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A COMPLEX STUDY OF GAS DIFFUSION PROCESSES IN VACUUM TECHNOLOGY MATERIALS. 2. THE PHENOMENOLOGICAL THEORY OF GAS PERMEABILITY OF METALS IN THE PRESENCE OF COMPLICATED SOLUTION AND OUTGASSING PROCESSES

ABSTRACT

The phenomenological theory of processes of plane membrane permeability by a dissociating diatomic gas (the hydrogen-metal system) is considered. The formalism is proposed for generalize boundary conditions of the 3-rd kind, which takes into account the molecular hydrogen adsorption, the reversible hydrogen dissociation-recombination reaction, the atomic hydrogen adsorption the process of overcoming the surface barrier and diffusion over a layer that contains disturbed sites of limited capacity. Under an assumption of mechanism of non-disturbed hydrogen diffusion over a metal volume the equations for Fick's first and second laws are solved using non-stationary boundary conditions proposed. The influence of separate stages of a complicated dissolution-outgassing process on concentration profiles and hydrogen permeability kinetics of metals is analyzed by simulation techniques. The proposed version of a phenomenological theory of dissociating gas diffusion is shown to explain practically all anomalies observed in metals' hydrogen permeability experiments carried out so far. Some new effects have also been predicted, such as the non-linear form of a hydrogen permeability curve plotted in a functional scale.

I. Introduction

The vacuum equipment is widely used now in hydrogen energetic and thermonuclear synthesis installations. In some cases however, the hydrogen can penetrate into vacuumized volumes, which is undesirable. To suppress those effects successfully and to develop effective methods for outgassing of construction and functional materials, used in vacuum technology, the mechanism of hydrogen transfer through metal partitions has to be studied.

As known, the phenomenological description of diatomic gas permeability subject to reversible dissociation-recombination reaction at the membrane surface, requires, that the equations for Fick's second law be solved under nonlinear, non-stationary boundary conditions of the 3-rd kind [1]. Different approaches are known, which consider a role of one or several stages of overcoming the gas-solid body interface by hydrogen [2—6]. Unfortunately, there is no formalism so far, which would allow to take into account the influence of the whole succession of elementary processes, occurring at input and output membrane surfaces, on metal hydrogen permeability kinetics. The feature of this problem lies in a complex hierarchy of micro- and macroscopic approaches in the description of general kinetics of reactions.

The purpose of this work is to develop the phenomenological theory of plane membrane permeability by a dissociating diatomic gas. A special attention is paid to developing the formalism for generalized non-stationary boundary conditions of the 3-rd kind, which take into account the molecular hydrogen adsorption, the reversible catalytic hydrogen dissociation-recombination reaction, the atomic hydrogen adsorption, the process of overcoming the near-surface barrier and the diffusion over a layer containing the disturbed sites of limited capacity. Under an assumption of mechanism of non-disturbed hydrogen diffusion over a metal volume, the equations for Fick's first and second laws are solved with using generalized non-stationary boundary conditions of the 3-rd kind. The influence of separate stages of a complicated solution-outgassing process on hydrogen permeability kinetics of metals is analyzed by simulation techniques.

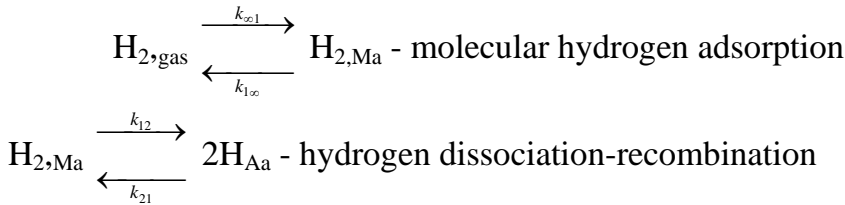
2. Dissolution-outgassing processes in the course of permeation

When hydrogen strikes the input surface of a membrane, the following processes occur:

