# TRANSFER EQUATIONS IN CAPILLARY-POROUS MEDIA FOR PROBLEMS IN NONISOTHERMAL DRYING, SORPTION, AND TWO-PHASE FILTRATION

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We derive a system of equations for problems in drying, sorption, and also nonisothermal filtration when there is incomplete saturation in undeformed porous media.

In theoretical investigations of transfer processes in porous media there is no single phenomenological process that is always used [1-3]. In the theories of drying, sorption, and two-phase filtration the divergences are of a fundamental nature, although insofar as their meaning goes, they all must reflect simultaneous heat and mass exchange in porous media during phase transformations.

In order to describe the above-mentioned processes, we must make use of the laws of conservation of mass and energy. The transfer equations obtained from the conservation laws are not closed. To close them, we must determine the intensity of the mass exchange between the phases, the additional specific heat of sorption (or desorption), the transfer potentials of the liquid and vapor, and the variation of the liquid pressure $P_l$ with the moisture content W and the temperature T, and we must clarify the physical mechanism of the heat and mass transfer and obtain a relation for calculating it.

In constructing a physical model, we shall consider only undeformed porous media without structural changes. We shall assume that the shrinkage of the specimen and the change in porosity during the drying process are insignificant and that the permeability coefficients of the liquid and the vapor are equal.

In the porous medium the boundary between the two phases is subdivided into a number of individual segments with different curvatures. Applying the mass-exchange analog of the Fourier criterion, we see that local thermodynamic equilibrium (LTE) in pores with cylindrical, spherical, or plane geometry occurs after a relaxation time of $\tau_r \approx 2\cdot 10^{-10}$—$7.5\cdot 10^{-10}$ sec for a pore radius of about $10^{-7}$ m, which is, as a rule, much less than the time required for the macroprocess of drying, and therefore the LTE hypothesis is valid in the case of "intensive" drying processes as well. Under conditions of dynamic equilibrium between the liquid and the vapor, the chemical potentials of the phases must be equal:

$$\mu_{\ell}(P_{\ell},\ T) = \mu_{\mathrm{v}}(P_{\mathrm{v}},\ T), \tag{1}$$

and the liquid pressure is determined by the vapor pressure according to Kelvin's formula [4]:

$$P_{\ell} = P_s + \frac{RT}{v_{\ell}} \ln \frac{P_{\mathrm{v}}}{P_s}. \tag{2}$$

Equation (2) was experimentally verified in [4, 5], in which the limits of the applicability of (2) are also indicated. The case in which the thickness of the liquid film is less than 10 Å will not be considered here; we shall assume that in this case the body is "dry."

Usually we know from experiments the sorption (desorption) isotherms W = f(φ, T). Knowing $P_s(T)$, we can represent the isotherms in the form

$$W = f(P_{\mathrm{v}},\ T), \tag{3}$$

where $P_{\mathrm{v}}$ is the intraporous vapor pressure. From (3) we can express $P_{\mathrm{v}}$ with the aid of the inverse function

$$P_{\mathrm{v}} = F(W,\ T). \tag{4}$$

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Consequently, taking account of (4), we can write Eq. (3) in the form

$$P_{\ell} = P_s(T) + \frac{RT}{v_{\ell}} \ln \frac{F(W,\,T)}{P_s(T)}\,. \tag{5}$$

Thus, formula (5) gives us the variation of the liquid pressure as a function of the moisture content and temperature in explicit form. Unlike Kelvin's formula (2), it takes account of the specific physicochemical properties of the porous specimen.

The experimental variation of the sorption isotherms as functions of temperature is such that as T increases, there is also an increase in the liquid pressure, which leads to a heat and moisture transfer effect.

The upper limit of applicability of (5) is determined by the difficulties in carrying out the experiments for obtaining the isotherms as $\varphi \to 1$. These difficulties led to the assertion that the macropores are not filled during sorption [1]. However, experiments [5] with special thermostating systems show that as $\varphi \to 1$, the macropores are also filled, and therefore (5) is valid all the way up to the point at which the pores are completely saturated with the liquid.

