

IDENTIFICATION OF A HYDROGEN TRANSFER MODEL WITH DYNAMICAL BOUNDARY CONDITIONS

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The nonlinear inverse problem of determining the hydrogen permeability parameters of stratified materials is considered. The model includes diffusion, invertible capture and sorption/desorption processes on surface, which leads to dynamical boundary conditions. For the concentration impulses method, the equation of stationary oscillations of concentration is obtained. Parametric identification scheme of the model is proposed. Techniques of Fourier series and conjugate equations are used.

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1. Mathematical model. There are many levels of interest in the interaction of hydrogen and its isotopes with various materials. It is sufficient to mention problems in power production, protection of construction materials from hydrogen corrosion, chemical reactor design, and vacuum technology. For those technological processes when metals contact with hydrogen medium it is necessary to design protecting coatings, which prevent hydrogen corrosion. Hydrogen is considered as a fuel, thus arise keeping and transporting problems. More about the question can be found in [1].

Classical diffusion models are often not sufficient, for it is necessary to consider physical and chemical processes on the surface. Sorption-desorption processes are modeled with dynamical boundary conditions [2]. A typical feature here is considering the most important integral characteristics of hydrogen transport in solids. They depend on technological peculiarities of material, on how the surface was processed. Thus it is not reasonable to head for tabulated data, but an algorithm for processing experimental curves is necessary. Coefficients estimation allows not only detailing physical conceptions (which, in the considered processes, are limitative for a given material) but also predicting the operating characteristics. The protecting, storage, and transport systems are multilayer. This makes the modeling and identification problem more difficult for direct measurements on the joint of layers are hardly possible. Layer structure can appear in the experiment, for instance, when it is necessary to study a material from which it is impossible to make a thin membrane. Then a plate from well-studied material is covered by an unknown one.

This paper is devoted to the proposition of a numerical algorithm for the parametric identification based on a well-studied [4, 2] method of concentration impulses (MCI). The considered model is rather general and the results may be applied to similar permeability problems. Specificity of hydrogen is only reflected in the fact that the desorption is square. A simplified scheme for rather homogeneous materials is briefly given

at the end of the paper. Great difficulties of solving nonlinear inverse problems are well known. Usually the discrepancy of experimental and model curves is minimized in the space of parameters. Various gradient algorithms are developed. But in the general case for distributed models it is necessary to integrate numerically the partial differential equations for current parameter approximations; it is difficult to study convergence. Thus it is necessary to benefit from the specificity of the accepted mathematical model.

2. Gas transfer model and concentration impulses method. At one side of the two-layer membrane (which divides a vacuum vessel into two parts), a rather high hydrogen pressure p_0 is made. At the outlet part of the vessel, penetrating gas is removed by a vacuum system. For the first layer, the mathematical model, considering diffusion in the volume of material (usually it is the metal) and physical/chemical processes on the surface, is assumed [2]:

$$c_t(t, x) = D(T)c_{xx}(t, x), \quad (t, x) \in \Omega, \quad (2.1)$$

$$\Omega = (0, t^+) \times (0, L), \quad c(0, x) = N_1(x), \quad (2.2)$$

$$c_0(t) = c(t, 0) = g(T)q(t), \quad T = T(t), \quad (2.3)$$

$$\dot{q}(t) = \mu s(T)p_0(t) - J_0(t) + D(T)c_x(t, 0), \quad (2.4)$$

$$J_0(t) = b(T)q^2(t), \quad c_0(0) = g(T(0))q(0) = N_1(0). \quad (2.5)$$

Here $c(t, x)$ is the concentration of diffusing (atomic for some metals) hydrogen, $q(t)$ is the surface concentration (number of atoms on cm^2 , $x = 0$ is for inlet side), $\dot{q} = dq/dt$, $D(T)$ is the diffusion coefficient, $g(T)$ is the matching coefficient between the concentrations on the surface and in the volume near the surface of the membrane, μ is a kinetic constant, $J_0(t)$ is the density of the outlet desorption flux, $b(T)$ is the desorption coefficient, and $T(t)$ is the temperature.

According to (2.3) dissolving is relatively fast, so the concentration near the surface $c_0(t)$ changes together with surface concentration $q(t)$. Equation (2.4) is the flux balance equation. The more the pressure $p_0(t)$ is, the faster a surface becomes saturated. The material of the layer is characterized by a value s . Some atoms, forming molecules, desorb back from the surface ($J_0(t)$), not going in the membrane. The last term in the right-hand side of (2.4) is for arriving from the volume of the diffusing atoms. Initial and boundary conditions are adjusted in the sense of (2.5). Equations (2.1)–(2.5) are rather general, parameters D , g , b , and s carry information about hydrogen transport. Further, adding variables to the model (at least the second layer parameters and that of processes on the joint are necessary) makes the identification problem hardly possible to solve.

Limitations of using the model will not be discussed. For metals and hydrogen, usually the Arrhenius law is used as the dependence of D , g , b , and s on temperature T : $D(T) = D_0 \exp(-E_D/RT)$, $g(T) = g_0 \exp(-E_g/RT)$, Other temperature dependencies are also possible. Mathematical basis of the boundary value problem with nonlinear dynamical boundary conditions (2.4) ($J_0 = bq^2$) is given in [7].

Similar equations are assumed for the second layer (two points of origin will be used for the x -axis): $\Omega_* = (0, t^+) \times (0, \ell)$,

$$u_t = D_*(T)u_{xx} - a_1(T)u + a_2(T)w, \quad (2.6)$$

$$w_t = a_1(T)u - a_2(T)w, \quad (t, x) \in \Omega_*, \quad (2.7)$$

$$u(0, x) = N_2(x), \quad w(0, x) = N_3(x), \quad (2.8)$$

$$u_\ell(t) = u(t, \ell) = g_*(T)v(t), \quad T = T(t), \quad (2.9)$$

$$\dot{v}(t) = \mu s_*(T)p_\ell(t) - J_\ell(t) - D_*(T)u_x(t, \ell), \quad (2.10)$$

$$J_\ell(t) = b_*(T)v^2(t), \quad u_\ell(0) = g_*(T(0))v(0) = N_2(\ell). \quad (2.11)$$

The value $x = \ell$ is for the outlet surface of the second layer, $\dot{v} = dv/dt$. The total width of the membrane is $L + \ell$. The difference from (2.1)-(2.5) is that trap interaction is considered (traps are different defects of the structure, which can capture hydrogen). In (2.6), (2.7), $w(t, x)$ is the concentration of the captured hydrogen, $a_i > 0$.

On the joint of the layers the following conditions are assumed:

$$D(T)c_x(t, L) = D_*(T)u_x(t, 0), \quad (2.12)$$

$$k(T)c_L(t) - k_*(T)u_0(t) = -D(T)c_x(t, L), \quad (2.13)$$

$c_L(t) = c(t, L)$, $u_0(t) = u(t, 0)$. Condition (2.12) (continuity of diffusion flux) means that hydrogen does not accumulate on the joint. Counter-current flows from one layer to another are proportional to concentration and their difference is the diffusion flux; thus (2.13) is obtained ((2.1), (2.6) are of the second order).

Now the measurements equations are defined:

$$p_\ell(t) = \theta_1 \int_0^t \exp\left\{-\frac{\tau-t}{\theta_0}\right\} J(\tau) d\tau, \quad (2.14)$$

$$J(t) = J_\ell(t) = b_*(T(t))v^2(t). \quad (2.15)$$

For concreteness, an experimental apparatus [3] will be taken as an example. A membrane is a vacuum vessel barrier and in the initial moment there is no hydrogen there ($t = 0$, $N_i(x) = 0$). At the outlet side a vacuum is provided. A mass spectrometer gives the hydrogen pressure $p_\ell(t)$, which is defined by the outlet desorption flux. We will usually omit the word *density* assuming that the surface has unit area. Equation (2.14) is defined by the experiment: hydrogen injection to the vessel (δ -impulse) implies a pressure jump and then an exponential fading. The values θ_0 , θ_1 are determined by the experimental apparatus. On $p_\ell(t)$ the flux J_ℓ is determined: $J_\ell(t) = (\dot{p}_\ell(t) + p_\ell(t)/\theta_0)/\theta_1$. On evacuation, we assume $\mu s_* p_\ell \approx 0$ in (2.10) since a high-capacity pump provides a very low hydrogen pressure $p_\ell(t)$ and the return to the surface is negligibly small. The density of the desorption flux $J(t) = J_\ell(t)$ is considered as experimental data. Obtaining J from an integral equation (2.14) while measurements of p_ℓ are noisy is not an easy problem [6].

Now the method of concentration impulses (MCI) is described [2, 4]. A membrane is heated till a fixed temperature $T(t) = \bar{T}$, the pressure $p_0(t) = \bar{p}$ is also constant. At

the outlet side a vacuum is provided. In some time the outlet flux $\bar{J} = \text{const}$ becomes stationary. After that, at the inlet side, a cracker is periodically turned on and off. This allows making rectangular impulses of hydrogen concentration near the surface. Time period is chosen such that while the cracker is off, the flux $J(t)$ has time to fall to the level \bar{J} , and while the cracker is on—to reach the horizontal asymptote ($J \approx \bar{J}_h = \text{const} > \bar{J}$).

Periodical turning the cracker on and off implies stepped concentration:

$$\begin{aligned}
 c_0(t) &= Q_0 + (-1)^j Q_1, \\
 t &\in \left(\frac{j\pi}{\omega}, \frac{(j+1)\pi}{\omega} \right), \quad j = 0, 1, \dots, \quad Q_0 > 0, \quad Q_1 > 0, \quad Q_0 - Q_1 > 0, \\
 c_0(t) &= Q_0 - iQ_1 \sum_{n=\pm 1, \pm 3, \dots} 2(n\pi)^{-1} \exp(in\omega t) \\
 &= Q_0 + Q_1 \sum_{n=1, 3, \dots} 4(n\pi)^{-1} \sin(n\omega t), \quad i = \sqrt{-1}
 \end{aligned} \tag{2.16}$$

(a time zero is moved). At times $j\pi/\omega$, fast transition processes hold, $c_0(t)$ changes with jumps. Frequency ω is chosen small. When the cracker is on, (2.4) is removed from the model for it is for the case when a surface contacts with molecular hydrogen. While knowing how $c_0(t)$ changes, in (2.16), we consider Q_i unknown.