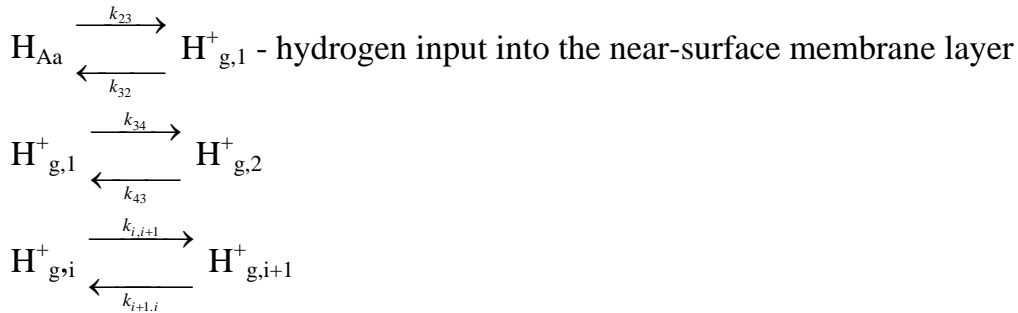
1. The physical adsorption of molecular hydrogen at the membrane surface.
2. The hydrogen dissociation-recombination reaction at catalytically active centers.
3. The chemical adsorption of atomic hydrogen at adsorptive-active centers.
4. The hydrogen transfer (in form of a proton, apparently) into the solid body volumes. In this case the hydrogen overcomes some extra potential barrier that arises either due to the difference between transport properties of a near-surface region and those of material volume (the surface can be considered to be some specific defect of metal), or due to the presence of any barrier layer (oxide, nitride, etc.) in the near-surface region of a membrane.
5. The migration over a thin, highly defective near-surface layer.
6. The hydrogen diffusion over a material volume, which is complicated to some degree by the process of hydrogen interaction with structure defects or by hydride formation reactions.

The elementary processes occurring in the hydrogen permeability of a membrane can be written as follows:

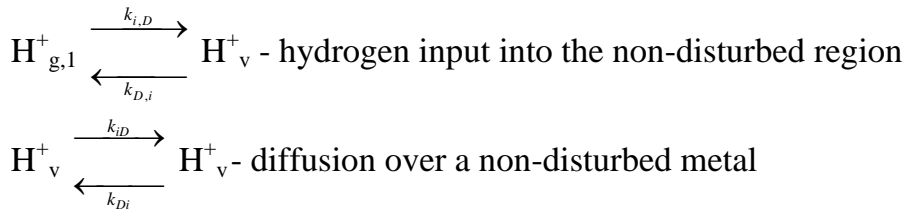
- 1) The processes at the membrane surface:



- 2) The hydrogen diffusion over a highly non-uniform near-surface layer of metal:



- 3) Non-disturbed diffusion over the metal volume



The scheme of energetic states of various positions accessible for hydrogen both at the surface and in the volume of metal is shown in Fig. 1. The process of hydrogen penetration into the solid body is considered to be a successive displacement of diffusant atoms through potential barriers from one site to another. We introduce the following notations: M_a - sites (adsorptive - active centers) which provide adsorption of hydrogen molecules (the catalytic reaction of hydrogen molecules' dissociation-recombination takes place at the same centers) Aa - the centers responsible for hydrogen atoms adsorption at the surface, g - sites accessible for hydrogen dissolution in the near-surface

layer of thickness Δ equal to some grid constants d , V – sites accessible for hydrogen solution in a non-disturbed material volume. G_{H_2} and G_{Ha} are free Gibbs energies (potential hole depths) for adsorption of hydrogen molecules and atoms, respectively, G_g – Gibbs energy for hydrogen solution in a near-surface (defective) metal layer, G_v – Gibbs energy for hydrogen solution in a metal volume, ΔG_k – the enthalpy of reaction of catalytic decomposition of hydrogen (the potential barrier height for transition from molecular to atomic hydrogen), ΔG_g and ΔG_D – potential barrier heights for hydrogen diffusion over the near-surface layer and volume of metal. Note that since the near-surface layer has highly defective structure, the diffusion over this layer is defined by a spectrum of local values G_g and ΔG_g . Such a diffusion over the near-surface layer can be described by the solution of diffusion Fick's equation with an account of functions $D(x)$ and $K_L(x)$, where D and K_L are the diffusion coefficient and the local solubility constant (as an example, those functions are expressed in Fig. 1 in terms of decreasing G_g and ΔG according to the Arrhenius law). However, since very thin layers are considered is here, it is more convenient, that the diffusion space be supposed to be discrete and the diffusion is described in the kinetic approximation. In this case each successive diffusion act takes place with its own G_g and ΔG values. We shall suppose that the adsorption positions and positions in the near-surface defective region can accommodate only limited number of hydrogen molecules or atoms, which means that these positions have limited capacity. In this case the adsorption isotherm obeys the Loungmour law, in which, however, p_0 should be replaced by $(p_0)^{1/2}$ due to the presence of atomization reaction. Sites in a non-disturbed metal matrix possess non-limited capacity, and the adsorption isotherm is described by Henry's isotherm for one-atomic hydrogen and by the Siverts law – for diatomic gas.