If the LTE hypothesis is satisfied when the phases in a nonequilibrium process go through a number of equilibrium states, we have [2-5]

$$I = \rho_t \frac{\partial W}{\partial \tau} = \rho_t \left[ \left( \frac{\partial W}{\partial p_v} \right)_T \frac{\partial P_v}{\partial \tau} + \left( \frac{\partial W}{\partial T} \right)_{P_v} \frac{\partial T}{\partial \tau} \right]. \tag{6}$$

Differentiating the equilibrium conditions (1) with respect to temperature, we obtain the well-known Clapeyron–Clausius relation for the specific heat of sorption

$$r_c = \frac{RT^2}{v^*_{\ell}} \left( \frac{\partial \ln P_v}{\partial T} \right)_W \tag{7}$$

or, using (3), (4), we can represent (7) in the form

$$r_c = \frac{RT^2}{v^*_{\ell}} \left( \frac{\partial \ln F(W,\,T)}{\partial T} \right)_W. \tag{8}$$

Thus, we must know the sorption isotherms in order to determine the intensity of mass exchange, i.e., the variation of the capillary pressure of the liquid as a function of the moisture content and the specific heat of sorption.

In order to explain the jump in moisture content at the boundary at which two porous bodies touch, Lykov [1] introduced the concept of the transfer potential $\theta_m$ of moisture in porous bodies.

In Vol'fkovich's experimental study [5] it was established that in the equilibrium state there is equality between the capillary pressures $P^k = P_v - P_l$ in the pores throughout the volume of the system for all porous bodies (including colloidal bodies), i.e., the vapor pressure and the liquid pressure can be regarded as potentials. It should be noted that although the chemical potentials of the phases are equal in the equilibrium state, they are independent functions, since the functional relations between the variables are different in the different phases, and therefore the number of equations depends on the number of phases [3]. We write out the laws of filtration for each of the phases in the form:

$$\begin{aligned} \mathbf{u}_v &= -\frac{k f_v(\theta_v)}{\eta_v} \nabla P_v, \\ \mathbf{u}_{\ell} &= -\frac{k f_{\ell}(\theta_{\ell})}{\eta_{\ell}} \nabla P_{\ell}, \end{aligned} \tag{9}$$

where $f_v(\theta_v)$, $f_l(\theta_l)$ are the relative phase permeabilities. We write $D_l(\theta_l) \equiv k f_l(\theta_l)/\eta_l$, where $f_l(\theta_l)$ is a monotone decreasing function of the saturation $\theta_l$ of the liquid phase, and at some limiting value $\theta_l^*$ we have $D_l(\theta_l) \equiv 0$. When $\theta_l < \theta_l^*$, the liquid passes from the capillary-connected mobile state into the immobile adsorption-bound state [3]. We can determine $\theta_l^*$ by the method of nuclear magnetic resonance (NMR). The NMR method can also be used for determining the self-diffusion coefficient of the liquid in the porous body, which is related to $D_l(\theta_l)$, for example, by Darken's equation [6].

For the one-dimensional case the equations of motion of the vapor and the liquid have the form

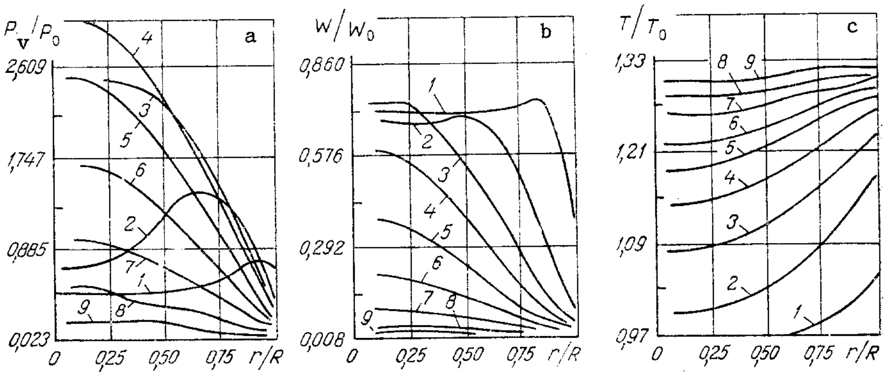

Fig. 1. Field of vapor pressures (a), moisture-content values (b), and temperatures (c) for: 1) $Fo_1 = 0.17$; 2) $Fo_2 = 0.34$; 3) $Fo_3 = 0.51$; 4) $Fo_4 = 0.68$; 5) $Fo_5 = 0.85$; 6) $Fo_6 = 1.02$; 7) $Fo_7 = 1.19$; 8) $Fo_8 = 1.36$; 9) $Fo_9 = 1.53$.

$$m\frac{\partial(\rho_v\theta_v)}{\partial\tau}=\frac{\partial}{\partial x}\left(\frac{k\rho_v f_v(\theta_v)}{\eta_v}\frac{\partial P_v}{\partial x}\right)+I, \tag{10}$$

$$m\frac{\partial(\rho_\ell\theta_\ell)}{\partial\tau}=\frac{\partial}{\partial x}\left(\frac{k\rho_\ell f_\ell(\theta_\ell)}{\eta_\ell}\frac{\partial P_\ell}{\partial x}\right)-I. \tag{11}$$

