FORMULATION OF A PROBLEM CLASS CONCERNING THE MASS TRANSFER IN GRANULAR BEDS WITH PHASE TRANSFORMATIONS AND CHEMICAL CONVERSIONS

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A system of differential equations is derived describing the mass transfer in a granular monodispersion bed, whereupon the basis characteristics of the mass transfer processes in such a bed are defined.

In the general theory of heat and mass transfer not sufficient attention has been paid to the kinetics of processes involving phase transformations and chemical conversions in a dense granular filtration bed [1].

As a consequence of this deficiency, the system of mass-transfer equations has not yet been properly generalized and individual problems as well as their solutions refer only to special cases [2-4].

At the same time, the similarity of transfer phenomena makes it possible to treat mass transfer processes in the same way.

In this article the author will consider only those processes involved in a heterogeneous interaction between phases where next to the reaction rate one may, with sufficient accuracy, take into account only the heat transfer rate or the mass transfer rate and disregard the other of the two, i.e., processes which occur either in the kinetic-thermal or in the kinetic diffusion mode.

We note that a gas – condensate system will be at equilibrium when the transfer potentials in both phases (the first and the second) are equal, i.e., when

$$\Pi_1 = \Pi_2. \tag{1}$$

It can be proved on the basis of nonequilibrium thermodynamics [5] that in a system only slightly deviating from equilibrium the reaction rate is proportional to this deviation. An experimental study of several mass transfer processes (evaporation, reduction – oxidation reactions, thermal decomposition, etc.) indicates that this relation remains valid also for a system far removed from equilibrium when first-order reactions occur.

We can, therefore, write for the rates of first-order reactions:

$$v_{\text{loc}} = kS(\Pi_{\text{loc}} - \Pi_e), \tag{2}$$

where the proportionality factor k signifies the reaction conductance [5].

Since thermodynamic equilibrium is a special case of the steady state reached when the boundary conditions are compatible with the equilibrium conditions [5], hence the quantity Π_e is phenomenologically equivalent to the equilibrium potential of the gaseous phase (e.g., the equilibrium concentration of the reacting component in the gas) or to the potential at the reaction surface of the condensate phase. Important is only that the potential difference in Eq. (2) characterizes the deviation of the gas – condensate system from equilibrium and determines the reaction-motive force. In view of this, the magnitude of Π_e may be treated empirically and defined as the magnitude at which the reaction rate is zero or falls below some prescribed low level.

According to its definition, the magnitude of potential Π_e is constant during a reaction process under prescribed conditions.

An analog of Π_e is, for example, the temperature of the evaporation surface in drying problems, where the psychrometric temperature difference may be interpreted as the evaporation motive force [6], inasmuch as, according to the Lykov method [6] and the Filonenko method [7], the drying rate during the slowdown period can be expressed in terms of the initial drying rate.

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When a heterogeneous mass transfer is isothermal, the concentration difference $(c - c_e)$ may be interpreted as the motive force in a first-order reversible reaction, while the magnitude of Π_e corresponds to the equilibrium concentration of the reacting component in the gaseous phase [4].

In highly endothermal reactions such as thermal decomposition, when all the incoming heat is expended essentially on the reaction and the temperature of the solid phase remains almost unchanged, the difference between the ambient temperature and the temperature of the reacting solid substance may be interpreted as the motive force, so that the magnitude of Π_e will determine the temperature at the time when the rate of the endothermal reaction begins to rise under prescribed conditions [8].

Thus, one can always define the transfer potential and the motive force in a specific mass transfer process on the basis of the physical mechanism of the attendant phenomena.

The stage of a physicochemical transformation in the particle of a solid phase can generally be measured in terms of the conversion coefficient

$$\psi = 1 - \frac{z}{z_0}. \tag{3}$$

For the solution of engineering problems it is usually most important to determine the mean (over the volume of a particle) conversion coefficient of the reacting condensate component:

$$\psi = \frac{1}{V} \int_{(V)} \psi_{\mathrm{loc}} dV. \tag{4}$$

By analogy to relation (2), the reaction rate expressed in terms of the mean (over the volume of a particle) conversion coefficient, we will multiply the total reaction conductance by the reaction motive force and rewrite the equation for the conversion rate as

$$V\beta z_0 \frac{\partial \psi}{\partial \tau} = gF(\Pi_x - \Pi_e). \tag{5}$$

The right-hand side of Eq. (5) represents the flow of mass or heat from the gaseous phase into the volume of solid particles.