Processes 1-5 occur again at the output surface of a membrane, but in the opposite order. Since the membrane surfaces are under different conditions in the permeability method, the chemical processes at input and output sides of a specimen are governed by kinetic equations with different values of parameters. Even for the same values of kinetic constants of surface reactions the contributions of processes, occurring at membrane input and output, into the general hydrogen permeability kinetics are different, because in the permeability method different partial pressures p^+ and p^- of hydrogen are maintained at different membrane surfaces.

3. Generalized boundary conditions in the problem of hydrogen permeability of metals.

Let us consider the membrane of thickness $L = L_D + \Delta_1 + \Delta_2 \approx L_D$, where L_D is the thickness of a non-disturbed material layer, over which the volume diffusion, described by solutions of Fick's equations, is accomplished; Δ_1 and Δ_2 are thicknesses of near-surface layers of highly defective material at membrane input and output respectively. The diffusion over these layers is described by the solution of kinetic equations. Practically non-dissociating, pure diatomic gas is present on both sides of a membrane at pressures p^+ and p^- ($p^+ > p^-$). We believe that any defects ("traps") are absent in the membrane volume, the atoms do not participate in chemical reactions, and their diffusion is one-channel, that is, it is accomplished according to a unique mechanism. We suppose also, that there exist adsorption positions of a single type only, and the elementary sites, occupied by sorbed molecule and atom, are nearly the same. The near-surface layer consists only of two layers, which are capable of accumulating hydrogen, and their characteristics differ from similar characteristics of non-disturbed sites in the metal volume. (This difference lies primarily in the fact, that the distorted sites possess limited

capacity, unlike the volume ones). Then the system of differential equations for boundary conditions takes the form

$$\begin{aligned}
\frac{dC_1}{dt} &= k_{\infty 1} p_0 (N_a - C_1 - C_2) - k_{1\infty} C_1 - k_{12} C_1 (N_a - C_1 - C_2) + k_{21} C_2^2 \\
\frac{dC_2}{dt} &= 2k_{12} C_1 (N_a - C_1 - C_2) - 2k_{21} C_2^2 - \frac{k_{23}}{g} C_2 (N_3 - C_3) + \frac{k_{32}}{g} C_3 (N_a - C_1 - C_2) \\
\frac{dC_3}{dt} &= k_{23} C_2 (N_3 - C_3) - k_{32} C_3 (N_a - C_1 - C_2) - \frac{k_{34}}{g} C_3 (N_4 - C_4) + \frac{k_{43}}{g} C_4 (N_3 - C_3) \\
\frac{\partial C_4}{\partial t} &= \frac{k_{34}}{g} C_3 (N_4 - C_4) - \frac{k_{43}}{g} C_4 (N_3 - C_3) + D_g \frac{\partial C_4}{\partial x}
\end{aligned} \quad (1)$$

where D is the hydrogen diffusion coefficient (cm^2/s), x is the diffusion coordinate, g is the dimensional factor that takes into account the transition from the surface concentration to volume one [$1/\text{cm}$], $C_1=C_{\text{Ma}}$ and $C_2=C_{\text{Aa}}$ are concentrations [$1/\text{cm}^2$] of hydrogen adsorbed in molecular and atomic forms, respectively, $C_3=C_g$ and $C_4=C_v$ are hydrogen concentrations [$1/\text{cm}^3$] in the near-surface material layer (site No 4 is supposed here to be the last defective layer position, that can be related to the first site from which the non-disturbed volume diffusion starts). This site is characterized by the fact, that the potential hole depth is equal to the depth of a potential hole of non-disturbed diffusion, i.e. $G_g = G_v$, but hole No. 4 is surrounded by potential barriers of different height ΔG_g and ΔG_D . Remind that the potential hole, in which hydrogen is solved in a non-disturbed material, is surrounded by potential barriers of the same height ΔG_D . N_a is here the concentration [$1/\text{cm}^2$] of adsorptive-active sites, where the adsorption of atoms and molecules takes place; N_3 and N_4 are concentrations [$1/\text{cm}^3$] of sites accessible for hydrogen solution in the near-surface layer; $k_{\infty 1} \left[\frac{1}{\text{atm} \cdot \text{s}} \right]$ is the adsorption rate constant for gas molecules; $k_{1\infty} [\text{s}^{-1}]$ is the desorption rate constant for gas molecules; k_{12} and $k_{21} [\text{cm}^2/\text{s}]$ are dissociation and recombination rate constant; k_{23} and $k_{32} [\text{cm}^2/\text{s}]$ are rate constants of solution and reverse adsorption of gas atoms from a near-surface layer; $k_{34} = k_D$ and $k_{43} [\text{cm}^2/\text{s}]$ are rate constants for direct and reverse transition from the near-surface layer to the non-disturbed metal volume. Here N_3 and N_4 are concentrations of internodes intervals accessible for hydrogen atoms in case of insertion solutions.

