# DYNAMICS OF NONSTATIONARY PHYSICOCHEMICAL PROCESSES IN A FLOW UNDER THE CONDITION OF A BIMOLECULAR RATE LAW FOR THE PROCESS

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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# DYNAMICS OF NONSTATIONARY PHYSICOCHEMICAL PROCESSES IN A FLOW UNDER THE CONDITION OF A BIMOLECULAR RATE LAW FOR THE PROCESS

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Questions concerning the dynamics of nonstationary chemical and physicochemical (for example, sorption, ion-exchange) processes are acquiring ever greater practical importance. However, because of mathematical difficulties they have not been developed sufficiently well. In the present article a method will be considered for solving the problem of the dynamics of a nonstationary physicochemical process under the condition that the rate of the process obeys a bimolecular law.

Let a substance that can be sorbed be passed through a tube (whose axis we choose as the coordinate axis and denote by $l$), filled with a sorbent at constant temperature. Let $C(l,t)$ denote the concentration of this substance located in the pores of the sorbent at a distance $l$ from the beginning of the sorbent layer. By $y(l,t)$ we shall denote the amount of this substance sorbed by a unit volume of sorbent by the time $t$. It is assumed that the sorbent fills the entire volume of the tube. Let the substance move in the sorbent with constant linear velocity $u$, sufficiently large that the process of longitudinal diffusion may be neglected.

If the concentration is calculated as the amount of substance in a unit volume free of sorbent, then in the material-balance equation one must use two cross sections: $\rho$, the total cross section of the tube, and $\rho' = \chi\rho$, the cross section free of sorbent. We shall consider the volume of sorbent at distances from $l_1$ to $l_2$ during the time interval from $t_1$ to $t_2$. The material-balance equation will be written as follows:

$$[(uC)_{l_1} - (uC)_{l_2}]\chi\rho\Delta t = [(y+\chi C)_{t_2} - (y+\chi C)_{t_1}]\rho\Delta l. \tag{1}$$

After division by $\Delta l\,\Delta t$ and passage to the limit as $\Delta l \to 0$, this equation takes the form

$$-u\chi\frac{\partial C}{\partial l} = \frac{\partial y}{\partial t} + \chi\frac{\partial C}{\partial t}. \tag{2}$$

The quantity $u\chi$ is equal to the linear rate of supply of the substance into the sorbent. We shall consider processes whose kinetics obey the equation

$$\frac{dy}{dt} = kCz, \qquad \text{where } z = y_0 - y; \tag{3}$$

$y_0$ is the equilibrium amount of substance sorbed by a unit volume of sorbent. From the expression $z = y_0 - y$ it follows that

$$\frac{dy}{dt} = -\frac{dz}{dt}. \tag{4}$$

Equation (3) is obeyed in many cases by the sorption of gases and vapors by porous sorbents ([1]), and also by ion exchange at low concentrations of electrolyte ([2]).

Substituting (4) into (3), we find that

$$\frac{dz}{dt} = -kCz. \tag{5}$$

The boundary and initial conditions are found as follows. From experiment it follows that

$$C(0,t) = C_0; \tag{6}$$

$$C(l,0) = 0 \quad \text{for } l > 0; \qquad C(l,0) = C_0 \quad \text{for } l \leq 0; \tag{7}$$

$$z(l,0) = z_0 = y_0 \quad \text{for } l \geq 0. \tag{8}$$

where $C_0$ is the concentration of the sorbed substance at the entrance to the tube. The expressions (7), which characterize one of the initial conditions, for $l > 0$ prove to be a discontinuous function. To simplify the problem of integrating the system of equations (2) and (5), the indicated initial condition may be replaced by a continuous function of the form

$$C(l,0) = C_0 e^{-al} \quad \text{for } l \geq 0, \tag{9}$$

which, for a sufficiently large value of the arbitrary constant, will give a result close to experiment.*

From (5), after substituting (6), it follows that

$$dz(0,t)/dt = -kC_0 z(0,t), \tag{10}$$

whence, after integration with account of (8),

$$z(0,t) = z_0 e^{-kC_0 t}. \tag{11}$$

Expressions (6), (11), (9), and (8) constitute the system of boundary and initial conditions necessary for solving equations (2) and (5), i.e., for finding the dependences of the concentration of the substance in the volume and on the surface of the sorbent as functions of the coordinate $l$ and time $t$.

From expression (5) it follows that

$$C = -\frac{1}{kz}\frac{\partial z}{\partial t}. \tag{12}$$

Substituting (12) and (4) into (2), we obtain

$$\frac{u\chi}{k}\frac{\partial}{\partial l}\left(\frac{1}{z}\frac{\partial z}{\partial t}\right) = -\frac{\partial z}{\partial t} - \frac{\chi}{k}\frac{\partial}{\partial t}\left(\frac{1}{z}\frac{\partial z}{\partial t}\right). \tag{13}$$

Differentiating, dividing by $\chi$, grouping, and denoting, we obtain $u\,\partial z/\partial l + \partial z/dt = w$,

$$z\frac{\partial w}{\partial t} = -\frac{k}{\chi}z^2\frac{\partial z}{\partial t} + \frac{\partial z}{\partial t}w \tag{14}$$

or

$$\frac{\partial}{\partial t}\left(\frac{w}{z}\right) = -\frac{k}{\chi}\frac{\partial z}{\partial t}. \tag{15}$$

Integrating (15), considering $l$ fixed and substituting $w$, we obtain

$$u\frac{\partial z}{\partial l} + \frac{\partial z}{\partial t} = -\frac{k}{\chi}z^2 + z\Phi(l), \tag{16}$$

where $\Phi(l)$ is some function of $l$.

