

DIFFUSIVE MASS TRANSFER IN A STATIONARY LAYER OF A GRANULATED MATERIAL

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Iu. A. BERMAN and R. F. NAGAEV
(Leningrad)

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The mechanism and kinetics of diffusion-controlled heterogeneous chemical reactions taking place in a dense layer of a granular permeable material, is investigated. Gas-solid chemical reactions of this type are encountered in such technological processes as calcining the iron ore pellets [1], manufacture of sponge iron [2 and 3], gasification of solid fuels with appreciable ash residues [4], e. a.

In the present paper we obtain a quasilinear system of partial differential equations describing diffusive mass transfer in a layer. The problem is complicated by the fact that the size of the zone in which the reaction takes place is not known in advance, therefore its boundaries must be determined in the course of solution. In the case of an isothermal mass transfer however, the solution can be obtained in a closed form. Variation of the similarity criteria with the dimensionless arguments, i. e. the time and the distribution coordinates, is shown graphically.

1. Basic physical premises and the chemical reaction equations.

The heterogeneous, diffusion-controlled reactions considered here possess a characteristic feature, namely their zonal character within each particle [1 and 4]. We can assume that at any instant of time the particle consists of two zones separated by the reaction interface. The outer zone consists of reaction products and the inner one – of the unreacted material. Convective diffusion is responsible for bringing the active gaseous component (oxygen in the oxidation processes, CO or H₂ in the reducing processes) to the surface of the particle, where molar or molecular diffusion takes over to bring it to the reaction interface where it reacts with the solid (Fig. 1).

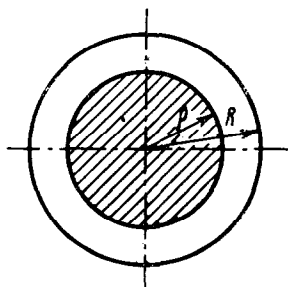


Fig. 1

We shall consider a layer composed of homogeneous spherical particles of the equivalent radius R . As we know, the quantity R can be derived from the experimental granularity measurements [5].

If we assume that the whole surface of the spherical particle is equally accessible to the reactive gas component and neglect its change in concentration in flowing over a distance of the order of the particle diameter, then we can assume that the reaction interface is also spherical. Rate of displacement of the reaction sphere defining the overall chemical reaction rate, can be found from the mass balance equation for the reacting gas at the solid-gas interface

$$-\zeta g(d\rho / d\tau) = \delta k c(\rho) \quad (1.1)$$

where ρ is the radius of the reaction sphere, τ is time, ζ is the stoichiometric extent of reaction parameter, γ is the volume weight of the particle, g is the content by weight of the reactive component in the solid reactant, δ is the density of the reactive gas, k is the reaction rate constant and $c(\rho)$ is the excess concentration of the reacting

gas

$$c(\rho) = c'(\rho) - c_0 \quad (1.2)$$

where $c'(\rho)$ is the actual concentration and c_0 is the equilibrium concentration. We shall assume that the equilibrium concentration c_0 is independent of the radius of the reaction sphere and, that the inequality $c'(\rho) > c_0$ holds.

In other words, we shall assume that the reaction proceeds with absorption of the gaseous phase.

In the following we shall regard the excess concentration $c(\rho)$ as the transport potential.

In the zone of products the gas is not used up, therefore its excess concentration $c(r)$ varies according to the usual law of diffusion

$$\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} = 0 \quad (1.3)$$

With the boundary conditions given by

$$D \frac{\partial c}{\partial r} \Big|_{r=R} = \beta [c_x - c(R)], \quad D \frac{\partial c}{\partial r} \Big|_{r=0} = kc(\rho) \quad (1.4)$$

where D is the effective diffusion coefficient, β is the convective mass transfer coefficient and c_x is the concentration of the reagent in the gas stream, we can solve (1.3) to obtain the law of distribution of concentration $c(r)$ throughout the thickness of the considered zone

$$c(r) = c_x \frac{(D/kR) + [1 - (\rho/r)](\rho/R)}{(D/kR) + (\rho/R) - [1 - (D/\beta R)](\rho/R)^2} \quad (1.5)$$

This is the distribution under the steady state conditions, when $\rho/R < 1$.

