lambda_{eff}^{+}$ , minimum and maximum values of the effective heat conductivity, W/(m·K);  $\mu$ , molecular mass of substance, kg/mole;  $\mu_1$ ,  $\mu_2$ , Lame coefficients, N/m<sup>2</sup>; N, thermoconcentration function; v, oscillation frequency,  $\sec^{-1}$ ; v', v'', v''', frequencies of photons absorbed by the particle moving in the direction of the axes x, y, z, sec<sup>-1</sup>; v<sub>P</sub>, Poisson coefficient;  $\rho$ , density, kg/m<sup>3</sup>;  $\sigma$ , surface tension, N/m;  $\phi$ , degree of saturation of the vapor-gas mixture;  $\chi_{v}$ , density of photons of frequency v,  $1/m^3$ ;  $\Psi$ , volume fraction of the porous system occupied by a phase component;  $\Psi_b$ , volume fraction of the plate layer with the ordinal number b;  $\omega$ , specific mass content (moisture content), %;  $\Omega$ , weight parameter of the difference equation;  $\nabla$ , Hamilton operator. Subscripts: w, water; g, gas; liq, liquid; e, evaporation; c, condensation; cap, capillary; sat, saturated state; v, vapor; eq, equilibrium state; env, environment; mix, mixture; alc, alcohol; s, solid; eff, efficiency; q, energy flux;  $\beta$ , ordinal number of the component;  $\zeta$ , phase of substance; 0, initial values (subscript) and pure (single-component) phase (superscript); d, diffusion; f, filtration. Notations of the form C'',  $\hat{C}$ ,  $\hat{C}$  ( $C = U, P, \rho$ ) pertain to vapor volatile, inert gas, and nonvolatile liquid components.

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