To make the equations for parameters more observable, we consider the material of the first layer already studied. The desorption flux density $J = J_\ell(t)$ and the parameters D , g , b , and s are known. The identification problem is to determine D_* , g_* , b_* , s_* , k , k_* , and a_i . The information about their values at different \bar{T} allows determining dependencies $D_*(T), \dots, k_*(T), a_i(T)$ (in the Arrhenius case $D_{*0}, E_{D_*}, \dots, b_{*0}, E_{b_*}$, etc.). Though s_* as a multiplier in $\mu s_* p_\ell = 0$ is not formally included in the model, it is determined by other parameters (see (3.1)). Applied to an experimental method of penetration the problem is studied in [8, 9].

Numerical experiments corroborate that the model is adequate with respect to physical conceptions and experimental data [2, 4]. From (2.16) it follows that a flux density $J(t)$ by some time becomes stationary oscillating, independently of initial gas distribution. A plot of $J(t)$ on a period of oscillations has a special look, see Figures 2.1 and 2.2.

Here are the main values of the parameters (the “highest” graph): $D = 10^{-5}$, $D_* = 10^{-9} \text{ cm}^2/\text{s}$, $g = 10^2$, $g_* = 10^3 \text{ cm}^{-1}$, $b = 10^{-17}$, $b_* = 10^{-16} \text{ cm}^2/\text{s}$, $s = 10^{-4}$, $s_* = 10^{-3}$, $k = 10^{-6}$, $k_* = 10^{-7} \text{ cm/s}$, $a_1 = 10^{-4}$, $a_2 = 10^{-5} \text{ s}^{-1}$, $\mu = 1.46 \cdot 10^{21} \text{ mol/cm}^2 \text{ s Torr}$, $\bar{p} = 1 \text{ Torr}$, $L = 0.02$, $\ell = 2 \cdot 10^{-4} \text{ cm}$, $Q_0 + Q_1 = 4(Q_0 - Q_1)$, $\sigma = 2\pi/\omega = 400 \text{ s}$.

While diffusion coefficients D , D_* decrease, so does the outlet hydrogen desorption flux and grows the time needed to reach the horizontal asymptotes. The oscillation phase changes. The delay between the moments of falls of concentration on inlet and outlet when the cracker turns off grows. Reversible capture implies the delay in saturation and more fluent transition to stationary states. The second highest graph on Figure 2.2 corresponds to $a_1 = 0.01$, $a_2 = 0.03$, and the lowest to $a_1 = 0.03$, $a_2 = 0.01$. Varying of other parameters also corresponds to physics.

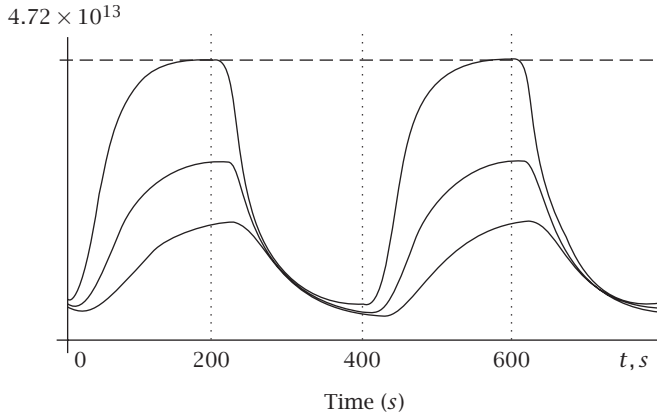


FIGURE 2.1. Influence of diffusion coefficient on outlet flux.

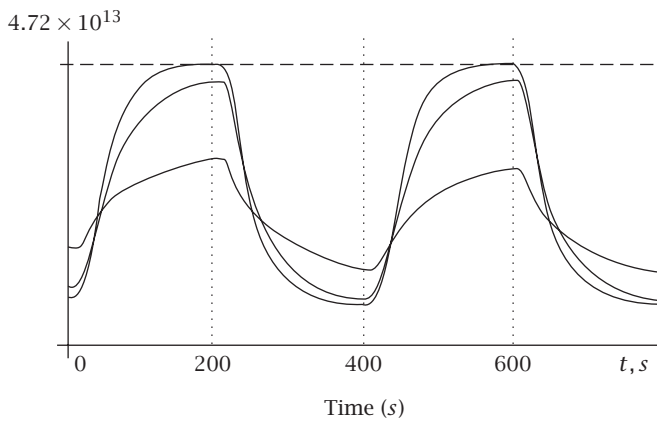


FIGURE 2.2. Influence of capturing and releasing the gas by traps.

3. Analysis of equilibrium and stationary states. The rate of joint crossing constants k, k_* is connected to $g, b, s, g_*, b_*,$ and s_* , which define the dynamics of surface processes. This connection will reduce the dimension of the estimation problem.

We, at the outlet side, make a pressure $p_\ell = p_0 = \bar{p}$ at $T = \bar{T}$ instead of vacuum. In some time equilibrium concentrations will be reached in both layers: $\bar{c}, \bar{u}, \bar{w}$. From (2.3), (2.4) (all derivatives are equal to zero), comes $\bar{c} = \gamma\sqrt{\bar{p}}, \gamma = g\sqrt{\mu s/b}$. In the same way, from (2.7), (2.9), (2.10), comes $a_1\bar{u} = a_2\bar{w}, \bar{u} = g_*\sqrt{\mu s_*/b_*}\sqrt{\bar{p}}$. Now from (2.13), comes

$$k\bar{c} = k_*\bar{u} \Rightarrow \frac{k}{k_*} = \frac{g_*\sqrt{s_*b}}{g\sqrt{sb_*}}. \tag{3.1}$$

The total concentration in the second layer is also proportional to $\sqrt{\bar{p}}$:

$$\bar{u} + \bar{w} = \bar{u} + \frac{a_1 \bar{u}}{a_2} = \gamma_* \sqrt{\bar{p}}, \quad \gamma_* \equiv \alpha g_* \sqrt{\frac{\mu s_*}{b_*}}, \quad \alpha \equiv \left(1 + \frac{a_1}{a_2}\right). \quad (3.2)$$

The coefficients of equilibrium dissolubility γ , γ_* are relatively easily obtained from saturation–degassing for each material separately. Thus for the more complicated problem being considered, they will be assumed to be known. Then due to (3.1), the value

$$\Gamma \equiv \frac{\gamma_*}{\gamma} = \left(1 + \frac{a_1}{a_2}\right) \frac{g_* \sqrt{s_* b_*}}{g \sqrt{s b_*}} = \frac{\alpha k}{k_*} \quad (3.3)$$

is known. Thus, a complex $\alpha k/k_* = \Gamma$ can be obtained experimentally, and k/k_* is connected with g , g_* , b , b_* , s , and s_* , by (3.1). It is enough now to know how to get the values D_* , g_* , b_* , k_* , and a_i at given temperature \bar{T} .

Let us see what information can the stationary state provide. At the inlet side $p_0(t) = \bar{p}$, at the outlet is the vacuum. By some time t_* a flux will be $J(t) = J_\ell(t) = \bar{J} = \text{const}$, $t \geq t_*$. In (2.1)–(2.10) all time derivatives will become zero. From (2.3), (2.4) it follows that $c_0(t) = \bar{c}_0 = \text{const}$ for $t \geq t_*$ and

$$\bar{c}_0 = g \left\{ \frac{\mu s \bar{p} - \bar{J}}{b} \right\}^{1/2}. \quad (3.4)$$

Actually, (2.10) implies that $\dot{v} = 0$, $\mu s_* p_\ell = 0 \Rightarrow \bar{J} = -D_* u_x$, $t \geq t_*$. Diffusion flux is equal to desorption one. From $c_t = u_t = w_t = 0$ linearity of concentrations with respect to depth follows, that is, the gradients c_x , u_x are constant. From (2.12), $Dc_x = -\bar{J}$, $t \geq t_*$ is obtained. After substituting Dc_x into (2.4) with $\dot{q} = 0$ and (2.3) taken into consideration, (3.4) can be found. Note that $\bar{c}_0 < \bar{c}$ because of subtracted \bar{J} . Equation (3.4) ($\bar{J} = \mu s \bar{p} - b \bar{q}_0^2$) means the equilibrium of fluxes.

REMARK 3.1. Enlarging L , ℓ , and \bar{p} , it is possible to make $\mu s \bar{p} \gg \bar{J}$. The flux that comes to the surface is much bigger than the carrying capacity of the membrane. Then from (3.4) it follows that $\bar{c}_0 \approx g \sqrt{\mu s \bar{p} / b}$, that is, $\bar{c}_0 \approx \bar{c} = \gamma \sqrt{\bar{p}}$. If, together with γ , the value s is also known, then $\bar{c}_0 = \gamma [(\mu s \bar{p} - \bar{J}) / (\mu s)]^{1/2}$.

Now it is possible to obtain analytical expressions for the stationary state:

$$\begin{aligned} \frac{\bar{c}_L - \bar{c}_0}{L} = c_x = -D^{-1} \bar{J} &\Rightarrow \bar{c}_L = \bar{c}_0 - LD^{-1} \bar{J}, \\ \bar{J} = b_* \bar{v}^2 = b_* \left(\frac{\bar{u}_\ell}{g_*} \right)^2 &\Rightarrow \bar{u}_\ell = g_* \left(\frac{\bar{J}}{b_*} \right)^{1/2}, \\ \frac{\bar{u}_\ell - \bar{u}_0}{\ell} = u_x = -D_*^{-1} \bar{J} &\Rightarrow \bar{u}_0 = \bar{u}_\ell + \ell D_*^{-1} \bar{J}. \end{aligned} \quad (3.5)$$

The following symbols will be used: $R(t) = J^{1/2}(t)$, $\bar{R} = \bar{J}^{1/2}$, and the new variables will be defined:

$$z_1 = \frac{\ell^2}{D_*}, \quad z_2 = \frac{1}{\sqrt{b_*}}, \quad z_3 = g_* \ell, \quad z_4 = \frac{\ell}{k_*}. \quad (3.6)$$

When $t \geq t_*$, (2.13) is written in the form $k\bar{c}_L - k_*\bar{u}_0 = \bar{J}$. After substituting the found \bar{c}_L , \bar{u}_0 and multiplying the equation by $\alpha\ell$, we obtain

$$\alpha(z_1 + z_4)\bar{J} + \alpha z_2 z_3 \bar{R} = \Gamma\ell(\bar{c}_0 - LD^{-1}\bar{J}). \tag{3.7}$$

This equation allows finding $\Sigma = \alpha(z_1 + z_4)$, $\Pi = \alpha z_2 z_3$ by two pressures \bar{p}_1 , \bar{p}_2 and the appropriate stationary values of the flux \bar{J}_1 , \bar{J}_2 . Then, multiplying (3.1) by $\alpha = (1 + a_1/a_2)$ and from $\Gamma = \Pi\sqrt{bs_*}/(\ell g\sqrt{s})$ or from $\gamma_* = \Pi\sqrt{\mu s_*}/\ell$, find s_* .