Since the convective transfer from the gaseous phase to the geometrical surface of particles usually follows Newton's law, hence the total conductance in Eq. (5) is

$$g = \alpha_F \varepsilon(R), \quad \text{where} \quad \varepsilon(R) = \frac{\Pi_x - \Pi_s}{\Pi_x - \Pi_e}. \tag{6}$$

When a reaction occurs only at the geometrical surface of particles and is limited by the external transfer conductance, then $\Pi_s = \Pi_e$ and

$$g = \alpha_F \delta(\psi), \tag{7}$$

with function $\delta(\psi)$ representing the variation of the reaction surface area, in fractions of the geometrical surface or in terms of the potential difference during the reaction.

We note that, according to (7), the formulas by Lykov [6] and Filonenko [7] for approximating the curves of the drying rate versus time during the slowdown period in the process may be treated as approximations of function $\delta(\psi)$.

It is characteristic of porous particles that reactions occur throughout their volume with a variable specific reaction surface [8-10]. In this case the total conductance consists of the transfer conductance from the gaseous phase to the surface of particles and the conductance inside the volume of particles, with the reaction taken into account.

Assuming the reaction to be a quasisteady process, which usually does not result in a large error [8-11], we determine the total conductance by combining the external and the volume component according to the general rule:

$$\frac{1}{g} = \frac{1}{g_{\mathrm{ext}}} + \frac{1}{g_{\mathrm{vol}}}. \tag{8}$$

According to (8)

$$g_{\text{ext}} = g\,|_{g_{\text{vol}}\to\infty} \text{ and, conversely, } g_{\text{vol}} = g\,|_{g_{\text{ext}}\to\infty}. \tag{9}$$

We now introduce into our analysis the dimensionless variables

$$\eta = \frac{a_{\Pi} F\,(\Pi_0 - \Pi_p)\,\tau}{V\beta z_0 R}; \quad g^* = g\,\frac{R}{a_{\Pi}}. \tag{10}$$

As a consequence of Eq. (5) and conditions (9), we have the following expressions for the dimensionless analogs of external and volume conductance

$$g^*_{\text{ext}} = \text{Bi}, \quad g^*_{\text{vol}} = \left(\frac{\partial\psi}{\partial\eta}\right)_{\Pi_S=\Pi_e}. \tag{11}$$

It follows from the second expression in (11) that, at constant transfer coefficients and geometrical particle parameters, the dimensionless analog of volume conductance is a continuous (or a piecewise continuous) function of the conversion coefficient.

The second expression in (11) can serve as the basis for experimentally determining the trend of $g^*_{\text{vol}}(\psi)$ and also, if possible in specific cases, as the basis for using the canonical equations of kinetics.

The functional relation $g^*_{\text{vol}}(\psi)$ can be determined, most generally, from the solution to the system of equations of quasisteady potential conduction through the volume of particles. As a consequence of similarity between heat and mass transfer phenomena, the equations of potential conduction and a reaction can be written out in the same general form.

For spherical bodies we have

$$\frac{\partial^2 \varkappa_{\text{loc}}}{\partial\varphi^2} + \frac{2}{\varphi}\,\frac{\partial\varkappa_{\text{loc}}}{\partial\varphi} - b^2 \varkappa_{\text{loc}}\, S(\psi) = 0, \tag{12}$$

$$\frac{\partial\psi_{\text{loc}}}{\partial\eta} = 1/3 b^2 \varkappa_{\text{loc}}\, S(\psi) \tag{13}$$

with the boundary conditions

$$\psi_{\text{loc}}|_{\eta=0} = 0, \quad \left.\frac{\partial\varkappa_{\text{loc}}}{\partial\varphi}\right|_{\varphi=0} = 0, \quad \varkappa_{\text{loc}}\,|_{\varphi=1} = 1. \tag{14}$$

Here

$$\varkappa_{\text{loc}} = \frac{\Pi_{\text{loc}} - \Pi_e}{\Pi_s - \Pi_e}; \quad b^2 = \frac{kS_0}{a_{\Pi}}\,R^2; \quad \varphi = \frac{r}{R}, \tag{15}$$

and function $S(\psi)$ represents the variation of specific surface during the reaction.

We note that the mass transfer coefficient b and the function $S(\psi)$ have been defined in accordance with the physical mechanism of the reaction in a single volume element of particles.