It is a well known fact, that in a diffusion-controlled reaction the value of the coefficient D/kR is much less than unity. On the other hand, the coefficient $D/\beta R$ is uniquely connected with the Nusselt number N_{Nu} by the relation $D/\beta R = 2/N_{Nu} \cdot D_0/D$ where D_0 is the outer diffusion coefficient.

Since under the conditions encountered in various technological processes the Nusselt number is sufficiently large ($N_{Nu} = 50 \div 100$), the outer diffusion which opposes the mass transfer process can also be neglected.

Thus in the case of heterogeneous chemical reactions whose limiting rate is governed by the diffusion of gas within the particle (inner diffusion mode), the following approximate analog of (1.5)

$$c(r) = c_x \frac{(D/kR) + [1 - (\rho/r)](\rho/R)}{(\rho/R) - (\rho/R)^2} \quad (1.6)$$

will cause a detectable error only for very small radii of the reaction sphere. Insertion of (1.6) into (1.1) leads to the following equation defining the law of variation of the radius of the reaction sphere with time

$$\frac{d\rho}{d\tau} = - \frac{D\delta}{\zeta \gamma g R} \frac{c_x}{(\rho/R) - (\rho/R)^2} \quad (1.7)$$

To construct an equation defining the concentration c_x of the reactive component in the gas stream, we shall require the mass balance equation for a unit area element dx of the reaction zone at the distance x from the layer surface (Fig. 2). We first note that the change in the amount of the reacting element in the gas stream after it has passed the element of the layer just mentioned, is equal to

$$dJ = -\omega \frac{\partial c_x}{\partial x} dx \quad (1.8)$$

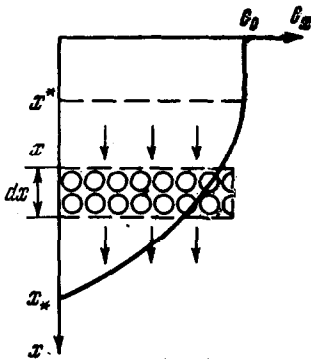


Fig. 2

where ω is the filtration rate computed over the whole cross section of the layer (*).

On the other hand, dJ is equal to the product of the reaction rate in a unit volume of the layer and the volume element $dV = 1 dx$. Reaction rate for a single particle is

$$v = \frac{4}{3} \pi R^3 \frac{\zeta g \gamma}{\delta} \frac{\partial}{\partial \tau} \left(1 - \frac{\rho^3}{R^3} \right) \quad (1.9)$$

Since the rate of reaction per unit layer volume is N times larger, where

$$N = \frac{3}{4} \frac{1-m}{\pi R^3} \quad (1.10)$$

is the total number of particles in the considered volume and m denotes the porosity of the layer, the required expression for dJ will become

$$dJ = \frac{(1-m) \zeta g \gamma}{\delta} \frac{\partial}{\partial \tau} \left(1 - \frac{\rho^3}{R^3} \right) dx \quad (1.11)$$

Equations defining the concentration c_x are obtained by combining (1, 8) and (1, 11) and can be written as

$$\frac{\partial c_x}{\partial x} = - \frac{(1-m) \zeta g \gamma}{\omega \delta} \frac{\partial}{\partial \tau} \left(1 - \frac{\rho^3}{R^3} \right) \quad (1.12)$$

Thus the diffusive mass transfer process in a granular layer can be described by a system of two quasilinear partial differential equations (1, 7) and (1, 12).

Values of the diffusion coefficient D appearing in (1, 7) and of the equilibrium concentration c_0 both depend, generally, on temperature. Within the range of temperatures encountered in various technological processes this dependence can be schematized using the Arrhenius (or other) type equations [1, 3 and 4]. This imposes the necessity of considering the mass transfer equations (1, 7) and (1, 12) together with the heat transfer equations in the presence of internal heat sources. In the present work, however, the mass transfer process in question is isothermal, therefore the quantities D and c_0 are constant. This is possible in particular when the transport phenomenon in the chemical processes has low activation energy or, when D and c_0 are computed at the temperature chosen in a certain definite manner.