It is assumed that:

- 1) the same adsorption position can not be occupied by a molecule and atom simultaneously;
- 2) two atoms are formed during the dissociation;
- 3) one of two positions required for chemisorption of atoms, appeared in a molecule dissociation, is supplied by this particular molecule, and
- 4) the near-surface region contains two layers of defective positions with limited capacity accessible for hydrogen solution. All constants except $k_{\infty 1}$ and $k_{1\infty}$ are normalized with respect to surface area unit, i.e. their dimension is [$\text{cm}^{-2} \text{s}^{-1}$].

In the dimensionless form system (1) is

$$\begin{aligned}
\frac{d\theta_1}{d\tau} &= \xi_{\infty 1} (1 - \theta_1 - \theta_2) - \xi_{1\infty} \theta_1 - \xi_{12} \theta_1 (1 - \theta_1 - \theta_2) + \xi_{21} \theta_2^2 \\
\frac{d\theta_2}{d\tau} &= 2\xi_{12} \theta_1 (1 - \theta_1 - \theta_2) - 2\xi_{21} \theta_2^2 - \xi_{23} \theta_2 (1 - \theta_3) + \xi_{32} \theta_3 (1 - \theta_1 - \theta_2) \\
\frac{d\theta_3}{d\tau} &= \xi_{23}^* \theta_2 (1 - \theta_3) - \xi_{32}^* (1 - \theta_1 - \theta_2) - \xi_{34} \theta_3 (1 - \theta_4) + \xi_{43} \theta_4 (1 - \theta_3)
\end{aligned} \quad (2)$$

$$\frac{d\theta_4}{d\tau} = \xi_{34}\theta_3(1-\theta_4) - \xi_{43}\theta_4(1-\theta_3) + G \frac{d\theta_4}{dX}$$

where $\theta_1 = \frac{C_1}{N_a}$ and $\theta_2 = \frac{C_2}{N_a}$ are occupation potential holes by molecules and atoms, respectively. $\theta_3 = \frac{C_3}{N_3}$ is the occupation fraction of potential holes in the near-surface region ($N_3=N_g$), $\theta_4 = \frac{C_4}{N_4}$ is the degree of occupation of the first position in a non-disturbed material ($N_4=N_v$). $\xi_{\infty 1} = \frac{k_{\infty 1}p_0}{D/L^2}$; $\xi_{1\infty} = \frac{k_{1\infty}}{D/L^2}$; $\xi_{12} = \frac{k_{12}N_a}{D/L^2}$; $\xi_{21} = \frac{k_{21}N_a}{D/L^2}$; $\xi_{23} = \frac{k_{23}N_{03}}{gD/L^2}$; $\xi_{32} = \frac{k_{32}N_3}{gD/L^2}$; $\xi_{23}^* = \frac{k_{23}N_a}{D/L^2}$; $\xi_{32}^* = \frac{k_{32}N_a}{D/L^2}$; $\xi_{34} = \frac{k_{34}N_4}{gD/L^2}$; $\xi_{43} = \frac{k_{43}N_4}{gD/L^2}$; $G=gL$; $X=x/L$; $\tau=Dt/L^2$.

(Here by $L \approx L_D$ is meant the thickness of a layer over which the non-disturbed diffusion takes place).

The diffusion in a membrane volume is

$$\frac{\partial \theta_4}{\partial \tau} = \frac{\partial^2 \theta_4}{\partial X^2} \quad (3)$$

The process of hydrogen transfer from metal into vacuum at the membrane output is described by a system of equations similar to (2), but parameters ξ_{ij}^L are used instead of ξ_{ij}^0 and p^- - instead of p^+ .

