

Approximate analytic solutions are obtained for the equations of equilibrium or non-equilibrium dynamics of sorption in the case of arbitrary convex or concave isotherms.

The isotherm sorption dynamics in a porous and nondeformable medium are described by the material-balance equation in which lengthwise diffusion is taken into account,

$$\frac{\partial a}{\partial t} + \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

and also by an equation which expresses the relation between the concentrations a and c . In the case of equilibrium dynamics one has $a = f(c)$ and in the case of nonequilibrium their interrelation is given by the kinetics equation in which the lack of equilibrium of the sorption process is expressed with the aid of the parameter l , the retardation path [1]:

$$a = f(c) - l \frac{df}{dc} \cdot \frac{\partial c}{\partial x} \quad (2)$$

The initial and boundary conditions for the equations of sorption frontal dynamics for a half-bounded column ($0 \leq x < \infty$) are given by

$$c(0, t) = 1; \quad c(x, 0) = c(\infty, t) = 0. \quad (3)$$

The solution of the system (1)-(3) depends on the shape of the sorption isotherm. For a linear isotherm γc analytic solutions were obtained [2, 3]. In the case of a nonlinear isotherm Eqs. (1) and (2) are also nonlinear, their solution giving rise to considerable difficulties of a mathematical nature. For convex or concave isotherms with only a slight deviation from linearity an approximate solution was obtained in [4] as well as statistical moments of the concentration curve [5, 6] which enable one to find estimates for the sorption front erosion when it is in motion in the column. An approximate solution of the equations of the equilibrium frontal dynamics of sorption was obtained in [7] for rectangular convex isotherms.

In the present article a distribution for the sorption front of concentration is assumed, with whose aid an approximate solution $c(x, t)$ of the system (1)-(3) is found in the case of any convex or concave isotherm including the cases of large deviations from linearity. This distribution was also employed to solve the equations of equilibrium dynamics in the case of lengthwise diffusion D or of nonequilibrium dynamics for $D = 0$.

The system (1) and (2) is given by

$$\frac{\partial f(c)}{\partial \tau} + \frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial \eta} = \frac{\partial^2 c}{\partial \eta^2}; \quad \tau = \frac{u^2 t}{D}; \quad \eta = \frac{ux}{D} \quad (4)$$

in the case of equilibrium dynamics and when the dimensionless time τ and the coordinates η are used. To solve the nonlinear equation (4) the integral-relations method [8] is used with such a modification that instead of a mobile boundary for the zero concentration one uses the mobile boundary $x_0(t)$ or $\delta(\tau) = ux_0/D$ for the concentration $c = 1$. The concentration distribution at the front is determined by the relations

$$\eta \leq \delta, c = 1; \quad \delta \leq \eta < \infty, \quad c = \exp \{-[b(\eta - \delta)]^2\}. \quad (5)$$

The slope of the concentration curve in (5) at any point $\eta > \delta$ is given by the coefficient $b(\tau)$ and by the mobile boundary $\delta(\tau)$ both being time-dependent. The profile of the concentration c can be regarded as an integral function of the random quantity η . Then the probability

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density of this distribution is given by $-\delta c/\partial\eta$ [5, 6, 9]. The width (standard deviation) σ and the location of the center of gravity of the decreasing portion of the concentration curve c in (5) are determined by the statistical moments for the curve $-\partial c/\partial\eta$:

$$\bar{\eta} = \frac{u\bar{x}}{D} = \int_{\delta}^{\infty} \eta \left(-\frac{\partial c}{\partial\eta} \right) d\eta = \delta + \frac{\sqrt{\pi}}{2b}, \quad \sigma^2 = \overline{(\eta - \bar{\eta})^2} = \frac{1}{b^2} \left(1 - \frac{\pi}{4} \right). \quad (6)$$

To determine the functions $b(\tau)$ and $\delta(\tau)$ it is required that the distribution (5) satisfies two integral relations (of the zeroth and of the first order) which express the law of mass conservation. The integral relation of the n -th order is obtained from (4) by multiplying both sides of the equation by η^n and integrating subsequently with respect to η from δ to ∞ :

$$n = 0; \quad \frac{d}{d\tau} \int_{\delta}^{\infty} (a + c) d\eta + [1 + f(1)] \frac{d\delta}{d\tau} = 1, \quad (7)$$

$$n = 1; \quad \frac{d}{d\tau} \int_{\delta}^{\infty} \eta(a + c) d\eta + [1 + f(1)] \delta \frac{d\delta}{d\tau} = 1 + \delta + \int_{\delta}^{\infty} c d\eta. \quad (8)$$