2. Similarity criterion of the isothermal mass transfer and the boundary conditions. When describing the reaction kinetics we find, that the extent of conversion of material is a more convenient parameter than the radius of the reaction sphere. We shall therefore adopt the extent of conversion of material equal to the ratio of the volume of the reacted material of the particle to its total volume

$$\psi = 1 - (\rho / R)^3 \quad (2.1)$$

and the reactive concentration

$$c = c_x / c_x^{(0)} \quad (2.2)$$

where $c_x^{(0)}$ is the excess concentration of the reactive gas component at the layer surface, as new dimensionless variables defining the similarity criterion. We note that the new variables ψ and c , by virtue of their physical nature, may vary within a unit interval (0, 1).

In addition we shall introduce new dimensionless variables defined by

$$\eta = \frac{3Dc_x^{(0)}\delta}{\zeta\gamma R^2} \tau, \quad \xi = \frac{3D(1-m)}{\omega R^2} x \quad (2.3)$$

*) We neglect the variation in the filtration rate caused by the fact that the quantity of the reactive component diminishes.

Now we can write the basic equations (1.7) and (1.12) describing the course of the chemical reaction within the layer, in dimensionless form

$$\frac{\partial \psi}{\partial \eta} = cF(\psi), \quad \frac{\partial c}{\partial \xi} = -cF(\psi), \quad F(\psi) = \frac{(1-\psi)^{1/2}}{1-(1-\psi)^{1/2}} \quad (2.4)$$

Here $F(\psi)$ is a continuous positive function monotonically over its interval of definition (0, 1) from infinity to zero.

Equations (2.4) are valid only within the reaction zone, which at any fixed instant η is defined by the inequality $\xi_*(\eta) < \xi < \xi_*(\eta)$ (2.5)

Boundaries of the reaction zone (in the following we shall discuss, for convenience, only their dimensionless analogs) are not known in advance and have to be determined in the course of solution of the problem. When $\xi > \xi_*(\eta)$, the material has not begun to react with the gaseous phase, therefore $c = \psi = 0$. On the other hand, the inequality $\xi < \xi_*(\eta)$ holds in the zone of reacted material ($c = \psi = 1$) (*).

At a fixed depth ξ the reaction starts at the instant $\eta = \eta_*(\xi)$ where $\eta_*(\xi)$ is the inverse of $\xi_*(\eta)$. Thus the initial conditions for the system (2.4) can be written as

$$\psi|_{\eta=\eta_*(\xi)} = c|_{\eta=\eta_*(\xi)} = 0 \quad (2.6)$$

Boundary conditions are somewhat more complicated. The difficulty lies in the fact that when $\eta < \eta^*(0)$, where $\eta^*(\xi)$ is the inverse of $\xi_*(\eta)$, then the material at the surface of the layer has not fully reacted and we have a special boundary condition

$$c|_{\xi=0} = 1 \quad (2.7)$$

If $\eta > \eta^*(0)$, then a zone of fully reacted material is situated next to the surface and the following two boundary conditions then hold

$$\psi|_{\xi=\xi^*(\eta)} = c|_{\xi=\xi^*(\eta)} = 1 \quad (2.8)$$

Although two boundary conditions (2.8) replace a single one, the problem does not become overdefined since the equation of the boundary $\xi = \xi^*(\eta)$ is not known. The same remark applies to the initial conditions (2.6).

The initial and boundary conditions predetermine the existence of two, essentially distinct stages of the mass transfer. The first, initial stage, is characterized by the fact that the reaction zone directly adjoins the layer surface and represents, on the plane of arguments, a triangular area bounded by the curves $\xi = 0$, $\eta = \eta^*(0)$ and $\eta = \eta_*(\xi)$. The next stage which we shall call the steady state stage, occurs in a semi-infinite zone situated within the layer and bounded by the curves $\xi = \xi^*(\eta)$, $\eta = \eta^*(0)$ and $\eta = \eta_*(\xi)$.

All the above argument reflects the physical nature of the problem and is, generally speaking, valid also in the general case of nonisothermal diffusion.

3. Integration of the chemical kinetics equations. Systems of nonlinear partial differential equations cannot, in general, be integrated by the classical methods and numerical methods are usually resorted to. In the present case however, the

) Keeping in mind the definition of applicability of the basic relation (1.6) given in Sect. 1 we note, that the actual values of c and ψ at the boundaries ξ_ and ξ^* of the reaction zone are, generally speaking, not equal to the values shown here, although the differences are not large.

problem which is essentially nonlinear, can nevertheless be solved completely by purely analytical ways using the following particular method.