To close the system of equations (10), (11), the theory of filtration uses the universal function of instantaneous saturation [3]:

$$P_v-P_\ell=\sigma\cos\alpha\,(m/k)\,J(\theta_\ell), \tag{12}$$

where $\alpha$ is the wetting angle. Representation (12) was first proposed in [7], and $J(\theta_\ell)$ is called the Leverett function. The surface tension $\sigma$ and the boundary angle of wetting $\alpha$ are complicated functions of temperature, and for real media they are unknown; therefore such problems as capillary impregnation in the temperature field are usually omitted from consideration. For the closure of Eqs. (10), (11) we shall use the relation (5), based on Kelvin's formula and sorption isotherms.

In investigating slow flows, we may disregard the terms that take account of the variation in pressure and in the specific volume of the gas, and also of the convective transfer of energy; the energy equation is greatly simplified, and in the one-dimensional case it has the form

$$[(1-m)c_{p_t}\rho_t+m(\theta_v\rho_v c_{p_v}+\theta_\ell\rho_\ell c_{p_\ell})]\frac{\partial T}{\partial\tau}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right)+LI-mP^{\kappa}\frac{\partial\theta_\ell}{\partial\tau}. \tag{13}$$

Expression (13) differs from the equations obtained in [1-3] cheifly in being closed. For calculating the specific heat of phase transition we can use the relation (9), and for determining the intensity of mass exchange we can use the relation (6).

The system consisting of Eqs. (10), (11), (13) and the closing relations (1)-(9) can be used in problems involving drying, sorption, and filtration with incomplete saturation.

As an example, let us consider the process of drying of a cylindrical specimen of K-120 electrocellulose paper with a radius r = 0.01 m. At the initial instant of time $W_0 = 6\%$, $P_{v_0} = 1052$ Pa, and $T_0 = 293$°K. The specimen is placed in a vacuum chamber with a vapor pressure of $P_s = 13.1$ Pa. All the parameters of the problem are close to the conditions of the experiment conducted in [8]. The surface of the specimen is acted upon by a heat flux resulting from radiant heat exchange between the external surface of the coil and the radiator at a temperature $T_{rad} = 420$°K. We must calculate the nonstationary fields of moisture content, vapor pressure, and temperature. The thermophysical and transfer properties of K-120 paper were determined in [8]. Experimental measurements of the coefficient of diffusion of the liquid $k\rho_\ell f_\ell(\theta_\ell)/\eta_\ell$ (which may perhaps better be called the generalized coefficient of permeability) are not available, and therefore for our estimates we shall use permeability values obtained on the basis of the vapor; then $k\rho_\ell/\eta_\ell = 10^{-15}$ sec. To calculate the relative phase permeability, we shall use, with certain assumptions, the well-known Aver'yanov formula

$$f_\ell(\theta_\ell)=\left(\frac{\theta_\ell-\theta_\ell^*}{1-\theta_\ell}\right)^{3,5}. \tag{14}$$

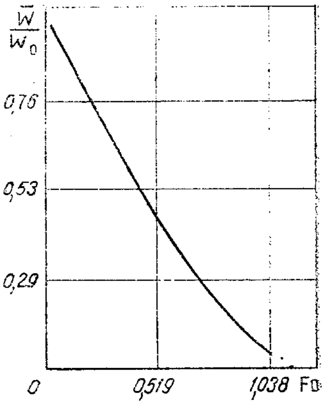

Fig. 2. Average moisture content as a function of the Fourier method.

The limiting saturation value $\theta_l^*$ for the paper was measured by the NMR method, and the corresponding value of the limiting moisture content was $W^* = m\rho_l\theta_l^* = 4\%$. Numerical calculations were carried out for the paper with a desorption isotherm of the form [8]:

$$W = A\exp(-\alpha T)(\beta P_v)^{(-\varkappa+\gamma T)}, \tag{15}$$

where A = 367935, $\alpha$ = 0.033, $\beta$ = 0.0076, $\chi$ = 0.96, $\gamma$ = 0.005. The specific heat of phase transfer of the moisture, according to (7) and taking account of (15), is:

$$r_c = \frac{RT^2}{v_\ell^*}\left[\frac{\alpha-\gamma\ln\beta}{-\varkappa+\gamma T} + \frac{\ln(W/A)+\alpha T+\varkappa-\gamma T}{(-\varkappa+\gamma T)^2}\right]. \tag{16}$$

The anisotropic liquid pressure can be calculated according to the relation (5); for isotherms of the form (15) it can be represented as

$$P_\ell = \frac{RTW}{v_\ell}\left[\frac{\ln(W/A)+\alpha T}{-\varkappa+\gamma T} - \ln(\beta C) - 15\ln\left(\frac{T}{373}\right)\right], \tag{17}$$

where C is a constant ($P_s = 10^5(T/373)^{15}$, $C = 10^5$).

