

ON THE KINETIC THEORY OF TRANSFER PROCESSES IN POROUS MEDIA

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This is a brief review of studies of mass transfer in porous media, using the kinetic approach.

Transfer equations in heterogeneous media (porous materials included) can be obtained by averaging the microequations for individual phases [1, 2]. However, because of the complexity of the resultant equations and expressions for the quantities describing interphase interactions, various approximate approaches and models are employed. In particular, the quasi-homogeneous approximation based on macroscopic equations similar to equations in a separate pore but with effective transfer coefficients is very popular [3].

As regards heat and mass transfer with phase transformations in porous materials, unsaturated porous media are most attractive as research objects (the relative pore volume occupied by a liquid is called the liquid saturation of the porous body). Under such conditions transfer processes become considerably more complicated because of the phase interaction inside the body. One of the methods used for the description of coupled heat and moisture transfer is based on a set of differential equations for the transfer potentials, obtained with the aid of irreversible thermodynamics [4]. This approach is widely used in drying theory. In the falling-drying-rate period the evaporation zone moves deeper into the material and evaporation occurs not only on a surface located at a depth, but also within a certain zone. This can be ascribed to different moisture-material bond forms, drying rates, and moisture recondensation inside the porous body. At a relatively high evaporation rate, when the capillary flow and recondensation fail to supply a sufficient amount of liquid to the pores being dried, the two-phase zone becomes a phase transition surface [3]. If variations of moisture contents in each of the zones are neglected, the mathematical description of heat and mass transfer in this case reduces to a Stefan-type problem.

However, in the above approach, coupled heat and moisture transfer equations do not reveal the real heat and moisture transfer mechanism and cannot be used to find the phase distribution in a porous body. Therefore, the theory of multiphase filtration is often used [2, 3, 5]. In this theory equations of Darcy type are written for the average velocities of each phase (liquid and gaseous). In this procedure, for completion of the whole set of equations of multiphase filtration, including phase changes, use is made of the expression for the pressure difference in the liquid and gaseous phases $p_{lq} - p_g = p_c(u^*)$, where, because of the assumption of local phase equilibrium between the capillary pressure p_c and the saturation u^* , the relation is expressed in terms of the Leverett function.

The main disadvantage of multiphase filtration theory is the assumption of independent motion of each phase. Therefore, of great interest are studies in which models are used to investigate the roles of the various physical processes in the phase interaction and distribution in a porous body. In particular, in [6], using the model of a pore space element, the authors analyze the roles of individual components of the mass flow (a diffusion steam flow, a thermocapillary film flow, and a viscous flow in the film induced by the gradient of capillary and wedging pressures) under local equilibrium between the liquid film and the vapor.

In the phenomenological theories of heat and mass transfer mentioned above, when they are used to treat phase transformations in porous materials, local phase equilibrium and local equilibrium mass transfer in the gas phase are assumed. However, in nonequilibrium conditions, when models of a continuum do not apply (the pore radii are comparable with the mean free path length, and transfer processes in the Knudsen layers and nonequilibrium physicochemical transformations at the pore walls are included), an adequate description of transfer processes in the

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gas phase in porous materials requires methods of physical kinetics.

The choice of kinetic methods for the description of gas flows depends on the porous body model used. In the case of a capillary model, the calculations are based on the expressions obtained in studies of gas flows in cylindrical channels for different Knudsen numbers Kn [3, 5, 7]. It should be noted that such expressions usually neglect peculiarities of the process associated with phase or chemical transformation, movable adsorbed layers in capillaries, and the evaporation boundary extended in porous materials. In [8] a study is carried out to investigate the kinetics of low-rate mass transfer in capillaries, with account of the processes mentioned above. In particular, the authors determined the range of validity of some phenomenological mass transfer relations.

It seems interesting to note that with different boundary conditions single-component gas flows in capillaries are characterized by essentially different asymptotic behavior at $\alpha \gg 1$ ($\alpha \approx 1/Kn$) (a continuum flow). When a filler evaporates from the bottom of a capillary with the radius r_0 and the length L with an impermeable cylindrical surface, the volume flow rate of gas N_z at the outlet at $\alpha \gg 8L/r_0\pi^{1/2}$ becomes constant (evaporation from the free surface). For a gas flow without evaporation N_z is proportional to α (the Poiseuille formula). However, in the case of evaporation from the inner surface

$$N_z = (1 - n_a) \frac{\sqrt{\alpha}}{2\pi^{1/4}}, \quad (1)$$

where n_a is averaged dimensionless particle density over the cross section $z = 0$. In this problem the molecular flow densities N_i in the axial and radial directions in the capillary are expressed by

$$N_i(z, r) = (n_a - 1) \exp(\beta z) f_i(r) \quad (i = z, r). \quad (2)$$

The coefficient $1/\beta$ in Eq. (2) characterizes the depth of the effective evaporation zone. For large α

$$\beta = \frac{4}{\pi^{1/4}} \frac{1}{\sqrt{\alpha}},$$

i.e. as the flow rarefaction decreases, the effective evaporation zone moves deeper. It is shown that the radial gas flow $N_r - \beta N_z$, i.e., at $\alpha \gg 1$ it is a value of a higher order of smallness than N_z .