From equation (16) it follows that the differential equations of the characteristics will be

$$dl/u = dt/1 = dz\Big/\left[-\frac{k}{\chi}z^2 + z\Phi(l)\right], \tag{17}$$

whence

$$l = ut + c_1. \tag{18}$$

$$z = \frac{b}{1 - c_2^b e^{-\frac{kb}{\chi} t}}, \tag{19}$$

where $b = \frac{\chi}{k}\Phi(l)$, and $c_1 c_2$ are constants of integration.

The value of $\Phi(l)$ can be found by substituting the value $z(0,t)$ into expression (16), i.e.,

$$u\frac{\partial z(l,0)}{\partial l} + \frac{\partial z(l,0)}{\partial t} = -\frac{k}{\chi}[z(l,0)]^2 + z(l,0)\Phi(l). \tag{20}$$

From (8) it follows that

$$\partial z(l,0)/\partial l = 0. \tag{21}$$

From (5) it follows

$$\partial z(l,0)/\partial t = -kC(l,0)z(l,0). \tag{22}$$

Substituting expressions (9) and (8) into (22), we obtain

$$\partial z(l,0)/\partial t = -kC_0 z_0 e^{-al}. \tag{23}$$

Substituting (23), (21), and (8) into (20), we find that

$$\Phi(l) = \frac{k}{\chi} z_0 - kuC_0 e^{-al}. \tag{24}$$

Therefore

$$b = \frac{\chi}{k}\Phi(l) = \frac{\chi}{k}\left[\frac{k}{\chi} z_0 - kuC_0 e^{-al}\right]. \tag{25}$$

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* This function could have been found by using expression (2), since according to (4), (5), and (8), $-u\chi\, dC(l,0)/dl = kC(l,0)z_0 + \chi\,\partial C(l,0)/\partial t$, but, according to (7), outside the region of discontinuity of the function $C(l,0)$, $\partial C(l,0)/\partial t = 0$. After substituting this value into the preceding expression and integrating, we obtain $C(l,0) = C(l,0) = C_0 e^{-\frac{kz_0}{\chi u} l}$. Consequently, in this case $a = kz_0/\chi u$. Such an approach is worse than the one adopted, since the discontinuity of the function is then neglected.

Substituting (25) and (18) into (19), we obtain

$$z = \frac{z_0 - \chi u C_0 e^{-a(ut+c_1)}}{1 - c_2^{z_0 - \chi u C_0 e^{-a(ut+c_1)}} e^{-[(k/\chi)z_0 - kuC_0 e^{-a(ut+c_1)}]t}}. \tag{26}$$

We shall consider the solution for the region where $l - ut \leq 0$. Let us set $t = t_0$ under the condition $l = 0$; then from (11) it follows that

$$z(0, t_0) = z_0 e^{-kC_0 t_0}. \tag{27}$$

From expression (18) it follows that, in this case,

$$t_0 = -c_1/u. \tag{28}$$

Substituting (28) into (27), we obtain

$$z(0, t_0) = z_0 e^{kC_0 \frac{c_1}{u}}. \tag{29}$$

Taking into account that $l = 0$ and $t = t_0$, substituting (29) into (26), we find

$$z_0 e^{kC_0 \frac{c_1}{u}} = \frac{z_0 - \chi u C_0 e^{-a(ut_0+c_1)}}{1 - c_2^{z_0 - \chi u C_0 e^{-a(ut_0+c_1)}} e^{-[(k/\chi)z_0 - kuC_0 e^{-a(ut_0+c_1)}]t}}. \tag{30}$$

Substituting the value $t_0$ from (28) into (30), we find the value of the constant

$$c_2 = \left[ \frac{\chi u C_0 + z_0 \{ e^{kC_0 \frac{c_1}{u}} - 1 \}}{z_0 e^{[kC_0 + (k/\chi)z_0 - kuC_0] c_1/u}} \right]^{\frac{1}{z_0 - \chi u C_0}}. \tag{31}$$

Substituting (31) and $c_1 = l - ut$ into (26), we obtain

$$z = \{ z_0 - \chi u C_0 e^{-al} \} \left\{ 1 - \left[ \frac{\chi u C_0 + z_0 \left[ e^{kC_0(l/u - t)} - 1 \right]}{z_0 e^{[kC_0 + (k/\chi)z_0 - kuC_0][(l/u) - t]}} \right]^{\frac{z_0 - \chi u C_0 e^{-al}}{z_0 - \chi u C_0}} \times e^{-[(k/\chi)z_0 - kuC_0 e^{-al}]t} \right\}^{-1}. \tag{32}$$

This is the solution of interest to us, valid for the region $l - ut \leq 0$.