Equations (7) and (8) are solved separately for polynomial convex or concave isotherms,

$$f(c) = \gamma c + \gamma_1 \varepsilon_1 c^m. \quad (9)$$

By integrating (7) and using (9) one obtains

$$\frac{\sqrt{\pi}}{2b} = \frac{\tau' - (1 + \varepsilon) \delta}{1 + \varepsilon/\sqrt{m}}; \quad \tau' = \frac{\tau}{1 + \gamma}, \quad \varepsilon = \frac{\gamma_1 \varepsilon_1}{1 + \gamma}. \quad (10)$$

Employing in the evaluation of the integrals in (8) the distribution (5) and the isotherm equation (9) and eliminating $b(\tau)$ with the aid of (10) one obtains from the ordinary differential equation for the function $\delta(\tau)$,

$$\frac{d\delta}{d\tau'} = \frac{1 + r\tau' + s\delta}{r_1\tau' + s_1\delta}, \quad (11)$$

$$s = -(1 + \varepsilon)r = \frac{1 + \varepsilon}{1 + \varepsilon/\sqrt{m}} \left[\frac{4}{\pi} \cdot \frac{1 + \varepsilon/m}{1 + \varepsilon/\sqrt{m}} - 1 \right],$$

$$s_1 = -(1 + \varepsilon)r_1 = (1 + \varepsilon) \left[\frac{4}{\pi} \cdot \frac{(1 + \varepsilon)(1 + \varepsilon/m)}{(1 + \varepsilon/\sqrt{m})^2} - 1 \right].$$

Integrating (11) together with $\delta(0) = 0$ yields the transcendental relation,

$$y - \ln|1 + y| = k\tau', \quad (12)$$

$$k = \frac{\varepsilon^2(1 - 1/\sqrt{m})^2}{1 + \varepsilon} \left[\frac{4}{\pi} (1 + \varepsilon) \left(1 + \frac{\varepsilon}{m} \right) - (1 + \varepsilon/\sqrt{m})^2 \right]^{-1},$$

$$y = \frac{\varepsilon(1 - 1/\sqrt{m})}{(1 + \varepsilon)(1 + \varepsilon/\sqrt{m})} [\tau' - (1 + \varepsilon)\delta]. \quad (13)$$

The solution (5) where b and δ are given by (10), (12), and (13) is applicable to isotherms of any curvature ε . Should the approximation accuracy of an isotherm as given by (9) be insufficient one can introduce more terms in (9) or modify the degree m of the polynomial. It can easily be seen that this does not change the form of the solution (5) or of the relations for $b(\tau)$, $\delta(\tau)$; the only change is in the constants k , ε , m which appear in the relations (10), (12), and (13). The latter is also true in the case of the Freundlich isotherm $\gamma = 0$, $\gamma_1 \varepsilon_1 > 0$ in (9).

For a linear isotherm ($\varepsilon = 0$) the parameters b and δ satisfy the relations

$$\frac{1}{b} = 2 \sqrt{\frac{2\tau'}{4 - \pi}}, \quad \delta = \tau' - \sqrt{\frac{2\tau'}{4 - \pi}}. \quad (14)$$

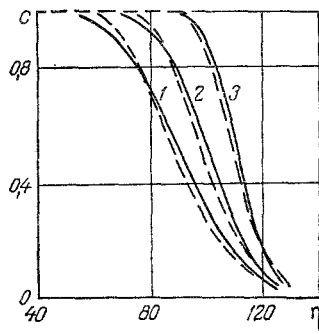


Fig. 1. Front of the concentration c in the case of concave (1) or linear (2) or convex (3) isotherm at the instant $\tau' = 100$: 1) $\varepsilon = 0.1$; 2) $\varepsilon = 0$; 3) $\varepsilon = -0.1$; $c, \eta, \tau, \varepsilon$ are dimensionless quantities.

At the initial stage of the front motion when $|y(\tau)| \ll 1$, $\tau' \ll 1/2k$ one obtains from (12), (13), (10)

$$y^2 = 2k\tau', \quad \frac{\sqrt{\pi}}{2b} = \frac{(1+\varepsilon)y}{\varepsilon(1-1/\sqrt{m})} = \frac{(1+\varepsilon)\sqrt{2k\tau'}}{\varepsilon(1-1/\sqrt{m})} \quad (15)$$

by employing the series expansion $\ln|1+y|$. In accordance with (14) and (15) one finds from (6) that at the initial stage of motion the front width $\sigma \sim 1/b$ increases proportionally to \sqrt{t} both for linear and for convex or concave isotherms.