REMARK 3.2. Stationary state can be analyzed also for the membrane when the layers are changed. Then in (3.7) the set of values D, g, b, s, L is replaced by that of D_*, g_*, b_*, s_*, ℓ and vice versa:

$$\Gamma\left(\frac{\bar{R}_*L}{D} + \frac{g}{\sqrt{b}}\right)\bar{R}_*\ell = \Pi(\mu s_*\bar{p} - \bar{J}_*)^{1/2} - \Sigma\bar{J}_*. \tag{3.8}$$

From known complexes Σ, Π , also s_* may be determined.

There is no additional information about unknown parameters. To determine them uniquely, it is necessary to study transition processes.

4. Stationary oscillations and conjugate equations. Due to (2.16), stationary oscillations of the flux $J(t)$, independent on $N_i(x)$, are formed on the outlet in some time t_* (Figures 2.1 and 2.2). We obtain the equation for this (asymptotic) mode.

Integrating the linear equation (2.7) and substituting $w(t, x)$ into (2.6), we obtain

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2} - a_1u + a_1a_2 \int_0^t \exp\{a_2 \cdot (\tau - t)\}u(\tau, x)d\tau + \chi(t, x). \tag{4.1}$$

While time t grows, influence of the initial data $u(0, x)$, $w(0, x)$ declines exponentially: in (4.1), $\chi(t, x) = a_2 \exp(-a_2t)N_3(x)$. Under an integral sign at $\tau = 0$, there is $\exp(-a_2t)N_2(x)$. Consider (4.1) while t formally grows till infinity. Firstly, consider integral term. Represent an integral as a sum

$$\exp(-a_2t) \int_0^t \exp(a_2\tau)u(\tau, x)d\tau = \exp(-a_2t) \int_0^{t_0} \dots + \exp(-a_2t) \int_{t_0}^t \dots \tag{4.2}$$

At any fixed t_0 the first term decreases exponentially. Choose $t_0 \geq t_*$ such that oscillations can be considered stationary. At that, the difference $t - t_0$ is also considered big enough, so that a first term ($t \geq t_1 \gg t_0 \geq t_* \gg 1$) becomes small. Represent as $t = t_0 + m\sigma + \tilde{t}$. Here, $\tilde{t} \in (0, \sigma)$, $\sigma = 2\pi/\omega$, is the period of oscillations and m is a

rather large natural number. Then due to the fact that $u(\tau + \sigma, x) = u(\tau, x)$ is periodic, we obtain

$$\begin{aligned} \int_{t_0}^t \dots &= \int_{t_0}^{t_0+\sigma} \exp(a_2\tau)u(\tau, x)d\tau + \int_{t_0+\sigma}^{t_0+2\sigma} \exp(a_2\tau)u(\tau, x)d\tau + \dots \\ &= \int_{t_0}^{t_0+\sigma} \exp(a_2\tau)u(\tau, x)d\tau + \exp(a_2\sigma) \int_{t_0}^{t_0+\sigma} \exp(a_2\tau)u(\tau, x)d\tau + \dots \\ &= FR + \exp(a_2m\sigma) \int_{t_0}^{t_0+\tilde{t}} \exp(a_2\tau)u(\tau, x)d\tau, \end{aligned} \quad (4.3)$$

$$F = \{1 + \exp(a_2\sigma) + \dots + \exp(a_2(m-1)\sigma)\} = \frac{1 - \exp(ma_2\sigma)}{1 - \exp(a_2\sigma)},$$

$$R = \int_{t_0}^{t_0+\sigma} \exp(a_2\tau)u(\tau, x)d\tau.$$

Multiply the result by $\exp(-a_2t)$ and let m tend to infinity:

$$\begin{aligned} \exp(-a_2t) \int_{t_0}^t \dots &\rightarrow -R \frac{\exp\{-a_2 \cdot (t_0 + \tilde{t})\}}{1 - \exp(a_2\sigma)} \\ &+ \int_{t_0}^{t_0+\tilde{t}} \exp\{a_2 \cdot (\tau - (t_0 + \tilde{t}))\}u(\tau, x)d\tau. \end{aligned} \quad (4.4)$$

So, the integral term in (4.1) for the large t has the form

$$\begin{aligned} a_1 a_2 \int_0^t \dots &= a_1 a_2 \int_{t_0}^{t_0+\tilde{t}} \exp\{a_2 \cdot (\tau - (t_0 + \tilde{t}))\}u(\tau, x)d\tau \\ &+ A \int_{t_0}^{t_0+\sigma} \exp\{a_2 \cdot (\tau - (t_0 + \tilde{t}))\}u(\tau, x)d\tau, \quad \tilde{t} \in (0, \sigma). \end{aligned} \quad (4.5)$$

Here $A = a_1 a_2 [\exp(a_2\sigma) - 1]^{-1}$. Now it is convenient to move the time zero to the point $t_0 + \sigma$ (for describing stationary oscillations that are not important). The new time $\tilde{t} \in (0, \sigma)$ will be named t for simplicity. Then on the period $(0, \sigma)$ the following equation for stationary oscillations in the second layer holds:

$$\begin{aligned} \frac{\partial u}{\partial t} &= D_* \frac{\partial^2 u}{\partial x^2} - a_1 u + A \int_{-\sigma}^0 \exp\{a_2 \cdot (\sigma + \tau - t)\}u(\tau, x)d\tau \\ &+ a_1 a_2 \int_{-\sigma}^{-\sigma+t} \exp\{a_2 \cdot (\sigma + \tau - t)\}u(\tau, x)d\tau, \quad t \in (0, \sigma). \end{aligned} \quad (4.6)$$

It is an equation with an aftereffect: the change in rate of concentration is influenced by history of that from the previous period. So, the capture influences the transfer not instantly, but integrally (some inertia corresponds to physical intuition). While $t \in (0, \sigma)$ grows, the further history influences less. Taking $u(\tau + \sigma, x) = u(\tau, x)$, $A \exp(a_2\sigma) = A + a_1 a_2$ into consideration, the equation is rewritten in the form

$$\begin{aligned} \frac{\partial u}{\partial t} = D_* \frac{\partial^2 u}{\partial x^2} - a_1 u + (a_1 a_2 + A) \int_0^t \exp\{a_2 \cdot (\tau - t)\} u(\tau, x) d\tau \\ + A \int_t^\sigma \exp\{a_2 \cdot (\tau - t)\} u(\tau, x) d\tau, \quad (t, x) \in (0, \sigma) \times (0, \ell). \end{aligned} \tag{4.7}$$

But later a more compact form will be used:

$$\begin{aligned} \frac{\partial u}{\partial t} = D_* \frac{\partial^2 u}{\partial x^2} - a_1 u + \int_0^\sigma H(t, \tau) u(\tau, x) d\tau, \quad t \in (0, \sigma), \\ H(t, \tau) = (a_1 a_2 + A) \exp\{a_2 \cdot (\tau - t)\}, \quad 0 \leq \tau \leq t, \\ H(t, \tau) = A \exp\{a_2 \cdot (\tau - t)\}, \quad \sigma \geq \tau > t. \end{aligned} \tag{4.8}$$

REMARK 4.1. Formally one can find a contradiction in (4.8): the rate of changing of $u(t, x)$ with respect to t is influenced by future values of $u(\tau, x)$. But due to being periodical, this future is the influence of the previous period. It must be noted that, unlike (4.1), it is not possible in (4.8) to grow t without limitations: the equation has been written for the interval of the length $\sigma = 2\pi/\omega$ with a new time zero $t_0 + \sigma$ ($t_0 \gg 1, \tilde{t} \in (0, \sigma)$), that is, for the period of stationary oscillations. Later, for other t , the solution $u(t, x)$ is continued periodically ($H(0, \tau) = H(\sigma, \tau)$). This limit mode of oscillations is reached asymptotically in the model.

Later it is convenient that a new time zero $t_0 + \sigma$ coincides with turning a cracker on. Then $(0, \sigma/2)$ corresponds to turning on and $(\sigma/2, \sigma)$ —to turning off. If by the initial moment $t = 0$ $J \approx \bar{J}, J \approx \bar{J}_h$ holds when $t = \sigma/2$, and by the end of the period ($t = \sigma$) $J \approx \bar{J}$ again, then the initial segment $[0, \sigma]$ may be taken as a stationary oscillation period. Exactly that period, at which $J(t)$ has time to reach an asymptote, will be used below: the levels \bar{J}, \bar{J}_h are corresponded by linear concentrations, which can be calculated explicitly.