The flow at the membrane output is

$$J = \xi_{1\infty}^L \theta_{1L} - \xi_{\infty 1}^L (1 - \theta_{1L} - \theta_{2L}) \quad (4)$$

Now we consider hydrogen solubility in a metal plate. We suppose that $\xi_{ij}^0 = \xi_{ij}^L$, $p^+ = p^- = p_0$. Under thermodynamic equilibrium $\frac{d\theta_1}{d\tau} = \frac{d\theta_2}{d\tau} = \frac{\theta_3}{d\tau} = \frac{\theta_4}{d\tau} = 0$ where from

$$\theta_1 = \frac{K_1 p_0}{1 + \sqrt{K_1 K_2 p_0} + K_1 p_0} \text{ for } p_0 \rightarrow 0, \theta_1 \rightarrow K_1 p_0$$

$$\theta_2 = \frac{\sqrt{K_1 K_2 p_0}}{1 + \sqrt{K_1 K_2 p_0} + K_1 p_0} \text{ for } p_0 \rightarrow 0, \theta_2 \rightarrow \sqrt{K_1 K_2 p_0}$$

$$\theta_3 = \frac{K_3 \sqrt{K_1 K_2 p_0}}{1 + K_3 \sqrt{K_1 K_2 p_0}} \text{ for } p_0 \rightarrow 0, \theta_3 \rightarrow K_3 \sqrt{K_1 K_2 p_0}$$

$$\theta_4 = \frac{K_3 K_4 \dots K_i \sqrt{K_1 K_2 p_0}}{1 + K_3 K_4 \dots K_i \sqrt{K_1 K_2 p_0}} \text{ for } p_0 \rightarrow 0, \theta_4 \rightarrow K_3 K_4 \dots K_i \sqrt{K_1 K_2 p_0}$$

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$$\theta_i = \frac{K_3 K_4 \dots K_i \sqrt{K_1 K_2 p_0}}{1 + K_3 K_4 \dots K_i \sqrt{K_1 K_2 p_0}} \text{ for } p_0 \rightarrow 0, \theta_i \rightarrow K_3 K_4 \dots K_i \sqrt{K_1 K_2 p_0} = K_{eff} \sqrt{p_0}$$

Here equilibrium constant are: $K_1 = \frac{k_{\infty 1}}{k_{1\infty}}$; $K_2 = \frac{k_{12}}{k_{21}}$; $K_3 = \frac{k_{23}}{k_{32}}$; $K_4 = \frac{k_{34}}{k_{43}}$ (here we assume that $k_{43}=k_D$).

Thus, the equilibrium solubility of is determined not only by gas pressure over a plate, but also by equilibrium constants of all surface processes. For sufficiently low

pressures $\theta_1(p_0)$ corresponds to Henry's law and for the other $\theta_i(p_0)$ values – to Siverts' law. The presence of maximum in $\theta_2(p_0)$ dependence is due to the fact, that for large p_0 a considerable part of surface occurs to be occupied by sorbed molecules and, hence, it is inaccessible for atoms. For low pressures $\theta_1 \ll \theta_2$ and hydrogen flows through a membrane can be abnormally low.

4. A mathematical simulation of hydrogen permeability kinetics of metals in the presence of generalized boundary conditions at membrane surfaces.

The differential equation (3) related to conditions of type (2), written for input and output membrane surfaces, has been solved numerically. In this case the second derivative with respect to X in equation (3) was replaced by a finite-difference operator

$$\frac{d\theta_i}{d\tau} = \frac{\theta_{i-1} - 2\theta_i + \theta_{i+1}}{h^2}; \quad i = 5, 6, \dots, n-4 \quad (5)$$

where $h = 1 / (n_x + 1)$ is the grid step in coordinate X , n_x is the number of internal nodes of this grid, $n = n_x + 8$ is the total number of differential equations describing the process (4 equations (2) for the input surface, 4 similar equations for the output surface and n_x equations - for internal points of a grid).

The system of n differential equations, obtained in the above manner, has been solved by the Kutta-Merson method [7]. In this case the "experimental" curves were calculated, such as equilibrium sorption isotherms, the effective permeability constant and effective diffusion coefficient as functions of membrane thickness and partial hydrogen pressure at the membrane input, concentration profiles and kinetic hydrogen permeability curves. The effective diffusion coefficient was calculated by the method of moments according to the formula:

$$D_{eff} = \frac{L^2}{6\tau_L} \quad (6)$$

where τ_L is the first statistic moment of the kinetic hydrogen permeability curve $J(t)$ equal to the delay time measured in the integral version of permeability:

$$\tau_L = \frac{1}{J_\infty} \int_0^\infty t \frac{dJ}{dt} dt = \frac{1}{J_\infty} \int_0^\infty [J_\infty - J(t)] dt$$

(here J_∞ through the membrane in a stationary state, i.e. for $t \rightarrow \infty$).