A comparison of the quasisteady-state equation (12) and the complete equation in [11] yields the following condition of quasisteadiness

$$\frac{M\,(\Pi_0 - \Pi_e)}{\beta z_0} \ll 1, \tag{16}$$

with M denoting the transfer inertia equal to the gas density during mass transfer or to the volume heat capacity during heat transfer.

For a reaction in the kinetic-diffusion mode, condition (16) becomes

$$\frac{\rho_G (c_0 - c_e)}{\beta q_0 \rho_M} \ll 1. \tag{17}$$

Since $\rho_G \ll \rho_M$, hence this condition is usually satisfied.

For a reaction in the kinetic-thermal mode, condition (16) becomes

$$\frac{\chi_M \rho\,(\vartheta_0 - t_e)}{Q_p z_0} \ll 1, \tag{18}$$

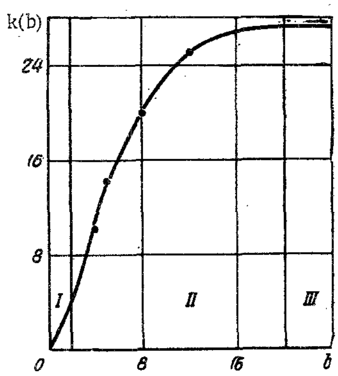

Fig. 1

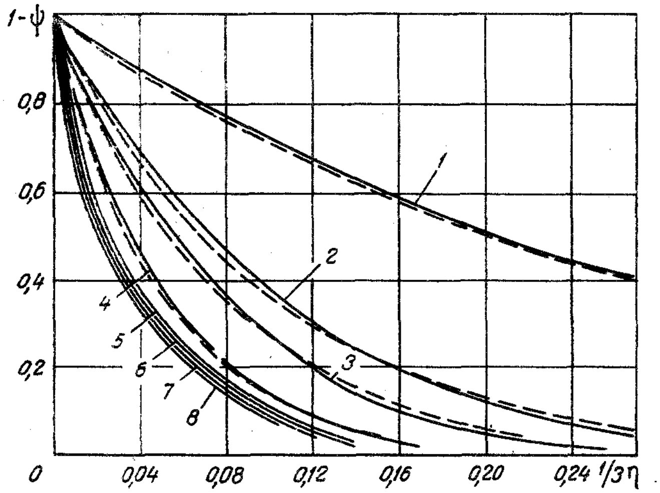

Fig. 2

Fig. 1. Coefficient k(b) in formula (23) as a function of the mass transfer coefficient b: kinetic mode of volume reaction (I), kinetic-diffusion or kinetic-thermal mode of reaction (II), diffusion or thermal mode of reaction (III).

Fig. 2. Curves of the conversion coefficient of material in porous particles during the various modes of volume reaction: b = 2 (1), 4 (2), 5 (3), 8 (4), 12 (5), 16 (6), 20 (7), 100 (8). Exact solution (solid lines), according to approximate formula (24) (dashed lines).

and is satisfied when the reaction is highly endothermal, with condition (16) expressed more precisely in terms of

$$Q_p^* = Q_p(1 + \mathrm{Rb}), \tag{19}$$

instead of Q_p and the Rebinder number being defined by the ratio

$$\mathrm{Rb} = \frac{\chi_M \rho_M}{Q_p z_0} \cdot \frac{\partial t}{\partial \psi}. \tag{20}$$

The transfer phenomena play no role in a kinetic reaction and the trend of $g_{vol}^*(\psi)$ at $\varkappa_{loc} = 1$ is determined by Eq. (13). Conversely, when mass or heat transfer rather than kinetics are limiting a properly chemical reaction, then

$$g_{vol}^* = \frac{(1-\psi)^{1/3}}{1-(1-\psi)^{1/3}}. \tag{21}$$

A reaction in the intermediate mode is more difficult to analyze, because the system of equations (12)-(13) is nonlinear and its solution presents a special problem. Function $S(\psi)$ can often be approximated [3, 6, 8, 10] by

$$S(\psi) = 1 - \psi. \tag{22}$$

With $S(\psi)$ expressed like this, Eqs. (12)-(13) have been solved numerically in [10].

Following the suggestions in [10] and an evaluation of the numerical solution to Eqs. (12)-(13), it has been possible to derive an approximate formula

$$g_{vol}^* = \frac{k(b)}{3}(1-\psi), \tag{23}$$

for the entire range of reaction modes with $S(\psi)$ defined according to (22).