We now construct a conjugate system. Methodology of conjugate equations in the mathematical physics is given, for instance, in [5]. Consider a system (2.1), (4.8) with the conditions (2.12), (2.13). Choose the functions $\varphi(t, x), \psi(t, x)$ with necessary analytical properties (below the integration by parts is used) and make the following transforms:

$$\begin{aligned} 0 = \int_0^\sigma \int_0^L \varphi \cdot (c_t - D c_{xx}) dx dt \\ + \eta \int_0^\sigma \int_0^\ell \psi \cdot \left\{ u_t - D_* u_{xx} + a_1 u - \int_0^\sigma H(t, \tau) u(\tau, x) d\tau \right\} dx dt \\ = \int_0^L \{ \varphi(t, x) c(t, x) \} \Big|_{t=0}^\sigma dx - \int_0^\sigma \{ \varphi(t, x) D c_x(t, x) \} \Big|_{x=0}^L dt \\ + \int_0^\sigma \{ D \varphi_x(t, x) c(t, x) \} \Big|_{x=0}^L dt + \eta \int_0^\ell \{ \psi(t, x) u(t, x) \} \Big|_{t=0}^\sigma dx \\ - \eta \int_0^\sigma \{ \psi(t, x) D_* u_x(t, x) \} \Big|_{x=0}^\ell dt + \eta \int_0^\sigma \{ D_* \psi_x(t, x) u(t, x) \} \Big|_{x=0}^\ell dt. \end{aligned} \tag{4.9}$$

Two double integrals are omitted here, for they vanish if we choose φ, ψ that satisfy the following equations conjugate to (2.1) and (4.8)

$$\frac{\partial \varphi}{\partial t} = -D \frac{\partial^2 \varphi}{\partial x^2}, \quad x \in (0, L), \quad t \in (0, \sigma), \tag{4.10}$$

$$\frac{\partial \psi}{\partial t} = -D_* \frac{\partial^2 \psi}{\partial x^2} + a_1 \psi - \int_0^\sigma H(\tau, t) \psi(\tau, x) d\tau. \tag{4.11}$$

In the integral, there is $H(\tau, t)$ instead of $H(t, \tau)$ in (4.8). In detail,

$$\begin{aligned} \int_0^\sigma \dots &= (a_1 a_2 + A) \int_t^\sigma \exp\{a_2 \cdot (t - \tau)\} \psi(\tau, x) d\tau \\ &+ A \int_0^t \exp\{a_2 \cdot (t - \tau)\} \psi(\tau, x) d\tau, \quad A = \frac{a_1 a_2}{\exp(a_2 \sigma) - 1}. \end{aligned} \tag{4.12}$$

The conjugate equations are constructed in the following way: the signs of the terms in the right-hand side are changed, the integration segment $[0, t]$ is replaced by $[t, \sigma]$ and vice versa, $\tau - t$ is replaced by $t - \tau$ and vice versa, that is, “everything is up side down.”

Further transforms of (4.9) are made to eliminate terms, which cannot be explicitly expressed via the model coefficients and the measurements. Having no experimental information about the fluxes at the joint of layers ($x = L$ for the first layer and $x = 0$ for the second), add the conjugate conditions, similar to (2.12), (2.13), to (4.10), (4.11):

$$D\varphi_x(t, L) = D_*\psi_x(t, 0), \quad \eta = \frac{k_*}{k} = \frac{\alpha}{\Gamma}, \tag{4.13}$$

$$k\varphi(t, L) - k_*\psi(t, 0) = -D\varphi_x(t, L). \tag{4.14}$$

Finally, (4.9) is in the form

$$\begin{aligned} 0 &= \int_0^L \{\varphi(t, x)c(t, x)\} |_{t=0}^\sigma dx + \int_0^\sigma \varphi(t, 0) Dc_x(t, 0) dt \\ &- \int_0^\sigma D\varphi_x(t, 0)c(t, 0) dt + \alpha\Gamma^{-1} \int_0^\ell \{\psi(t, x)u(t, x)\} |_{t=0}^\sigma dx \\ &- \alpha\Gamma^{-1} \int_0^\sigma \psi(t, \ell) D_*u_x(t, \ell) dt + \alpha\Gamma^{-1} \int_0^\sigma D_*\psi_x(t, \ell) u(t, \ell) dt. \end{aligned} \tag{4.15}$$

REMARK 4.2. For conjugate equations (4.10), (4.11) there are no boundary conditions. As (4.10)–(4.14) are homogeneous, the solutions φ, ψ are defined up to the multiplier. There are infinitely many of those; it is convenient to use separation of variables: $\varphi = \beta(t)r(x), \psi = \beta_*(t)r_*(x)$.

Here are some most simple solutions to (4.11). The integral of $H(\tau, t)$ on $\tau \in [0, \sigma]$ does not depend on t and is equal to a_1 . Thus the functions $\psi = 1, \psi = x$ are solutions. Other variants: $\psi = \beta(t) \cos(\nu x) (\sin(\nu x)), \beta(t) \exp(\nu x)$, where ν is a parameter. For the case $\beta(t) \cos(\nu x)$, for instance, obtain

$$\dot{\beta} = D_*\nu^2\beta + a_1\beta - \int_0^\sigma H(\tau, t)\beta(\tau) d\tau. \tag{4.16}$$

Divide by $\exp(a_2 t)$ and define a new variable $\xi(t) = \exp(-a_2 t)\beta(t)$:

$$\dot{\xi} + a_2 \xi = (D_* v^2 + a_1)\xi - A \int_0^t \xi(\tau) d\tau - (a_1 a_2 + A) \int_t^\sigma \xi(\tau) d\tau. \tag{4.17}$$

Differentiating on t , obtain a linear equation of the second order:

$$\xi^{(2)}(t) + (a_2 - a_1 - D_* v^2)\dot{\xi}(t) - a_1 a_2 \xi(t) = 0. \tag{4.18}$$

Substituting ξ back to (4.17) one arbitrary constant disappears. For $\psi = \beta(t) \exp(vx)$ it is only necessary to change the sign at D_* . A linear combination of solutions is also a solution. The parameter v is arbitrary and may be determined as a function of estimated quantities $v = v(D_*, a_i)$. For instance, for $\psi = \beta(t) \cos(vx)$, it is better to take $v^2 = D_*^{-1}(a_2 - a_1)$, if $a_2 > a_1$. Otherwise for $\psi = \beta(t) \exp(vx)$, $v^2 = D_*^{-1}(a_1 - a_2)$ if $a_2 < a_1$. Then $\xi^{(2)} = a_1 a_2 \xi$.

In (4.15) no information about a stationary mode $c(\sigma/2, x)$ is used. Thus one more method of constructing conjugate systems is reasonable.

Consider two semiperiods $[\tau_1, \tau_2] = [0, \sigma/2]$ and $[\tau_1, \tau_2] = [\sigma/2, \sigma]$, $\sigma = 2\pi/\omega$. Integrate (2.7) on a segment $[\tau_1, \tau_2]$, taking $a_1 c(\tau_i, x) = a_2 w(\tau_i, x)$ for the stationary modes into consideration, and substitute w into (2.6). In the same way as in (4.9),

$$\begin{aligned} 0 = & \int_{\tau_1}^{\tau_2} \int_0^L \varphi \cdot (c_t - D c_{xx}) dx dt \\ & + \eta \int_{\tau_1}^{\tau_2} \int_0^\ell \psi \cdot \left\{ u_t - D_* u_{xx} + a_1 u - a_1 a_2 \int_{\tau_1}^t \exp\{a_2 \cdot (\tau - t)\} u(\tau, x) d\tau \right. \\ & \left. - a_1 \exp\{a_2 \cdot (\tau_1 - t)\} u(\tau_1, x) \right\} dx dt = \dots \end{aligned} \tag{4.19}$$

Finally instead of (4.15), the following equation is obtained ($\chi = \Gamma/\alpha = k/k_*$):

$$\begin{aligned} 0 = & \int_0^L \{ \varphi(t, x) c(t, x) \} |_{t=\tau_1}^{\tau_2} dx + \int_{\tau_1}^{\tau_2} \varphi(t, 0) D c_x(t, 0) dt \\ & - \int_{\tau_1}^{\tau_2} D \varphi_x(t, 0) c(t, 0) dt + \chi^{-1} \int_0^\ell \{ \psi(t, x) u(t, x) \} |_{t=\tau_1}^{\tau_2} dx \\ & - \chi^{-1} \int_{\tau_1}^{\tau_2} \psi(t, \ell) D_* u_x(t, \ell) dt + \chi^{-1} \int_{\tau_1}^{\tau_2} D_* \psi_x(t, \ell) u(t, \ell) dt \\ & - a_1 \chi^{-1} \int_{\tau_1}^{\tau_2} \int_0^\ell \psi(t, x) \exp\{a_2 \cdot (\tau_1 - t)\} u(\tau_1, x) dx dt. \end{aligned} \tag{4.20}$$

At that, the conditions on the joint (4.13), (4.14) are preserved, and instead of (4.11) there will be

$$\frac{\partial \psi}{\partial t} = -D_* \frac{\partial^2 \psi}{\partial x^2} + a_1 \psi - a_1 a_2 \int_t^{\tau_2} \exp\{a_2 \cdot (t - \tau)\} \psi(\tau, x) d\tau, \tag{4.21}$$

$x \in (0, \ell)$, $t \in (\tau_1, \tau_2)$. The simplest solutions to these equations $\psi_1 = \beta(t)$, $\psi_2 = \beta(t)x$, $\psi_3 = \beta(t) \sin(vx)$, and $\psi_4 = \beta(t) \exp(vx)$ are also obtained by integration of (4.18) ($\psi_{1,2} \Rightarrow v = 0$). The only difference is that one of two arbitrary constants is eliminated using other conditions.

5. Parametric identification of the model. Here are the methods of obtaining explicit equations (nondifferential), connecting estimated parameters with the measurements.