As an example, Fig. 1 shows the equilibrium hydrogen concentrations in different types of states as functions of partial hydrogen pressure ($p^+ = p^- = p_0$). For better visuality Fig. 2a shows curves for low p_0 values, and Fig. 2b - those within a wide range of pressures. It is seen that if θ_1 , θ_3 and θ_4 increase with pressure and approach the external value, then θ_2 (the quality of atomic hydrogen adsorbed at the membrane surface) passes through a maximum. Fig. 3 demonstrates a stationary hydrogen flow through the membrane as a function of partial hydrogen pressure at the membrane input. For low pressures the flow is abnormally small, but as the pressure grows, the flow increases and seems to be reached (Fig. 3a) an external value. However, the simulation within a wide range of pressures has shown (Fig. 3b) that curve $J_\infty(p_0)$ passes through a maximum. Now we shall consider the kinetics of nonstationary hydrogen permeability through metal membranes.

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In concentration profiles calculations the generalized boundary conditions of the 3-rd kind were supposed to take place on both membrane surfaces; parameters $k_{ij}^0 = k_{ij}^L$, $p^+ = p_0$, $p^- = 0$.

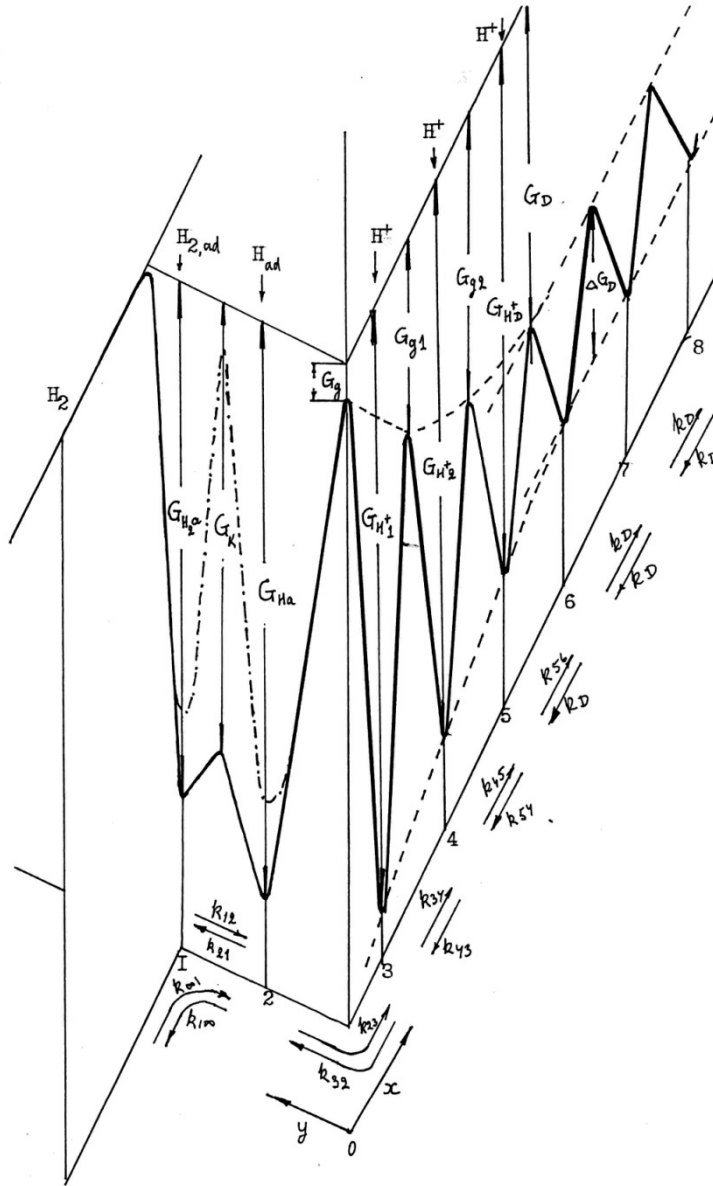


Fig. 1. The diagram of energy states of hydrogen in gas phase, adsorbed at the surface (in form of molecules and the diagram of energy states of hydrogen solved in a defective near-surface layer and in the non-disturbed metal volume (G - Gibbs energy for hydrogen solution, ΔG potential barrier heights for hydrogen diffusion).