Coefficient k(b) is shown in Fig. 1 as a function of the mass transfer coefficient b, while the $\psi(\eta)$ curves in Fig. 2 represent respectively the exact solution and the approximate formula

$$\psi = 1 - \exp\left(-\frac{k(b)}{3}\eta\right), \tag{24}$$

derived from (23) and by integrating the second expression in (11). We note that formula (24) can be used for determining, from tests, the reaction constants in the expression for the mass transfer coefficient b.

Thus, in the most general case, relation (8) yields the dimensionless analog of the total conductance as a function of the conversion coefficient:

$$g^* \equiv F(\psi).$$

Function $F(\psi)$ as well as the transfer potential must be considered the fundamental characteristics of mass transfer processes and, as a most general rule, expressions for the dimensionless analog of the total conductance $F(\psi)$ will vary from case to case.

The preceding discussion dealt with basic problems concerning the reaction kinetics at a constant transfer potential in the gaseous phase. When the mass transfer processes in a bed of particles are quasisteady, then Π_x = var, but the balance equation is also valid then,

$$\sigma w \frac{\partial \Pi_x}{\partial x} = -\beta z_0 V N \frac{\partial \psi}{\partial \tau}$$

being its quasisteady approximation with assumed zero losses and zero lengthwise transfer by either diffusion or conduction.

We have $\sigma = \chi_G/\rho_G$ if the transfer potential is represented by temperature, or $\sigma = \rho_G$ if it is represented by concentration.

In dimensionless variables

$$\varkappa = \frac{\Pi_x - \Pi_e}{\Pi_0 - \Pi_e}, \quad \xi = \frac{a_\Pi (1-m) x}{\sigma w R^2}.$$

The system of equations describing the mass transfer in a bed can, according to (5) and (26), be written as

$$\frac{\partial \psi}{\partial \eta} = \varkappa F(\psi), \quad \frac{\partial \varkappa}{\partial \xi} = -\varkappa F(\psi).$$

We note that using Eq. (28) implies a negligible, as compared to the total reaction time, delay ($\Delta\tau = x(1-m)/w$ in the beginning of a reaction at various bed levels owing to the finite velocity of the stream through the porous volume (this assumption of a negligible time delay is always valid in practice), and it implies the validity of the second quasisteadiness condition

$$\frac{R^2 M}{a_\Pi} < \frac{2R}{u_\varkappa}.$$

The latter inequality means that any concentration or temperature change in a gas stream within a distance of the order of a particle dimension may be disregarded. The quantity $u_\varkappa$ will be determined after system (28) has been solved.

For a reaction in a moving bed (parallel flow or counterflow) there appears no difficulty in solving system (28), by virtue of the steady potential field of transfer in the direction of the bed flow.

The general solution to the quasilinear system (28) for a stationary bed with an arbitrary form of function $F(\psi)$ presents a special problem.

The author thanks Professor M. A. Gurevich for discussing a number of questions here, for supplying tables with the aid of which the results of the numerical integration of Eqs. (12)-(13) with the boundary condition (14) and the approximation (22) could be analyzed.

NOTATION

Π	is the transfer potential;
v	is the reaction rate;
k	is the reaction constant;
S	is the specific reaction surface in a particle volume;
ψ	is the material conversion coefficient;
z_0	is the volume concentration of the reacting component in the condensate phase of particles;
V	is the volume of a particle;

τ	is the time;
β	is the stoichiometric mass or energy flow rate necessary to convert a unit mass of the condensate phase;
F	is the geometrical surface of a particle;
g	is the total conductance;
g_{ext}	is the external-transfer conductance;
g_{vol}	is the volume conductance in a particle, with the chemical reaction taken into account;
α_F	is the coefficient of external heat or mass transfer;
a_{Π}	is the potential conductivity (per particle volume);
R	is the radius of spherical particles;
r	is the radial coordinate;
c	is the concentration of the reacting component in the gaseous phase;
ρ	is the density;
q_0	is the initial weight content of the reacting component in the condensate phase, per unit mass of material in the particles;
χ	is the heat capacity (per weight);
Q_p	is the specific heat of the endothermal reaction;
t	is the temperature of the material;
x	is the distance from the bed surface;
w	is the velocity of the gas stream;
N	is the number of particles per unit bed volume;
m	is the bed porosity;
$U_{\varkappa}$	is the velocity of the stream front at a fixed potential.

Subscripts

loc	denotes local;
e	denotes equilibrium;
0	denotes initial at entrance to the bed;
x	denotes distance from the bed surface;
s	denotes bed surface;
G	denotes gas;
M	denotes bed material.

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