It is known [1] that there exists an asymptotic ($t \rightarrow \infty$) solution for convex isotherms, this being the stationary state of the front motion when the function c only depends on the single variable z . Employing (12) one can easily find the steady time τ_{st} of the state:

$$\begin{aligned} \varepsilon > 0, m < 1 \quad \text{or} \quad \varepsilon < 0, m > 1, \quad \lim_{\tau \rightarrow \infty} y = -1, \\ \lim_{\tau \rightarrow \infty} c(\eta, \tau) = c(z) = \exp[-(bz)^2], \\ z = \eta - \frac{\tau'}{1+\varepsilon} + \frac{1+\varepsilon/\sqrt{m}}{\varepsilon(1-1/\sqrt{m})}. \end{aligned} \quad (16)$$

With the error not exceeding 1% ($y_{st} = -0.99$) the front width $\sigma \sim |y|$ (6), (10) becomes constant for $\tau' > \tau'_{st}$ where

$$\tau'_{st} = \frac{3.6}{k}, \quad \delta_{st} = \frac{\tau'_{st}}{1+\varepsilon} - \frac{1+\varepsilon/\sqrt{m}}{\varepsilon(1-1/\sqrt{m})}. \quad (17)$$

The estimates (17) agree with those obtained in [4-6, 9] for convex isotherms $\gamma(c + \varepsilon_1 c^2)$ of low curvature $|\varepsilon| \ll 1$. However, the estimates (17) can also be applied in the case of isotherms of high curvature, for example,

$$\begin{aligned} m = 2, \quad \gamma = \gamma_i; \quad \varepsilon = -0.5 \quad \tau'_{st} = 4.2, \quad \delta_{st} = 4.8; \\ \varepsilon = -0.4 \quad \tau'_{st} = 15, \quad \delta_{st} = 19. \end{aligned} \quad (18)$$

In the case of convex isotherms the sorption front gets progressively eroded. It follows from (12), (6) that for long times, $\tau' \geq 100/k$ when $y \geq 100 \gg \ln|1+y|$, one has

$$\varepsilon > 0, m > 1 \quad \text{or} \quad \varepsilon < 0, m < 1, \quad (19)$$

$$y = k\tau', \quad \sigma = \sqrt{\frac{4}{\pi} - 1} \frac{(1+\varepsilon)k\tau'}{\varepsilon(1-1/\sqrt{m})}.$$

Consequently, in the case of concave isotherms for $\tau' \geq 100/k$ the width of the sorption front grows proportionally to t (19).

The estimation of the error in the approximate solution (5), (10), (12), (13) is carried out by comparing it with a known solution for a linear isotherm [2],

$$\varepsilon = 0, \quad c(\eta, \tau) = \frac{1}{2} \left[\operatorname{erfc} \frac{\eta - \tau'}{2\sqrt{\tau'}} + \exp(\eta) \operatorname{erfc} \frac{\eta + \tau'}{2\sqrt{\tau'}} \right], \quad (20)$$

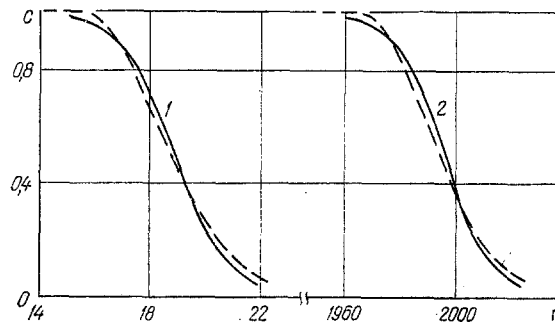


Fig. 2. Fronts of the concentration c for convex isotherms in the stationary state: 1) $\tau' = 10$, $\varepsilon = -0.5$; 2) $\tau' = 1800$, $\varepsilon = -0.1$; c , η , τ , ε are dimensionless quantities.

and also with the solution for isotherms of the type (9) ($\gamma = \gamma_1$, $m = 2$) of low nonlinearity, $|\varepsilon| \ll 1$ [4]. The solution in [4] was obtained with the aid of an integral transformation of the function c which transforms a nonlinear problem into a linear one for another function. Using the notation given in that article the solution of [4] can be written as

$$c(\eta, \tau) = \frac{\exp\left(\frac{\varepsilon p}{1+\varepsilon}\right) \operatorname{erfc} \frac{1}{2} (g + p/h)}{2 + \exp\left(\frac{\varepsilon p}{1+\varepsilon}\right) \operatorname{erfc} \frac{1}{2} (g + p/h) - \operatorname{erfc} \frac{1}{2} \left(\frac{p}{h} - g\right)}, \quad (21)$$

$$p = \eta - \frac{\tau'}{1+\varepsilon}, \quad h = \sqrt{\tau'(1+\varepsilon)}, \quad g = \frac{\varepsilon h}{1+\varepsilon}.$$

In Fig. 1 the solid lines correspond to the concentration fronts at an arbitrary time instant as evaluated for a linear isotherm by using the formula (20) (curve 2), and for low-curvature ($m = 2$, $\varepsilon = \pm 0.1$) isotherms by using the formula (21) (curves 1, 3). If one compares them with the corresponding curves (dashed) evaluated by using (5), (10), (12), (13), a good agreement is observed for linear isotherms or isotherms with slight nonlinearity. One notes that the stationary state of the motion in the case of a convex isotherm ($\varepsilon = -0.1$) prior to this instant has yet to be attained: $\varepsilon = -0.1$, $\tau'_{st} = 860$ (17).