As an example, Fig. 4 shows non-stationary concentration hydrogen profiles represented as θ_i , that is, as fractions of sites of i -th type occupied by hydrogen (the degree of occupation of corresponding sites of capture is expressed in atomic fractions). Fig. 4 reflects the time variation of occupation degree for two types of adsorption centers at an input membrane surface (θ_1^0 and θ_2^0) in defective sites at the membrane input or output, respectively ($\theta_3^0 = \theta_3^L$) as well as in adsorption centers at an output membrane surface (θ_2^L and θ_1^L). The same plots demonstrate time variation of a hydrogen concentration distribution over a non-disturbed metal layer, $\theta_D(X, \tau)$. Some specific

properties of sites No 4 at membrane input and output have already been mentioned above).

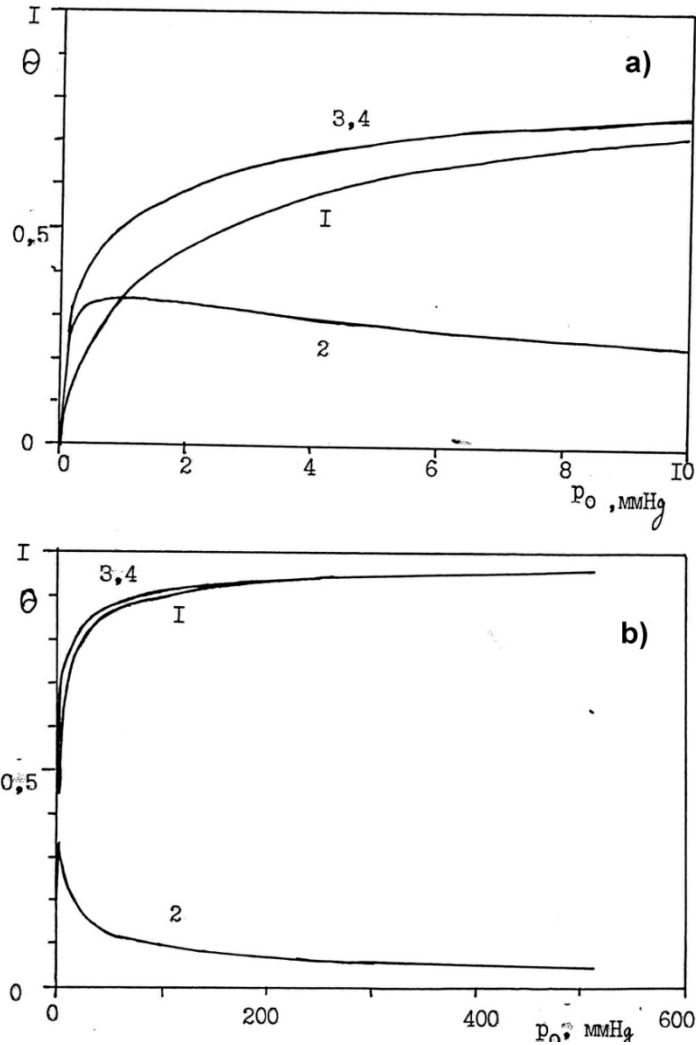


Fig. 2. The hydrogen quantity in different types of sites, (occupied fraction) as a function of partial hydrogen pressure at plate surfaces (the equilibrium sorption; calculations for values of parameters: $\frac{N_3}{gN_1} = 1$, $\frac{N_3}{N_1} = 1$, $\xi_{ij} = 10$, where $i=\infty, 1, 2, 3, 4$; $j=\infty, 1, 2, 3, 4$; $g_L=10$; $0.2 \leq p_0 \leq 512$ mmHg, $k_{\infty 1}$ is expressed in units $\text{s}^{-1} (\text{mm Hg})^{-1}$, $\theta_1(1)$, $\theta_2(2)$, $\theta_3(3)$, $\theta_4(4)$, a - low pressures; b - wide range of pressures.

It is seen that, unlike the boundary conditions of the 1-s kind, the hydrogen concentration at the first site belonging a non-disturbed metal (Mo. 4) is established by no means instantaneously, but increases for sufficiently long time. The difference between notions of "dynamic" and "equilibrium" concentrations is obvious: in the stationary state of hydrogen permeability the hydrogen concentrations, adsorbed at membrane surfaces in atomic or molecular form, as well as in the defective near-surface layer with limited capacity of sites, drastically differ from hydrogen concentrations in a metal volume. As under boundary conditions of the 1-st kind, for large times the rectilinear concentration distribution is established over a non-disturbed metal volume; however in this case the concentration gradient is considerably lower than that under boundary conditions of the 1-st kind.