The solution for the region $l - ut \geq 0$ is found as follows. Taking $t = 0$ and substituting expression (8) into (26), we obtain

$$c_2 = \left[ \frac{\chi u C_0 e^{-ac_1}}{z_0} \right]^{\frac{1}{z_0 - \chi u C_0 e^{-ac_1}}} . \tag{33}$$

Substituting (33) and the value of the constant $c_1$, from expression (18), into (26), we find the solution of interest to us for the region $l - ut \geq 0$:

$$z = \{z_0 - \chi u C_0 e^{-al}\} \left\{ 1 - \left[ \frac{\chi u C_0 e^{-a(l-ut)}}{z_0} \right]^{\frac{z_0 - \chi u C_0 e^{-al}}{z_0 - \chi u C_0 e^{-a(l-ut)}}} \times e^{-[(k/\chi) z_0 - k u C_0 e^{-al}]t} \right\}^{-1} . \tag{34}$$

The limiting transition under the condition that $a \to \infty$ leads, as is seen from expressions (32) and (34), to the function of interest to us in the form

$$z(l,t) = z_0 \left\{ 1 - \left[ \frac{z_0 \{e^{kC_0(l/u-t)} - 1\} + \chi u C_0}{z_0 e^{[kC_0 + (k/\chi) z_0 - k u C_0](l/u-t)}} \right]^{\frac{z_0}{z_0 - \chi u C_0}} e^{-\frac{k}{\chi} z_0 t} \right\}^{-1} \quad \text{for } l—ut \leq 0; \tag{35}$$

$$z(l,t) = z_0 \quad \text{for } l - ut \geq 0. \tag{36}$$

The solution for $l - ut \leq 0$ is the one that must be used when the length of the tube is sufficiently large. The obtained solution (32) and (34) satisfies both the initial and boundary conditions and the original differential equation. For practical calculations we are interested in expression (35) for the region $l—ut \leq 0$. For the region $l - ut \geq 0$ the solution, as is seen from (36), is trivial.

To find the distribution of the concentration $C(l,t)$ of the sorbed substance in the volume for any time $t$ and coordinate $l$, it is necessary to use expression (12), into which the values of $z$ and its derivative must be substituted, using expressions (32) and (34). For practical calculations only the region $l - ut \leq 0$ is of interest to us, for which we find:

$$\begin{aligned} C(l,t) = \Bigg\{ & \frac{z_0 - \chi u C_0 e^{-al}}{z_0 - \chi u C_0} \frac{\left(kC_0 + \frac{k}{\chi} z_0 - k u C_0\right) \left[\chi u C_0 + z_0 \left(e^{kC_0(l/u-t)} - 1\right)\right] - k C_0 z_0 e^{kC_0(l/u-t)}}{\chi u C_0 + z_0 \left[e^{kC_0(l/u-t)} - 1\right]} \\ & - \frac{k}{\chi} z_0 - k u C_0 e^{-al} \Bigg\} \left\{ k - k \left[ \frac{z_0 e^{(kC_0 + (k/\chi) z_0 - k u C_0)(l/u-t)}}{\chi u C_0 + z_0 \left[e^{kC_0(l/u-t)} - 1\right]} \right]^{\frac{z_0 - \chi u C_0 e^{-al}}{z_0 - \chi u C_0}} \right. \\ & \left. \times e^{\left(\frac{k}{\chi} z_0 - k u C_0 e^{-al}\right)t} \right\}^{-1} . \end{aligned} \tag{37}$$

Since, according to condition (9), $a$ must be very large, the limiting transition gives the final formula for calculating the distribution of the concentration of the sorbed substance along the tube under the condition that $l - ut \leq 1$:

$$C(l,t) = \left\{ \frac{z_0}{z_0 - \chi u C_0} \frac{\left(kC_0 + \frac{k}{\chi} z_0 - kuC_0\right) \left[\chi u C_0 + z_0 \left(e^{kC_0(l/u-t)} - 1\right)\right] - kC_0 z_0 e^{kC_0(l/u-t)}}{\chi u C_0 + z_0 \left[e^{kC_0(l/u-t)} - 1\right]} - \frac{k}{\chi} z_0 \right\} \times \left\{ k - k \left[ \frac{z_0 e^{(kC_0 + (k/\chi) z_0 - kuC_0)(l/u-t)}}{\chi u C_0 + z_0 \left[e^{kC_0(l/u-t)} - 1\right]} \right]^{\frac{z_0}{z_0 - \chi u C_0}} e^{\frac{k}{\chi} z_0} \right\}^{-1}. \tag{37}$$

The solutions considered are valid not only for sorption or ion-exchange processes, but may also be applied to chemical reactions in a flow between a solution or gas and a solid body, provided that the kinetics of the process obeys equation (3).

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*Note: Figure translations are in progress. See original paper for figures.*

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