USAGE OF FOURIER SERIES. Consider $t \geq t_* \gg 1$ ($t \neq j\pi/\omega$) and take only one period. For distinctness, let its first half be for the cracker turned on. Move the time zero ($t \in [0, \sigma]$) and find c, u in the form ($i = \sqrt{-1}$):

$$c(t, x) = \sum_{-\infty}^{+\infty} c_n(x) \exp(in\omega t), \quad u(t, x) = \sum_{-\infty}^{+\infty} u_n(x) \exp(in\omega t). \quad (5.1)$$

Being nonlinear does not allow using superposition of oscillations. Being real of c, u implies c_n and $c_{-n}, u_n,$ and u_{-n} become complex conjugate. Thus consider only $n \geq 0$. Due to the smoothing effect of the diffusion equation we are interested only in harmonics with small n . High harmonics are difficult to determine experimentally. The quantities with similar names $c_{0,L} = c_{0,L}(t), c_n = c_n(x), c_x = c_x(t, x)$ and $u_{0,\ell} = u_{0,\ell}(t), u_n = u_n(x), u_x = u_x(t, x)$ are distinguished by context. Substituting into (2.1), (4.8), we obtain, for stationary oscillations,

$$\begin{aligned} c_n(x)in\omega &= Dc_n''(x), \quad x \in (0, L), \\ c_n(x) &= A_n \exp(\lambda x) + B_n \exp(-\lambda x), \quad \lambda^2 = \frac{in\omega}{D}, \\ u_n(x)in\omega &= D_*u_n''(x) - a_1u_n(x) + \frac{a_1a_2u_n(x)}{in\omega + a_2}, \\ u_n(x) &= A_{*n} \exp(\lambda_*x) + B_{*n} \exp(-\lambda_*x), \quad x \in (0, \ell), \\ \lambda_*^2 &= \frac{in\omega + a_1 - a_1a_2/(in\omega + a_2)}{D_*}. \end{aligned} \quad (5.2)$$

Here $f' \equiv f_x$, the constants $A_n, B_n, A_{*n},$ and B_{*n} are to be determined. It is not important which root of the number $in\omega/D$ is taken as λ . The same is true for λ_* (let $\Re > 0$). The initial condition (2.16) gives the initial data $c_0(0) = Q_0, c_n(0) = -2iQ_1/(n\pi)$ (n is odd), and $c_n(0) = 0$ (n is even, $n > 0$). From here the following holds for the odd natural n (for even formally $Q_1 = 0$):

$$c_n(x) = 2A_n \sinh(\lambda x) - 2iQ_1(n\pi)^{-1} \exp(-\lambda x). \quad (5.3)$$

Then, using a boundary condition (2.10) due to (2.9) and $\mu s_* p_\ell = 0$, obtain

$$\begin{aligned} \dot{u}_\ell &= -g_*J - g_*D_*u_x(t, \ell), \quad in\omega u_n(\ell) = -g_*J_{(n)} - g_*D_*u'_n(\ell), \\ \sigma J_{(n)} &= \langle J(t), \exp(in\omega t) \rangle_{L_2}, \quad \sigma = \frac{2\pi}{\omega}, \quad L_2 = L_2([0, \sigma], \mathbb{C}). \end{aligned} \quad (5.4)$$

Besides,

$$Dc'_n(L) = D_*u'_n(0), \quad kc_n(L) - k_*u_n(0) = -Dc'_n(L). \quad (5.5)$$

Substituting to these equations the expressions for $c_n(x)$, $u_n(x)$, obtain a system of linear algebraic equations for A_n , A_{*n} , and B_{*n} :

$$\begin{aligned} D\lambda[2A_n \cosh(\lambda L) + 2iQ_1(n\pi)^{-1} \exp(-\lambda L)] &= D_*\lambda_*(A_{*n} - B_{*n}), \\ k[2A_n \sinh(\lambda L) - 2iQ_1(n\pi)^{-1} \exp(-\lambda L)] - k_*(A_{*n} + B_{*n}) & \\ &= -D_*\lambda_*(A_{*n} - B_{*n}), \\ in\omega[A_{*n} \exp(\lambda_*\ell) + B_{*n} \exp(-\lambda_*\ell)] & \\ &= -g_*J_{(n)} - g_*D_*\lambda_*[A_{*n} \exp(\lambda_*\ell) - B_{*n} \exp(-\lambda_*\ell)]. \end{aligned} \quad (5.6)$$

When determining the expressions A_{*n} , B_{*n} obtain

$$u_n(\ell) = A_{*n} \exp(\lambda_*\ell) + B_{*n} \exp(-\lambda_*\ell) = U_n(D_*, g_*, k, k_*, a_i, Q_1). \quad (5.7)$$

The explicit expression for U_n is too cumbersome to be presented here.

On the other hand, from the measurement equation (2.15) follows that

$$u(t, \ell) = u_\ell(t) = \frac{g_*R(t)}{\sqrt{b_*}} \Rightarrow u_n(\ell) = \frac{\Pi R_{(n)}}{\alpha\ell}. \quad (5.8)$$

Equating the two expressions for $u_n(\ell)$, obtain the equations in the form

$$f_n(D_*, g_*, a_i, Q_1) = U_n - \frac{\Pi R_{(n)}}{\alpha\ell} = 0. \quad (5.9)$$

The variables k , k_* are eliminated with the help of known Γ , Σ .

When $n = 0$, in the similar way, the equation is obtained:

$$\left(Q_0 - \frac{J_{(0)}L\ell}{D}\right)\Gamma - J_{(0)}\Sigma = \Pi R_{(0)}, \quad (5.10)$$

which allows determining the unknown concentration Q_0 .

REMARK 5.1. Each equation is transformed to two: $\Re f_n = 0$, $\Im f_n = 0$. Other variants are also possible. Present a harmonics $u_{-n}(\ell) \exp(-in\omega t) + u_n(\ell) \exp(in\omega t)$ in a real form $\Omega_n \sin(n\omega t + \varphi_n)$. In the same way this harmonics must be treated in Fourier series expansion $g_*R(t)/\sqrt{b_*}$. Equating amplitudes or/and phases for $n \geq 1$, obtain the equations for the unknown parameters. Phases are calculated more precisely. Equations for even natural n are simpler: $Q_1 = 0$ should be assumed formally. But if the membrane is very thin, then due to $c_n(0) = 0$ at small n the even harmonics will be weak and gives poor information compared to odd ones ($c_n(0) = -2Q_1/(n\pi)$). While n grows, odd harmonics becomes less different (and thus less informative) also.

The value $2Q_1$ of amplitude of oscillation $c_0(t)$ is determined via the model parameters and the oscillation period. The value $Q_0 - Q_1 = \bar{c}_0$ is obtained from (3.4). Substituting Q_0 , we calculate Q_1 . It is possible to act in other way also. When $J \approx \bar{J}, \bar{J}_h$,

the concentrations $c(t, x)$, $u(t, x)$ are linear in layers (see Section 3). Writing the expressions $\bar{c}_0(\bar{J})$, $\bar{c}_0(\bar{J}_h)$ explicitly ($2Q_1 = \bar{c}_0(\bar{J}_h) - \bar{c}_0(\bar{J})$), obtain

$$\begin{aligned} \frac{\bar{c}_L - \bar{c}_0}{L} = c_x = -D^{-1}\bar{J}, \quad \frac{\bar{u}_\ell - \bar{u}_0}{\ell} = u_x = -D_*^{-1}\bar{J}, \\ k\bar{c}_L - k_*\bar{u}_0 = \bar{J}, \quad \bar{u}_\ell = g_* \left(\frac{\bar{J}}{b_*} \right)^{1/2} = \frac{\Pi \bar{R}}{\ell} \\ \Rightarrow 2Q_1 \Gamma \ell = (\bar{J}_h - \bar{J})\Sigma + (\bar{R}_h - \bar{R})\Pi + \Gamma L \ell D^{-1}(\bar{J}_h - \bar{J}). \end{aligned} \quad (5.11)$$

The concentration Q_1 should be determined beforehand and substituted to $f_n = 0$.

Thus, the identification problem is reduced to a system of equations for elementary functions. In case if the capture is small ($w = 0$, $a_i = 0$), there will be $\alpha = 1$ instead of $\alpha = (1 + a_1/a_2)$. Equations $f_n = 0$ become simpler and will contain only D_* , g_* . Eliminating g_* , obtain a scalar equation for the diffusion coefficient D_* , yet cumbersome. It can be relatively easily solved in physically reasonable range for D_* . When D_* , g_* , and a_i (if the capture is considered) are already determined, other parameters k , k_* , and b_* are calculated on known values Σ , Γ , and Π .

CONJUGATE EQUATIONS METHOD. A strategy of using (4.15), (4.20) is as follows. Choose specific solutions φ , ψ of conjugate equations, taking joint conditions (4.13), (4.14) into consideration. Important here is the fact that the equations are linear homogeneous with no boundary conditions. Thus there are infinitely many possible variants. Substitute φ , ψ to (4.15) or (4.20) according to which form is used. The equations were obtained such that there is no concentration or flows in the volume in (4.15), (4.20). Only stationary concentrations are present (they can be calculated explicitly) and the values connected with surface processes. Note that the measurements are connected exactly with desorption on the surface. The only thing to do is to obtain explicit dependencies between the model parameters from (4.15), (4.20) using the model equations.

Taking capture into consideration ($a_i \neq 0$) leads to very complicated equations for the parameters. Their theoretical analysis is hardly possible. In applications, usually the traps formed by the material defects are considered as a small perturbation. Limitative parameters are the main parameters connected with diffusion and sorption. Here is an algorithm of model identification for $a_i = 0$. Obtained parameters will be a good initial estimation for perturbed problem $a_i \neq 0$. The locally convergent solver of systems of equations is sufficient.

So, let the defects of the second layer be negligible: $a_i = 0$, $N_3(x) = 0$, and $w = 0$. The parameters D_* , g_* , b_* , s_* , k , and k_* must be estimated on the measurements $J(t)$. Formally, if $a_i = 0$, it is necessary to put $\alpha = 1$, the quotient a_1/a_2 appeared from $a_1\bar{u} = a_2\bar{w}$. Equation (3.1) allows eliminating s_* . The coefficients of equilibrium dissolubility allow obtaining $\Gamma = \gamma_*/\gamma = \chi = k/k_*$. Only four parameters D_* , g_* , b_* , and k_* remain undetermined. Stationary linear distributions of diffusing hydrogen do not depend on existence of reversible capture: equation (3.7) ($\alpha = 1$) remains unchanged. This allows finding

$$\Sigma = z_1 + z_4, \quad \Pi = z_2 z_3, \quad z_1 = \frac{\ell^2}{D_*}, \quad z_2 = \frac{1}{\sqrt{b_*}}, \quad z_3 = g_* \ell, \quad z_4 = \frac{\ell}{k_*}. \quad (5.12)$$

At least two equations are necessary. They can be obtained from the transition process. The change $\lambda_* = (1 + i)\sqrt{n\omega/(2D_*)}$ should be made in the previous subsection. But even with these simplifications, $f_n = 0$ remain very cumbersome. But conjugate equations method allows solving the problem analytically.