Let us introduce the function
$$h(\psi) = 3/2[1 - (1 - \psi)^{2/3}] - \psi \quad (3.1)$$

continuous and increasing monotonically from zero at $\psi = 0$ to $1/2$ at $\psi = 1$. Then the first equation of (2.4) can be written in the form

$$\partial h / \partial \eta = c \quad (3.2)$$

Performing partial differentiation with respect to ξ , after certain manipulations and with (2.4) taken into account, we easily obtain

$$\frac{\partial}{\partial \eta} \left(\frac{\partial h}{\partial \xi} + \psi \right) = 0 \quad (3.3)$$

The derivative $d h / d \psi |_{\psi=0} = 0$, therefore by virtue of the initial conditions (2.7) the following relation will always hold within the reaction zone

$$\partial h / \partial \xi + \psi = 0 \quad (3.4)$$

Let us now write (3.4) in the form of the following ordinary first order differential equation

$$\partial h / \partial \xi + \psi F(\psi) = 0 \quad (3.5)$$

Integrating this equation for the initial reaction stage when the boundary condition (2.8) holds, we obtain the required integral in the following implicit form

$$\xi = \Phi(\psi_0) - \Phi(\psi) \quad (3.6)$$

where

$$\Phi(\psi) = \frac{3}{2} \ln \left[3 \frac{1 - (1 - \psi)^{1/3}}{\psi} \right] + \sqrt{3} \operatorname{arctg} \left[\sqrt{3} \frac{1 + (1 - \psi)^{1/3}}{1 - (1 - \psi)^{1/3}} \right] - \frac{\pi \sqrt{3}}{2} \quad (3.7)$$

Function $\Phi(\psi)$ increases monotonically in the interval (0, 1) from zero to $3/2 \ln 3 - 1/2 \pi \sqrt{3}$. The extent of conversion of material at the layer surface $\psi_0 = \psi |_{\xi=0}$ can be obtained in accordance with the first equation of (2.4), from

$$d\psi_0 / d\eta = F(\psi_0) \quad (3.8)$$

Since $\psi |_{\eta=\eta_*(0)} = 0$ and $\eta_*(0) = 0$, the integral of (3.8) which defines the dependence of ψ_0 on the dimensionless time η , in an implicit form, is

$$h(\psi_0) = \eta \quad (3.9)$$

This describes the reaction kinetics in a diffusion-controlled process for particles distributed at the surface of the layer appearing, basically, as discrete particles.

Thus the relations (3.6) and (3.9) fully define the character of variation of the extent of conversion ψ (ξ , η) in the initial stage of the reaction. Simultaneous solution of these equations is best performed graphically.

The resulting relation
$$\psi = \Phi^*[\Phi(\psi_0) - \xi] \quad (3.10)$$

where Φ^* is the inverse of Φ , has the form of a travelling wave which propagates without distortion into the layer with a varying velocity

$$d\Phi(\psi_0) / d\eta = 1 / \psi_0 \quad (3.11)$$

The latter expression is easily obtained from (3.7) and (3.8). Differentiating now (3.6) partially with respect to η performing some manipulations and taking into account (3.11) and the first equation of (2.4), we obtain the following formula for the dimensionless concentration of the reacting gas

$$c = \psi / \psi_0 \quad (3.12)$$

Thus the process of varying the concentration c with time, also exhibits a wave character. However, since the extent of conversion of material ψ_0 on the layer surface increases monotonically from zero at $\eta = 0$ to unity at $\eta = 1/2$, it follows that the intensity of the concentration wave gradually diminishes. When $\eta > 1/2$, Eq. (3, 9) forbids physically meaningful solutions. Therefore the duration $\eta^*(0)$ of the initial stage of the reaction is equal to $1/2$. At the completion of the initial stage we have the following characteristic equality $c = \psi$.