The boundary conditions are:

$$\tau = 0,\ T(r,\ 0) = T_0;\ P_v(r,\ 0) = P_{v0};\ P_\ell(r,\ 0) = P_{\ell 0}, \tag{18}$$

$$r = 0,\ \left.\frac{\partial P_v}{\partial r}\right|_{r=0} = \left.\frac{\partial P_\ell}{\partial r}\right|_{r=0} = 0;\quad \left.\frac{\partial T}{\partial r}\right|_{r=0} = 0; \tag{19}$$

$$r = 1,\ P_v(1,\ \tau) = P_c;\ P_{\ell c} = P_s(T_c) + \frac{RT_c(\tau)}{v_\ell}\ln\left(\frac{P_c}{P_s}\right), \tag{20}$$

$$\lambda\left.\frac{\partial T}{\partial r}\right|_{r=1} = \sigma^*\varepsilon^*(T_{\mathrm{rad}}^4 - T_c^4(1,\ \tau)). \tag{21}$$

For the solution of the system of equations, we used the combined Euler—Lagrange (CEL) method, which was used originally to solve nonstationary hydrodynamic problems involving a moving common liquid boundary [9].

To solve the energy and motion equations for the vapor, we used numerical schemes in the Euler representation, and for the equation of motion of the liquid, when deformation of the physical system may take place as a result of capillary overflow, we used Lagrangian variables. The system of equations was solved by the method of successive approximations, and therefore the iterative cycles were organized for all equations of the system.

The calculations showed that for Fo = 1.56 the drying process comes to an end and the parameters are close to the equilibrium values, and therefore we obtained on a graph-plotter graphs up to Fo = 1.56 for 9 instants of time (k = 1, 2, ..., 9, $\Delta Fo_k = k\Delta Fo$, where Fo = 1.56/9), in order to follow the evolution of the local values of the parameters. In the graphs r = 0 corresponds to a point at a distance of 0.5h from the axis of symmetry, where h is the magnitude of the step, space (h = 1/20), r = 1 is a point at a distance of 0.5h from the surface.

Figure 1a shows that at the initial instant of time (curves 1-4) there is a wave motion of the vapor, and the front of maximum pressure is displaced into the interior of the specimen and reaches a maximum value on the axis of symmetry. Figure 1b shows the fields of moisture-content values. As a result of processes which may be characterized as "heat and moisture conduction," the moisture content may increase somewhat in the central, "cold" parts of the specimen.

Figures 1c and 2 show the temperature fields and the variation of the average moisture content of the material as a function of time. Comparison of the results of the calculations with the experimental data of [8] shows that the error in the determination of the variation of the average moisture content as a function of time up to moisture content values of W = 1.5% is no more than 15%. However, at the stage of the drying of the K-120 paper to W = 0.5%, the error increases to 30-40%, while the "theoretical" drying process comes to an end more rapidly. The divergence in the heating curves is 25-30%, and the heating time of the specimen, according to the calculations, is longer. The curves describing the variation of the local vapor pressure with time are in general difficult to compare, since it proved impossible to determine the time at which the pressure passed through the value of maximum pressure at the center of the specimen. In [8] the small vapor pressure values were measured with ordinary manometers with a large excursion and a free volume connected with tubes to medical needles, which could have led to significant distortions of the vapor pressure fields; consequently we shall not compare the calculations to the experimental data. However, it should be noted that there was good qualitative agreement between the theory and the experimental data. The vapor-pressure peaks were observed at the same instants of time, and the increase in the vapor pressure and its relaxation took place in a similar manner.

## NOTATION

k, permeability, $m^3$; m, porosity, $\theta_i$, saturation of porous medium with vapor (v) and liquid ($l$); $\sigma^*$, Stefan–Boltzmann constant; $\varepsilon^*$, emissivity; $v_l$, molar volume of liquid, $m^3$/mole; $v_l^*$, molar mass of liquid, kg/mole; R, universal gas constant; $\rho_T$, density of dry porous specimen; W, moisture content, kg/kg.

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