A conjugate system appears in the form

$$\begin{aligned} \varphi_t &= -D\varphi_{xx}, \quad x \in (0, L), \quad \psi_t = -D_*\psi_{xx}, \quad x \in (0, \ell), \quad t > 0, \\ D\varphi_x(t, L) &= D_*\psi_x(t, 0), \quad k\varphi(t, L) - k_*\psi(t, 0) = -D\varphi_x(t, L). \end{aligned} \tag{5.13}$$

Equation (4.15) coincides with (4.20) without the last term in the right-hand side (for $a_i = 0$), if $[0, \sigma]$ is replaced by $[\tau_1, \tau_2]$.

We consider how the method can be realized. If $J(t) = \bar{J}$ and $J(t) = \bar{J}_h$, then concentrations in the layers are distributed linearly and thus can be easily calculated:

$$\begin{aligned} c(0, x) &= c(\sigma, x) = \bar{c}_0 - xD^{-1}\bar{J}, \\ u(0, x) &= u(\sigma, x) = \chi\bar{c}_0 - (\chi LD^{-1} + k_*^{-1} + xD_*^{-1})\bar{J}, \\ c\left(\frac{\sigma}{2}, x\right) &= Q_0 + Q_1 - xD^{-1}\bar{J}_h = \bar{c}_0 + 2Q_1 - xD^{-1}\bar{J}_h, \\ u\left(\frac{\sigma}{2}, x\right) &= \chi(\bar{c}_0 + 2Q_1) - (\chi LD^{-1} + k_*^{-1} + xD_*^{-1})\bar{J}_h, \\ \bar{c}_0 &= Q_0 - Q_1 = g\left\{\frac{\mu s \bar{p} - \bar{J}}{b}\right\}^{1/2}, \quad \chi = \frac{k}{k_*}. \end{aligned} \tag{5.14}$$

Stationary mode is reached asymptotically. If $x = 0, t = 0$, and $\sigma/2$, then due to (2.16), there are concentration jumps $c(+0, 0) - c(-0, 0) = c(\sigma + 0, 0) - c(\sigma - 0, 0) = 2Q_1$, $c(\sigma/2 + 0, 0) - c(\sigma/2 - 0, 0) = -2Q_1$. This detail is not very significant, for the expressions $c(0, x)$, $c(\sigma/2, x)$, and $c(\sigma, x)$ will be used only under the integral on $x \in [0, L]$ sign. To obtain, for instance, $u(0, x)$, it is necessary to substitute \bar{u}_0 from $k\bar{c}_L - k_*\bar{u}_0 = \bar{J}$, where $\bar{c}_L = \bar{c}_0 - LD^{-1}\bar{J}$, to the linear expression $u(0, x) = \bar{u}_0 - xD_*^{-1}\bar{J}$ for the stationary initial concentration in the second layer. When a significant capture is present ($a_i \neq 0$), the equations in (5.14) remain unchanged.

(I) Firstly consider a simplest case $\varphi = \text{const}$. As (4.15) and (4.20) are homogeneous with respect to φ, ψ , let $\varphi = 1$. Then $\psi = \chi$ and on a period $[0, \sigma]$, (4.15) has a simple physical meaning:

$$\int_0^\sigma Dc_x(t, 0) dt = \int_0^\sigma D_*u_x(t, \ell) dt. \tag{5.15}$$

Turning a cracker ON implies a concentration jump on the surface and a quick establishment of the inlet flux:

$$\begin{aligned} c(t, 0) &= Q_0 + Q_1, \quad t \in \left(0, \frac{\sigma}{2}\right), \\ Dc_x(t, 0) &\approx -\bar{J}_h, \quad t \in \left(\varepsilon, \frac{\sigma}{2}\right), \quad \varepsilon \ll \sigma. \end{aligned} \tag{5.16}$$

On the interval $(\sigma/2, \sigma)$, due to (2.4) it holds that $Dc_x(t, 0) = \dot{q} - \mu s \bar{p} + bq^2$. The integral at a relatively large segment $[0, \sigma]$ of $bq^2(t)$ is calculated as an integral of $b[\bar{c}_0/g]^2$, with taken (3.4) into consideration. A jump of surface concentration is limited by $(2Q_1/g)$ and a transition time is negligibly small. But while calculating an integral of \dot{q} it is not possible to assume $\dot{q} = 0$. While transition time reduces, \dot{q} grows. The integral of \dot{q} remains equal to $q(\sigma) - q(\sigma/2)$ in the limit also, when the transition period is considered momentary. Such ideas are formalized in terms of δ -functions. While calculating the right-hand side, use (2.10) at $\mu s_* p_\ell = 0$: $-D_* u_x(t, \ell) = \dot{v}(t) + J(t)$. Finally obtain an equilibrium equation $(\bar{J} + \bar{J}_h)\pi/\omega + 2Q_1/g = S$, S is the integral of $J(t)$ on a segment $[0, \sigma]$. This gives one more possibility to estimate Q_1, Q_0 . But there is no additional information about the estimated parameters. Thus we consider (4.20) on semiperiods. When $[\tau_1, \tau_2] = [0, \sigma/2]$, an expression for the flux $-Dc_x(t, 0)$, which establishes slower than inlet concentration, is needed. It is reasonable from the point of view of precision to choose φ from an additional condition $\varphi(t, 0) = 0$ (this will eliminate $Dc_x(t, 0)$ from (4.20)) or $[\tau_1, \tau_2] = [\sigma/2, \sigma]$, when the inlet surface contacts with the molecular hydrogen according to (2.4).

Let $[\tau_1, \tau_2] = [\sigma/2, \sigma]$ and calculate the integrals I_1, \dots, I_7 in (4.20):

$$\begin{aligned}
 I_1 &= \int_0^L \left\{ c(\sigma, x) - c\left(\frac{\sigma}{2}, x\right) \right\} dx = -2Q_1L - \frac{(\bar{J} - \bar{J}_h)D^{-1}L^2}{2}, \\
 I_2 &= \int_{\sigma/2}^{\sigma} Dc_x(t, 0) dt = \int_{\sigma/2}^{\sigma} (\dot{q} - \mu s \bar{p} + bq^2) dt = -\frac{2Q_1}{g} - \frac{\bar{J}\pi}{\omega}, \\
 I_4 &= \int_0^{\ell} \left\{ u(\sigma, x) - u\left(\frac{\sigma}{2}, x\right) \right\} dx = \Pi(\bar{R} - \bar{R}_h) + \frac{D_*^{-1}\ell^2(\bar{J} - \bar{J}_h)}{2}, \\
 I_5 &= -\int_{\sigma/2}^{\sigma} D_* u_x(t, \ell) dt = \int_{\sigma/2}^{\sigma} (\dot{v} + J) dt = \frac{\bar{R} - \bar{R}_h}{\sqrt{b_*}} + S.
 \end{aligned} \tag{5.17}$$

The integrals I_3, I_6 , and I_7 are zero; here S is for the integral of $J(t)$ on the time segment $[\sigma/2, \sigma]$. In variables z_i , (4.20) for $\varphi = 1$, $\psi = \chi$, $[\tau_1, \tau_2] = [\sigma/2, \sigma]$, $a_i = 0$ is linear algebraic:

$$\begin{aligned}
 f_1 &= \frac{z_1(\bar{J} - \bar{J}_h)}{2} + z_2(\bar{R} - \bar{R}_h) + B + S = 0, \\
 B &= -2Q_1L - \frac{D^{-1}L^2(\bar{J} - \bar{J}_h)}{2} - \frac{2Q_1}{g} - \frac{\bar{J}\pi}{\omega} + \Pi(\bar{R} - \bar{R}_h).
 \end{aligned} \tag{5.18}$$

(II) Let $[\tau_1, \tau_2] = [0, \sigma/2]$ and $\varphi = x/L$. Then, for a linear $\psi = \alpha x + \beta$, the following is obtained from the conjugate system: $\psi = DD_*^{-1}x/L + (kL + D)/(k_*L)$. After calculating the integrals in (4.20), $f_2 = d_1z_1^2 + d_2z_1 + d_3z_2 + d_4 = 0$ is obtained. Here

$$\begin{aligned}
 d_1 &= -\frac{DM\xi}{3}, \quad M = \bar{J}_h - \bar{J}, \quad \xi = \frac{1}{\chi\ell L}, \\
 d_2 &= DM\Sigma\xi - \frac{DQ_1}{L} + M, \quad d_3 = (D\Sigma\xi + 1)(\bar{R}_h - \bar{R}),
 \end{aligned}$$

$$\begin{aligned}
 d_4 = & Q_1 L - \frac{MD^{-1}L^2}{3} - \frac{(\bar{c}_0 + 2Q_1)D\pi}{\omega L} - DM\Sigma^2\xi \\
 & + 2\Sigma\left(\frac{Q_1 D}{L} - M\right) + 2Q_1\chi\ell - \frac{M}{D\xi} + (D\Sigma\xi + 1)S + D\Pi\xi S_{1/2},
 \end{aligned}
 \tag{5.19}$$

The values $S, S_{1/2}$ are the integrals of $J(t)$ and $R(t) = J^{1/2}(t)$ on the time segment $[\tau_1, \tau_2]$.

For the period $[0, \sigma]$, $\varphi = x/L$, the equation from the previous paragraph is obtained from (4.15) ($n = 0$). The case $[\tau_1, \tau_2] = [\sigma/2, \sigma]$, $\varphi = x/L$, does not give any new information about z_1, z_2 . Also there is no need to detail $[\tau_1, \tau_2] = [\sigma/2, \sigma]$, $\varphi = (x - L)/L$, $\psi = DD_*^{-1}x/L + D/(k_*L)$ for it is a combination of $\varphi = 1, \varphi = x/L$.

(III) The solutions of conjugate equations ($a_i = 0$) will be determined in the form

$$\begin{aligned}
 \varphi &= (t - \tau_0)\varphi_1(x) + \varphi_0(x), \quad \psi = (t - \tau_0)\psi_1(x) + \psi_0(x) \\
 \Rightarrow \varphi_1 &= -D[(t - \tau_0)\varphi_1'' + \varphi_0''], \quad \psi_1 = -D_*[(t - \tau_0)\psi_1'' + \psi_0''].
 \end{aligned}
 \tag{5.20}$$

Let $\varphi_1'' = 0, \psi_1'' = 0$: $\varphi_1 = d_1(x - L) + d_0, \psi_1 = d_{*1}x + d_{*0}$. Then

$$\begin{aligned}
 \varphi_0 &= h_3(x - L)^3 + h_2(x - L)^2 + h_1(x - L) + h_0, \\
 \psi_0 &= h_{*3}x^3 + h_{*2}x^2 + h_{*1}x + h_{*0},
 \end{aligned}
 \tag{5.21}$$

and $d_1 = -6Dh_3, d_0 = -2Dh_2, d_{*1} = -6D_*h_{*3}, d_{*0} = -2D_*h_{*2}$. After substitution to the joint conditions and equating functions of x and what is at $(t - \tau_0)$, four linear equations for h_i, h_{*i} will be obtained. The parameters d_i, d_{*i} , and h_{*i} are uniquely represented via h_0, \dots, h_3 . These can be considered as arbitrary constants.