An error estimate for the obtained solution in the case of isotherms with strong deviation from linearity can be found by comparing it with the solution of Eq. (4) for long times when the stationary state occurs:

$$t \rightarrow \infty, \quad \frac{\partial c}{\partial \eta} = \frac{dc}{dz}, \quad \frac{\partial c}{\partial \tau} = - \frac{1}{(1+\gamma)(1+\varepsilon)} \cdot \frac{dc}{dz}, \quad (22)$$

$$m = 2, \quad \gamma = \gamma_1, \quad \varepsilon < 0, \quad \ln c - \ln |1-c| = \frac{\varepsilon z}{1+\varepsilon} + K.$$

A stationary state is attained for $\varepsilon = -0.5$, $\tau' \geq 4.2$; $\varepsilon = -0.1$, $\tau' \geq 860$ [(17), (18)]. In Fig. 2 the solid lines represent the profiles of the concentration c evaluated with the aid of (22) and the dashed lines those evaluated with the aid of (5), (10), (12), (13). The agreement is good both in the case of isotherms of pronounced ($\varepsilon = -0.5$) and weak ($\varepsilon = -0.1$) nonlinearity.

For solving the system of equations for nonequilibrium frontal dynamics of sorption with $D = 0$ one substitutes (2) in (1) and the obtained solution is written in the dimensionless time $\tau = ut/l$ and dimensionless coordinate $\eta = x/l$:

$$\frac{\partial f(c)}{\partial \tau} + \frac{\partial c}{\partial \tau} + \frac{\partial^2 f(c)}{\partial \tau \partial \eta} = - \frac{\partial c}{\partial \eta}. \quad (23)$$

Integral relations can be obtained from (23) by the procedure described above. For $\gamma \gg 1$ (this being an important case in applications) the equations for $b(\tau)$ and $\delta(\tau)$ derived from the integral relations are of the form (10), (12), (13), in the case under consideration of nonequilibrium dynamics, the only difference being that now the coordinate and time are expressed not in the units D/u , but in the units of l ; all the previous results or estimates are now applicable to the case of frontal nonequilibrium dynamics of sorption without being modified.

NOTATION

c , dimensionless (in inlet concentration units) concentration of sorbed gas or liquid in mobile phase; α , dimensionless (in inlet concentration units) concentration of matter in sorbent per unit volume of the mobile phase; $f(c)$, isotherm equation of sorption; x , coordinate; η , dimensionless coordinate; t , time; τ , τ' , dimensionless times; u , mean flow velocity; D , lengthwise diffusion coefficient; l , kinetic parameter—retardation path; γ , Henry coefficient; ϵ , isotherm nonlinearity parameter; m , exponent; $x_0(t)$, mobile boundary of concentration $c = 1$; $\delta(\tau)$, dimensionless mobile boundary of concentration $c = 1$; K , constant.

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AN APPROXIMATE MATHEMATICAL MODEL OF HEAT AND MASS TRANSFER IN TWO-PHASE FLOW

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We propose an approximate method for studying transport processes in one-dimensional two-phase flow which permits the determination of the system output as a function of input and the system parameters. The error of the method is estimated.

A mathematical description of transport processes in steady two-phase flows characterized both by mixing and the presence of arbitrary sources whose strengths depend only on the potentials of the entities being transported is important for the chemical industry. For simplicity we consider only one-dimensional flows. It is known that such a description cannot generally be given in exact closed analytic form even for one-phase systems. There is evidence, however, that for a certain heuristic reinterpretation of the differential equation to be solved and its boundary conditions, an approximate method of describing the system analytically can be constructed [1].

In the present paper we investigate such a method in a general form suitable for a mathematical description of two-phase heat and mass transfer. The proposed method can be used not only for an approximate analytic study of heat and mass transfer in two interacting phases, but also for an approximate study of heat- and mass-transfer processes taking place simultaneously in a single phase. In addition, this method can in principle be generalized to include an arbitrary number of equations. There then arises the problem of comparing the approximate and exact results. In this paper we restrict ourselves to the most important practical case of two equations.

It is known [2] that transport processes in the systems under consideration can be described in the usual approximation by the equations

$$-F\mathcal{K} \frac{d^2u}{dx^{*2}} + V \frac{du}{dx^*} - f^*(u, u') = 0, \quad (1)$$

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