Investigation of the heavy mass transfer kinetics in evaporation is a more complicated problem. In [9] direct statistical modeling was used to solve the problem of heavy evaporation of a filler in a porous two-dimensional body with semi-infinite periodic channels, whose thickness and depth are assumed equal to the mean molecular pathway in their order of magnitude. It is shown that the dimensionless limiting flow rates (at $M_\infty = 1$, M_∞ is the Mach number) and vapor densities at the outer boundary of the Knudsen layer are smaller than the corresponding values in the case of one-dimensional evaporation from the free surface. These values decrease with the depth. A similar problem but with evaporation from the whole inner surface of the channels is considered in [10]. In this case the limiting dimensionless flow rate is higher than that in the case when the filler evaporates only from the bottom of the channels.

When high-concentration energy fluxes act upon materials, hollows (wells) are produced because of metal melting. Analysis of numerical results obtained from solutions of the problem [11] on gas outflow into a vacuum from a well in evaporation of material from its inner surface (its temperature T_w is assumed constant) and comparison of them with results of a similar problem on evaporation in a long capillary allows the following conclusion. At $Kn = 0.2$ and $q/kT_w > 3$ (q is the energy necessary for evaporation of one atom) conditions of vapor supersaturation occur already inside the well; at distances exceeding the diameter, the vapor density is practically the same as the equilibrium density (the result obtained in the problem of low-rate evaporation is qualitatively the same). Therefore, if the well depth is larger than its diameter, then, generally speaking, it is necessary to take into consideration the effect of the gas dynamics of vapor outflow on the development of the well.

The ratio of the molecular flow Γ incident on the inner surface of the well to the maximum unilateral flow I_e ($I_e = n_e \sqrt{kT_w/2\pi m}$), n_e is the saturated vapor density at T_w) characterizes the reverse particle flow that reduces the net evaporation rate. In particular, at the edge of the well at $Kn = 0.66$ $\Gamma/I_e \approx 0.3$; at $Kn \rightarrow \infty$, $\Gamma/I_e \approx 0.5$. It should be noted that for a free molecular flow in a cylindrical capillary the equality $\Gamma/I_e = 0.5$ holds. Thus, the density of the reverse molecular flow onto the evaporating surface of the well, even at its edge, exceeds the corresponding value

in one-dimensional evaporation into a vacuum from a flat surface (in the latter case it is about 18%).

For $0 < 1/Kn < 0.1$, the ratio of the net particle flow from the well to I_e is close to unity; then it starts to rise slowly as $1/Kn$ increases.

In [12] a model is suggested for mass transfer in porous media under the action of laser radiation, but in the regime of a continuum. It uses some results of the kinetic theory of evaporation. The vapor flow from pores is considered for two limiting cases. For materials with a high permeability vapor flows out of the pore rapidly as compared with the rate of pressure increase (a "sand" model). In the other limiting case pressure rises in pores (a "tree" model). In the latter model of treelike pores very fine branches behave as if they all were cut away, and the main contribution to the outflow is made by pores from where vapor flows out very quickly.

Another model of porous materials, which allows the method of the kinetic theory of gases to be used for the description of mass transfer, is a globular model of "dusty" gas [13, 14]. In [15, 16], a new approach is applied for the description of low-intensity isothermal mass transfer for the statistical model of a highly porous body mentioned earlier. In the one-dimensional kinetic equation the collision integral is replaced by a term with an effective "external" force that results from cumulative interaction of gas molecules with immovable particles, simulating the porous framework. This approach allows simple expressions for the evaporation and gas filtration rates in the porous layer and the permeability and density drops (the inlet and outlet resistances) at the gas-porous material interface to be found as a function of the Knudsen number.

As regards the kinetics of high-rate transfer processes in evaporation (condensation) in such a model porous body, studies [17, 18] are among the first in this field. In particular, their authors determine the location of the boundaries of the moist zone in a porous layer, the flow values, and the angular distribution of gas particles as a function of the temperature drop and the condensation coefficient. It should be noted that in the published proceedings of the "Euromech-285" colloquium (Minsk, September, 1991) and of the International Workshop "The Kinetic Theory of Transfer Processes in Evaporation and Condensation" urgent problems of the kinetics of heavy evaporation and condensation, homogeneous nucleation in gases, and adsorption and desorption of gases are discussed.

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