The only thing to do is to substitute φ, ψ to (4.15), (4.20), and calculate the integrals. Stationary distributions $c(\tau_i, x), u(\tau_i, x)$ are substituted from (5.14). The flux $-Dc_x(t, 0)$ on the time interval $(0, \sigma/2)$ is replaced by \bar{J}_h , and on the interval $(\sigma/2, \sigma)$ — by $-\dot{q} + \mu s \bar{p} - bq^2$ due to (2.4). At that, $q(t) = \bar{c}_0/g$ due to (3.4), that is, $\mu s \bar{p} - bq^2 = \bar{J}$ on $(\sigma/2, \sigma)$. It is not possible to assume $\dot{q} = 0$ due to jumps of $c(t, 0)$. The flux $-D_*u_x(t, \ell)$ is replaced by $\dot{v} + J$. The integrals with \dot{q}, \dot{v} are transformed by integration by parts. The functions $u(t, \ell), v(t)$ are determined from $J = b_*v^2$ and $g_*v = u(t, \ell)$. To eliminate, for instance, $Dc_x(t, 0)$, it is necessary to choose $h_0 = 0, h_2 = 0$ ($\varphi(t, 0) = 0$). Detailed explanation is omitted.

(IV) Other variants may also be considered:

$$\begin{aligned}
 \varphi &= \beta(t) \sin(vx)(\cos), \quad \beta(t) \exp(vx), (t - \tau_0)^m \varphi_m(x) + \dots + \varphi_0(x), \\
 &\sin(\alpha t)\varphi_1(x) + \cos(\alpha t)\varphi_2(x), (t - \tau_0) \exp\{\alpha(t - \tau_0)\}\varphi_1(x) \\
 &\quad + \exp\{\alpha(t - \tau_0)\}\varphi_2(x).
 \end{aligned}
 \tag{5.22}$$

The meaning of choosing different φ, ψ (test functions) is the following. In the variant (I) there are no terms with boundary concentrations $c_0(t), u_\ell(t)$ in (4.15), (4.20). The value $\varphi(t, 0) = 0$ allows eliminating the flux $-Dc_x(t, 0)$. Different weight is given to stationary concentrations $c(\tau_i, x), u(\tau_i, x)$ in integrals, and so on. It is possible to choose which quantities will influence mostly on the equations $f_i = 0$.

The obtained equations are enough to determine uniquely the model coefficients D_* , g_* , b_* , s_* , k , and k_* when $a_i = 0$. Let the values D , g/\sqrt{b} , y , and y_* be known ($\sqrt{\mu s} = y\sqrt{b/g}$). For preliminary analysis of hydrogen permeability by a permeability method, it is possible to use the results of [8]. The experiment is held for two pressures $\bar{p} = \bar{p}_1$, $\bar{p} = \bar{p}_2$. From (3.7) ($\alpha = 1$) for $\bar{J} = \bar{J}_1$, $\bar{J} = \bar{J}_2$, and \bar{c}_{01} , \bar{c}_{02} , the values $\Sigma = \ell^2/D_* + \ell/k_*$, $\Pi = \ell g_*/\sqrt{b_*}$ are obtained. The equations are linear with respect to Σ and Π . From (3.1) it follows that $s_* = (\chi y \ell / \Pi)^2 / \mu$. The concentrations \bar{c}_{0i} are determined according to (3.4) or more roughly $\bar{c}_{0i} \approx y \sqrt{\bar{p}_i}$ (and then g/\sqrt{b} and s are not necessary). Unknown values Q_i are estimated by $\bar{c}_0 = Q_0 - Q_1$, equations from the previous paragraph, and Section 3. To determine z_1 , z_2 , it is enough to use linear equations (5.18). Other variants are also possible. Averaging and the least squares methods are reasonable here. Those integrals that contain the measurements $J(t)$, $R(t) = J^{1/2}(t)$ are calculated beforehand. Finally, the estimated parameters are obtained:

$$\begin{aligned} D_* &= \frac{\ell^2}{z_1}, & k_* &= \frac{\ell}{z_4} = \frac{\ell}{\Sigma - z_1}, & b_* &= \frac{1}{z_2^2}, \\ g_* &= \frac{z_3}{\ell} = \frac{\Pi}{z_2 \ell}, & k &= \chi k_*. \end{aligned} \quad (5.23)$$

For the perturbed system, when $a_i \neq 0$, obtained estimations should be taken as initial approximations. The equations of the form $f_n = 0$ are obtained in the same way as when $a_i = 0$ using the conjugate equations method, yet these equations are far more cumbersome. But these are the equations of the different class: in the initial form, the parameters are connected by a differential model, and the given method reduces it to a numerical solving of systems of equations. Calculating one-dimensional integrals is relatively easy.

6. Remarks and some simplifications. (1) If the model (2.16) is adequate for the material of the second layer, then it is possible to exchange the layers—providing pressure \bar{p} at the side of the second layer. Formally it is necessary to exchange the parameters D , g , b , s , k , L and D_* , g_* , b_* , s_* , k_* , ℓ in all the equations $f_n = 0$. To enlarge the flux often glow discharge is used instead of the cracker.

(2) A bit simple is the case of easier coming out of hydrogen from the second layer to the vessel. At the outlet, let a flux balance model be used:

$$\mu s_*(T) p_\ell(t) - b_*(T) u^2(t, \ell) - D_*(T) u_x(t, \ell) = 0. \quad (6.1)$$

Hydrogen does not accumulate on the surface, but desorbs immediately. The flux density is known: $J(t) = b_* u^2(t, \ell)$. Formally it corresponds to the case $g_* = 1$, $\dot{v} = 0$. In the vacuum, assume $\mu s_* p_\ell = 0$. The identification algorithm is simplified significantly. There will be no terms with z_2 in (5.18) (they appeared as a result of integration of \dot{v}).

(3) The algorithm of parameter estimation on measurements will be numerically stable if the terms in the equations have similar number exponents. This depends on the materials and L , ℓ . In particular, number exponents of L^2/D , ℓ^2/D_* should be more or less similar, or the system of equations will be ill-posed. Inverse problems are usually not immune to experimental and numerical errors.

(4) The given algorithm needs a significant experimental and numerical work. It is reasonable to study the material of the first layer (usually it is a metal substrate) beforehand. It is also possible to consider a multilayer material as a single membrane and thus estimate the parameters integrally and more roughly. In any case, practically even simplified single-layer variant may be sufficient. Thus, to help the reader to avoid studying all given materials here it is given independently in a rather brief form. Mathematical model:

$$\begin{aligned} c_t &= Dc_{xx}, \quad x \in (0, \ell), \quad c(0, x) = \varphi(x), \quad c_{0, \ell}(t) = gq_{0, \ell}(t), \\ \dot{q}_{0, \ell}(t) &= \mu s p_{0, \ell}(t) - b q_{0, \ell}^2(t) \pm Dc_x|_{x=0, \ell}, \quad J(t) = b q_{\ell}^2(t). \end{aligned} \quad (6.2)$$

In the conditions of the experiment, the equilibrium concentration of dissolved-in-metal hydrogen is proportional to the square root of the molecular hydrogen pressure on the surface. The coefficient of equilibrium dissolvability γ may be determined as follows. Place a membrane (not a barrier) to the vacuum vessel with gas hydrogen with pressure \bar{p} . Heat the membrane to intensify adsorption-desorption processes and diffusion. In some time, a constant concentration $c(t, x) = \bar{c}$ will establish. For the model ($p_0 = p_{\ell} = \bar{p}$), it means that all derivatives are zero: $\bar{c} = g\sqrt{\mu s \bar{p}/b} = \gamma\sqrt{\bar{p}}$. Quickly cool the membrane (turning the electric current off), at room temperature the rates of the studied processes are very low. Pump out the gas, almost all dissolved hydrogen will remain in the membrane. Now heat the membrane to a high temperature to degas it. Since \bar{p} , the total amount of captured hydrogen and geometry of the membrane, is known, it is possible to calculate \bar{c} and, thus, the coefficient of equilibrium dissolvability $\gamma = g\sqrt{\mu s/b}$, $\gamma = \gamma(\bar{T})$, where \bar{T} is the temperature at which saturation and the MCI experiment are held.

Return back to MCI when the membrane is a barrier and at the outlet side a vacuum is provided. Firstly analyze a mapping $\bar{p} \rightarrow \bar{J}$: at constant pressure $p_0(t) = \bar{p}$, a stationary flux $J(t) = \bar{J}$, $t \geq t_*$, establishes at the outlet by some time t_* . For $t \geq t_*$, all time derivatives may be considered zero, which implies a linear stationary concentration distribution $c(t, x) = c(t_*, x)$, $t \geq t_*$, $c(t_*, x) = \xi_1 \cdot (x - \ell) + \xi_2$. Calculate ξ_1 , ξ_2 . From the measurement equation $J = b q_{\ell}^2$, it follows that

$$\xi_2 = c(t_*, \ell) = g q_{\ell}(t_*) = g \left(\frac{\bar{J}}{b} \right)^{1/2} = g r \bar{L}, \quad r = b^{-1/2}, \quad L = J^{1/2}. \quad (6.3)$$

An angular coefficient ξ_1 is equal to $c_x(t, \ell) = -D^{-1} \bar{J}$ ($\dot{q}_{\ell} = 0$, $t \geq t_*$):

$$c(t, x) = c(t_*, x) = D^{-1} \bar{J} \cdot (\ell - x) + g r \bar{L}, \quad t \geq t_*. \quad (6.4)$$

At the outlet ($x = \ell$) the concentration \bar{c}_{ℓ} , proportional to $\bar{J}^{1/2}$, establishes and the diffusion flux $Dc_x(t, x)$ does not change with respect to the width of the membrane and is equal to the desorption flux \bar{J} by absolute value.