The boundary $\xi_*(\eta)$ of the reaction zone is obtained from the basic relation (3, 6) by putting $\psi = 0$, and has the form $\xi_*(\eta) = \Phi(\psi_0)$ (3.13)

We note that at the end of the initial stage

$$\xi_*(1/2) = 3/2 \ln 3 - 1/6 \pi \sqrt{3}$$

At small values of the arguments we can also use the following approximate formulas

$$\psi = \sqrt{6\eta} - 3\xi, \quad c = 1 - \sqrt{3/2} \eta^{-1} \xi, \quad \xi_*(\eta) = \sqrt{2/3} \eta \quad (3.14)$$

We also note that at small values of η the law governing the translation of the lower boundary $\xi_*(\eta)$ of the reaction zone is analogous to the law of translation of the interphase boundary in the Stefan's problem [6].

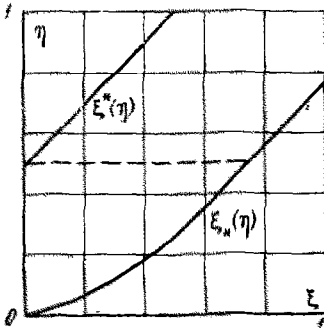


Fig. 3

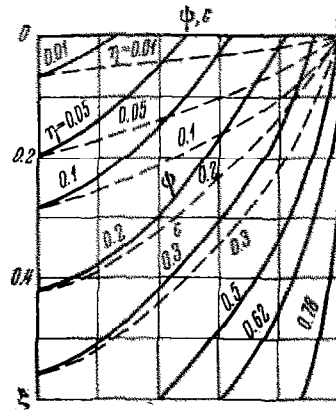


Fig. 4

In the second stage when $\eta > 1/2$ the integral of (3, 5) satisfying the boundary condition (2, 9) has the form $\xi - \xi^*(\eta) = 3/6 \ln 3 - 1/6 \pi \sqrt{3} - \Phi(\psi)$ (3.15)

which on partial differentiation with respect to η , yields

$$c = (d\xi^* / d\eta) \psi \quad (3.16)$$

Putting $\xi = \xi^*(\eta)$, we obtain $d\xi^* / d\eta = 1$ (3.17)

But $\xi^* = 0$ when $\eta = 1/2$. Consequently the reaction zone boundary has the form

$$\xi^*(\eta) = \eta - 1/2 \quad (3.18)$$

The other boundary is obtained from (3, 15) by putting $\psi = 0$, and is

$$\xi_*(\eta) = \eta - 1/2 + 3/2 \ln 3 - 1/6 \pi \sqrt{3} \quad (3.19)$$

Thus it follows from (3, 15) and (3, 16) that the dimensionless concentration c of the reacting gas and the extent of conversion of the material ψ in the second stage of reaction are equal to each other and depend on the difference of the arguments $\eta - \xi$. The

process assumes the character of a travelling wave propagating at a constant velocity. Boundaries of the reaction zone consist, at this stage, of mutually parallel straight lines. Therefore its width

$$\xi_*(\eta) - \xi^*(\eta) = \frac{3}{2} \ln 3 - \frac{1}{6} \pi \sqrt{3} \quad (3.20)$$

is constant and so is the duration of reaction for all particles which are deeper than $\frac{3}{2} \ln 3 - \frac{1}{6} \pi \sqrt{3}$ (Fig. 3). Comparing (3.6) with (3.15) and (3.13) with (3.19) we see, that the quantities c and ψ remain continuous during the transition from the initial to the steady state and the boundary of the reaction zone remains unbroken.

Figure 4 shows the variation of the relative concentration c and of the extent of conversion of material ψ versus the dimensionless distribution coordinate ξ (on the figure $\zeta \equiv \xi$) for various values of the dimensionless time η . We see that the curves for c and ψ are essentially different during the initial stage of the mass transfer ($\eta < 1/2$); they merge into each other during the second stage.

We note that the distribution of the concentration and of the extent of conversion of the solid throughout the thickness of the reaction zone in the second stage of the mass transfer ($\eta > 1/2$) also defines the distribution of the corresponding quantities when the gas and the solid move in opposite directions. Parameters of the counter-current mechanism (rate of delivery of the solid, gas consumption, etc.) are then obtained from the condition (3.7) which represents a dimensionless mass balance equation in the reaction zone with the mass transfer completed.

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