PRESENTATION OF CERTAIN CONJUGATE PROBLEMS
OF HEAT AND MASS TRANSFER DURING PHASE AND
CHEMICAL TRANSFORMATIONS

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The problem of allowing for the kinetics of mass transfer in porous solids in the presenta-
tion of certain conjugate problems is considered.

It is well known that conjugate heat-transfer problems [1] involve the simultaneous solution of the
heat-conduction equations for the solid and the liquid flowing around it (the velocity distribution in the
liquid is determined by solving the corresponding hydrodynamic problem), i.e., the temperature or ther-
mal flux at the solid/liquid interface is not specified in advance but determined from the solution of the
problem. This approach is more correct for transient and high-intensity heat transfer [2]. It is a char-
acteristic feature that in this case the solution depends on the properties of both the liquid and the solid
around which it is flowing.

In a number of cases involving gas flow around a solid it is interesting to study heat transfer under
conditions in which phase or chemical transformations are taking place on the solid surface (especially in
sublimation or the combustion of the wall material), or in which some substance differing from the main
gas flow passes through a porous surface (in the presence of deep evaporation zones in capillary-porous
solids). Such problems are generally considered as conjugate with respect to heat transfer, i.e., the
equations of the boundary layer in the gas and the heat-conduction equation in the solid are solved simul-
taneously [3-5]. However, the mass-transfer equation in the solid is usually absent, and the mass-trans-
fer condition is specified at the gas/solid interface (for example, the condition of equilibrium or nonequilib-
rium evaporation).

In this article (which is based on investigations carried out in the Mathematical Transport Theory
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show that in certain cases, when formulating such conjugate problems for both polycrystalline and capil-
ary-porous solids, it is essential to consider the mass-transfer equation and also to allow for the kinet-
ics of transfer processes inside the solid.

1. During the high-temperature reaction of carbon on a solid surface the density of the sample was
found to alter [6, 7]. The authors in question attributed this effect to the existence of a substantial solid-
phase diffusion of atoms from the interior of the solid to its surface. The atoms from inside the solid
tended to occupy the vacancies formed in the lattice at the surface as a result of the reaction, so that the
vacancies in effect diffused into the interior.

A certain mathematical model was employed in [8] in an attempt to discover the conditions under
which a substantial contribution might be made by the diffusive flow of atoms (vacancies) through the solid
to the loosening of the structure in the presence of a surface reaction. The boundary condition for the
vacancy diffusion equation allows for the fact that, in addition to ordinary evaporation, which corresponds
to the complete removal of a surface atom from the crystal, incomplete evaporation processes have to be
taken into consideration [9]. Atoms diffusing from the inside of the solid replace vacancies formed on the

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surface, and the velocity of the reaction front diminishes. The vacancy diffusion equation and boundary condition take the form

\[
D_v \frac{d^2 c}{dx^2} = \frac{c - c_o}{\tau_1},
\]

\[
\omega_v (c - c_o) - v_0 = D_v \frac{dc}{dx} \bigg|_{(x=0)}.
\]

It follows from the solution to the diffusion equation (1.1) that cases may arise in which the velocity of the reaction front tends to zero, and the material loses mass from inside by the diffusion of the solid atoms to the surface. This arises, in particular, as a result of the fact that real crystals have paths of easy diffusion, associated with the development of networks of boundaries between various elements of their structure, including microcracks and pores, these defects being linked to the outer surface by way of microcapillaries [7, 10, 11]. We thus have to consider the boundary problem of the loosening of a solid, i.e., the change in its density with time. The expression for the density of the diffusive flow of atoms has to include a term allowing for the dependence of the mobility of the atoms on the vacancy concentration [9, 12]. The approximate solution given in [13] for the loosening of material yields qualitative agreement between the calculated surface density and experimental measurements [6].

Thus, a consideration of the vacancy kinetics within the framework of the model employed enables us to make a correct presentation of the problem both for the diffusion (mass transfer) equation and for the energy equation in the solid [14] in the presence of a surface reaction.

II. Now let us consider some questions relating to the transfer kinetics of moisture in vapor form inside a capillary–porous solid in the presence of a deep evaporation zone.

1. As already noted, in certain cases surface diffusion has a considerable influence on transfer processes in porous solids. Experimental investigations into the flow of gases in capillaries under free-molecular conditions reveal a marked difference between the measured conductivity and that calculated by the Knudsen formula. One of the reasons for this difference is surface diffusion [15, 16]. The free-molecular flow of a vapor (with due allowance for surface diffusion) in a cylindrical capillary of radius R bounded on one side (X = 0) by the plane surface of the evaporating liquid and connected to a reservoir filled with vapor of the same liquid on the other (X = L), may be given an approximate analytical description by means of the following integrodifferential equation for the surface density of the adsorbed molecules \( n_{ad} \) as a function of the dimensionless coordinate \( x = X/L \) [11]:

\[
\frac{1}{E^2} \frac{dn_{ad}}{dx^2} = \frac{1}{6} n_{ad}(x) - \int_{0}^{x} \frac{1}{6} n_{ad}(\xi) K_i(|x - \xi|) + \alpha K_i(x + \xi) d\xi - N_1 \tau K(x) - N_1 \tau [K(1 - x) - \alpha K(1 + x)],
\]

where \( \tau \) is the adsorption time; \( E = (1/\tau D_0) \), \( i = L/R \), \( \alpha \) is the specular reflection coefficient of the liquid surface,

\[
K(x) = \frac{p_0^2 + 2}{2(p_0^2 + 4)^{1/2}} - \frac{1}{2} x, \quad K_i(x) = -\frac{dK(x)}{dx};
\]

\[
N_1 = (1 - \alpha) \frac{p_1}{(2 \pi m k T)^{1/2}}, \quad N_2
\]

are, respectively, the flows of molecules diffusely emitted by unit area of the liquid meniscus and molecules passing through unit area of the open end from the reservoir.

The boundary conditions have the form [11, 17]

\[
\frac{dn_{ad}}{dx} = L \sqrt{E} (n_{ead} - n_{ad}); \quad n_{ead} = N_1 \tau.
\]

\[
n_{ad}(0) = n_0.
\]

It follows from Eq. (2.1) that, on the one hand, the greater the dimensionless parameter \( G_L = 1/EL^2 \), the more significant is the role of surface diffusion in the distribution of \( n_{ad} \) over the surface of the capillary. On the other hand, if \( G_L \ll 1 \) Eq. (2.1) has a small parameter attached to the leading derivative.