On the other hand, $\dot{q}_0 = 0 \Rightarrow c(t, 0) = \bar{c}_0 = g r (\mu s \bar{p} - \bar{J})^{1/2}$, $t \geq t_*$. Under the root, there is a positive number: flux is the difference between the coming to the inlet surface flux $\mu s \bar{p}$ and the desorption back to the vessel.

Comparing the two expressions for \bar{c}_0 , obtain an equation $f(D, g, b, s) = 0$, which explicitly connects the unknown parameters in algebraic form:

$$\begin{aligned} gr(\mu s \bar{p} - \bar{J})^{1/2} - gr\bar{L} - \ell D^{-1}\bar{J} &= 0 \\ \Rightarrow X[(\mu s \bar{p} - \bar{J})^{1/2} - \bar{L}] = \bar{J}, \quad X &= \frac{Dgr}{\ell}. \end{aligned} \quad (6.5)$$

The two equations (6.5), for different pressures \bar{p}_i , allow determining uniquely s and a complex X . Using γ , s , and X , obtain $D = \sqrt{\mu s X \ell} / \gamma$, $gr = \gamma / (\sqrt{\mu s \ell}) = \ell X / D$.

When $\mu s \bar{p} \gg \bar{J}$, it is possible to replace the first term in (6.5) by $\gamma \sqrt{\bar{p}}$. These two linear, with respect to D^{-1} and gr , equations allow determining D and gr , when $\bar{p} = \bar{p}_i$, $\bar{J} = \bar{J}_i$. The parameter s is later found using $\gamma = gr \sqrt{\mu s}$.

Nothing more can be obtained from the analysis of equilibrium and stationary modes: the parameters g , b are impossible to be split. Thus the transition process must be studied. At least one more equation is necessary. Here are two ways to provide any number of equations $f(D, g, b) = 0$.

FOURIER SERIES. Due to (2.16), by some time t_* , the stationary oscillations of the flux $J(t)$ appear at the outlet, independent of the initial distribution $c(0, x) = \varphi(x)$. For the Fourier coefficients, obtain

$$c_n(x) in\omega = Dc_n''(x), \quad in\omega c_n(\ell) = -gDc_n'(\ell) - gJ_{(n)}, \quad (6.6)$$

$c_n(0) = -2iQ_1 / (n\pi)$ (n is odd), $c_n(0) = 0$ (n is even, $n \neq 0$). It implies

$$\begin{aligned} c_0(x) &= -D^{-1}J_{(0)}x + Q_0, \\ c_n(x) &= 2A_n \sinh(\lambda x) - 2iQ_1(n\pi)^{-1} \exp(-\lambda x). \end{aligned} \quad (6.7)$$

Here $\lambda = (1+i)[n\omega/(2D)]^{1/2}$. The values A_n are determined by

$$\begin{aligned} A_n(in\omega \sinh(\lambda \ell) + \lambda gD \cosh(\lambda \ell)) \\ = -gJ_{(n)}/2 + iQ_1[n\pi \exp(\lambda \ell)]^{-1}(in\omega - \lambda gD). \end{aligned} \quad (6.8)$$

Here n is odd natural (for the even ones the terms with Q_1 are absent).

On the other hand, $c(t, \ell) = g(J/b)^{1/2}(t) \Rightarrow c_n(\ell) = grL_{(n)}$. Equating $grL_{(n)}$ to the above-obtained equation for $c_n(x)$ at $x = \ell$, obtain on $r = b^{-1/2}$, Q_1 linear equations $f_n(D, g, b) = 0$ ($\lambda^2 D = in\omega$). Details are omitted. For each n , they can be transformed into two equations, equating real or imaginary parts to zero. Eliminating Q_1 , obtain b , and using gr , determine g . If the oscillation period is not arbitrary, but is exactly that for which $J(t)$ has enough time to reach the asymptotes $J = \bar{J}_h$, $J = \bar{J}$ while the cracker turns on and off, then $2Q_1 = D^{-1}[\bar{J}_h - \bar{J}]\ell + gr[\bar{L}_h - \bar{L}]$. Using known X , D , the explicit formula gives r . Then, using X , γ , the parameter g is obtained.

While n grows, even and odd harmonics in $c(t, x)$ are distinguished less. For even $n > 1$, there is no term with Q_1 . But if the membrane is thin enough, then due to $c_n(0) = 0$, the even harmonics will be weak even for small n and thus carries a little information.

CONJUGATE EQUATIONS. Consider an arbitrary solution $\psi(t, x)$ of conjugate to $c_t = Dc_{xx}$ equation $\psi_t = -D\psi_{xx}$ without initial or boundary conditions. Using the integration by parts formula, obtain

$$\begin{aligned}
 0 &= \int_{\tau_1}^{\tau_2} \int_0^\ell \psi \cdot (c_t - Dc_{xx}) dx dt \\
 &= \int_0^\ell (\psi c)|_{t=\tau_1}^{\tau_2} dx - \int_{\tau_1}^{\tau_2} D(c_x \psi)|_{x=0}^\ell dt + \int_{\tau_1}^{\tau_2} D(\psi_x c)|_{x=0}^\ell dt.
 \end{aligned}
 \tag{6.9}$$

For the specific ψ , the equation becomes more detailed. The simplest solutions $\psi = 1$, $\psi = x/\ell$ may be taken as well as more complicated $\psi = \beta(t) \sin(\sigma x)$ (cos, exp). They are defined up to the multiplier $\beta(t) = \exp(\pm D\sigma^2 t)$. There are infinitely many solutions ψ as there are no boundary conditions for the equation $\psi_t = -D\psi_{xx}$. This allows constructing infinitely many equations for the parameters.

Here are some variants: $[\tau_1, \tau_2] = [0, \pi/\omega]$, $[\tau_1, \tau_2] = [\pi/\omega, \sigma]$. The flux grows monotonically on the first time segment from \bar{J} , reaching by the time π/ω the asymptote $J = \bar{J}_h > \bar{J}$. On the second, when the cracker is off, it declines monotonically from \bar{J}_h to \bar{J} . For the first time segment and $\psi = 1$, the outlet flux $Dc_x(t, 0)$ will be present in (6.9). When the cracker is on, the author does not have an adequate model for $Dc_x(t, 0)$. Thus we take a solution $\psi = x/\ell$:

$$\frac{z[\bar{J}_h - \bar{J}]}{6} + \frac{zX[\bar{L}_h - \bar{L}]}{2} + r[\bar{L}_h - \bar{L}] + S - \frac{\bar{J}_h \pi}{\omega} + X \left(S_{1/2} - \frac{\bar{L}_h \pi}{\omega} \right) = 0.
 \tag{6.10}$$

Here $z = \ell^2/D$, S is an integral of $J(t)$, and $S_{1/2}$ is an integral of $L(t)$ on the segment $[\tau_1, \tau_2]$. The expression

$$\begin{aligned}
 c_\ell &= gq_\ell, \quad q_\ell = rL, \quad c_0 = Q_0 + Q_1 = D^{-1}\bar{J}_h\ell + gr\bar{L}_h, \\
 Dc_x(t, \ell) &= -\dot{q}_\ell - J
 \end{aligned}
 \tag{6.11}$$

and $c(\tau_i, x)$ (for the levels \bar{J} , \bar{J}_h) should be substituted to (6.9).

The choice $\psi = 1$ for $[\tau_1, \tau_2] = [\pi/\omega, \sigma]$ provides

$$\frac{z[\bar{J} - \bar{J}_h]}{2} + zX[\bar{L} - \bar{L}_h] + S - \frac{\bar{J}\pi}{\omega} + 2r[\bar{L} - \bar{L}_h] + rX^{-1}(\bar{J} - \bar{J}_h) = 0.
 \tag{6.12}$$

In (6.9) it is necessary to take $bq_0^2 = \mu s \bar{p} - \bar{J}$ ($q_0(t) = g^{-1}(Q_0 - Q_1) = g^{-1}\bar{c}_0$) and

$$q_0(\tau_2) - q_0(\tau_1) = -2Q_1 g^{-1}, \quad 2Q_1 = D^{-1}[\bar{J}_h - \bar{J}]\ell + gr[\bar{L}_h - \bar{L}],
 \tag{6.13}$$

into consideration.

The equations are linear on z , r , it is possible to determine D , b , and the parameter g is obtained from $X = Dgr/\ell$ or $y = gr\sqrt{\mu s}$. Thus, the initial nonlinear inverse problem for the system of differential equations is reduced to algebraic equations for the unknown parameters. Equilibrium and stationary modes allow obtaining D , s , and gr . Considering only stationary mode allows obtaining s and X . To split g , b (D , g , b), it is sufficient to use one (two) of the obtained equations.

In the equations there are only the differences $\bar{J}_h - \bar{J}$, $\bar{L}_h - \bar{L}$,

$$\begin{aligned} S - \frac{\bar{J}_h \pi}{\omega} &= S - \frac{\bar{J} \pi}{\omega} - \frac{(\bar{J}_h - \bar{J}) \pi}{\omega}, \\ S_{1/2} - \frac{\bar{L}_h \pi}{\omega} &= S_{1/2} - \frac{\bar{L} \pi}{\omega} - \frac{(\bar{L}_h - \bar{L}) \pi}{\omega}. \end{aligned} \quad (6.14)$$

The values $S - \bar{J} \pi / \omega$, $S_{1/2} - \bar{L} \pi / \omega$ are the integrals of $J(t) - \bar{J}$, $L(t) - \bar{L}$ on the appropriate time segments of the length π / ω . Thus it is enough to have information about the level of exceeding of $J(t)$, $L(t)$ over the background values \bar{J} , \bar{L} .

Thus, an inverse parametric identification problem of the hydrogen transfer through the stratified materials model with nonlinear dynamical boundary conditions in the form of differential equations, which model sorption-desorption processes on the surface, is reduced to solving a system of nondifferential equations. The measurements are under an integral sign, which provides some immunity of identification for noises. The amount of the experimental work is significant, but, unlike the methods which study surface processes and diffusion separately, here their close connection is taken into consideration.

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