Obviously, in the presence of "traps", which "catch" molecular or atomic hydrogen, hydrogen concentrations at the surface or in near-surface metal layers (both at the membrane input and output) can reach high values. The abnormal increase of hydrogen

concentration, in its turn, causes bristling of near-surface metal layers and also gives rise to intensive outgassing processes when hydrogen-containing materials are affected by light or ionizing radiation.

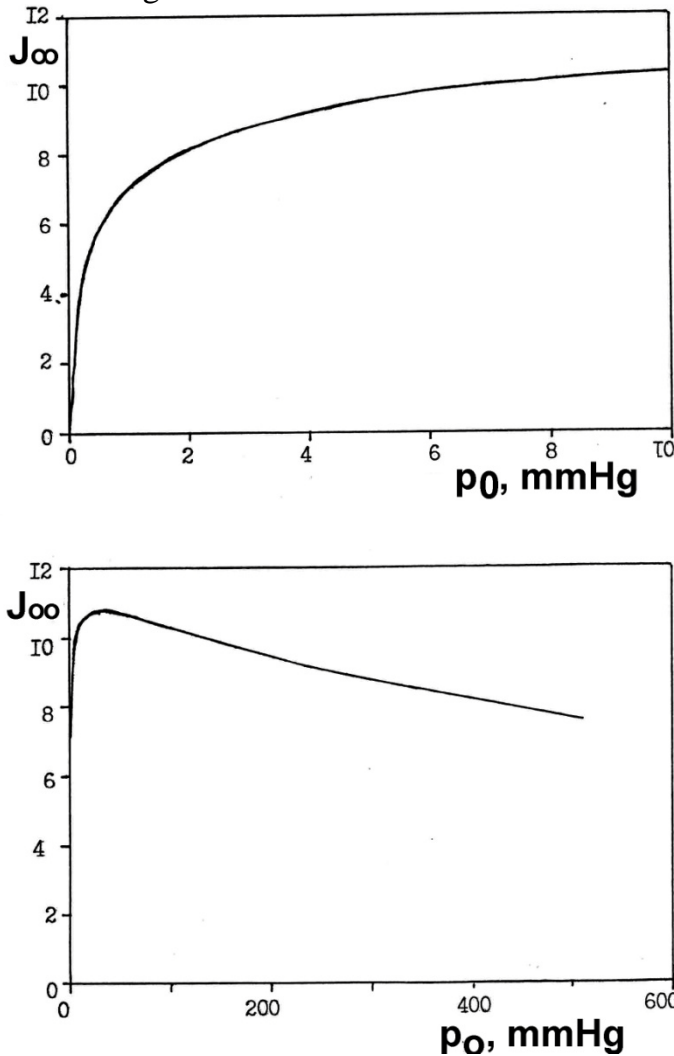


Fig. 3. The stationary hydrogen flow through the membrane as a function of partial hydrogen pressure at the membrane input; a - low pressure b - wide range of pressures (parameters as in Fig.2).

Fig. 4 also demonstrates the influence of partial hydrogen pressure on non-stationary concentration profiles. Pressure p_0 greatly influences the shape of a concentration profile. As p_0 grows, the concentration of hydrogen, adsorbed in atomic form, first increases and then diminishes. For low p_0 the hydrogen concentration θ_2 grows with time, whereas for high p_0 values θ_2 remains nearly constant.

Fig. 5a illustrates the influence of partial pressure of hydrogen at the membrane input on kinetic permeability curves normalized with respect to a stationary flow value. It is seen that as the pressure grows, the time of reaching a stationary state first decreases and then grows. For better visuality Fig. 5b shows the some curves, but plotted in a functional scale (remind that when we have plotted in the same scale the kinetic hydrogen permeability curve calculated within the frame-work of a non-disturbed diffusion model with boundary conditions of the 1-st kind, the straight line with slope, angle tangent $\text{tg}\alpha = DL^2$ arises on the plot). It is seen that under non-stationary, non-linear boundary conditions of the 3-rd kind the kinetic curves, plotted in a functional scale, can be S-shaped, and in this case the plot curvature first increases and then diminishes as pressure grows.

As the hydrogen pressure at the membrane input grows, the effective diffusion coefficient first increases (Fig. 6 a), the plot being resembling a similar dependence for the model of diffusion in a medium containing the dispersion of point-like defects of limited capacity. For high pressures, however (Fig. 6 b), the $D_{\text{eff}}(p_0)$ dependence reaches a maximum, after which D_{eff} diminishes.

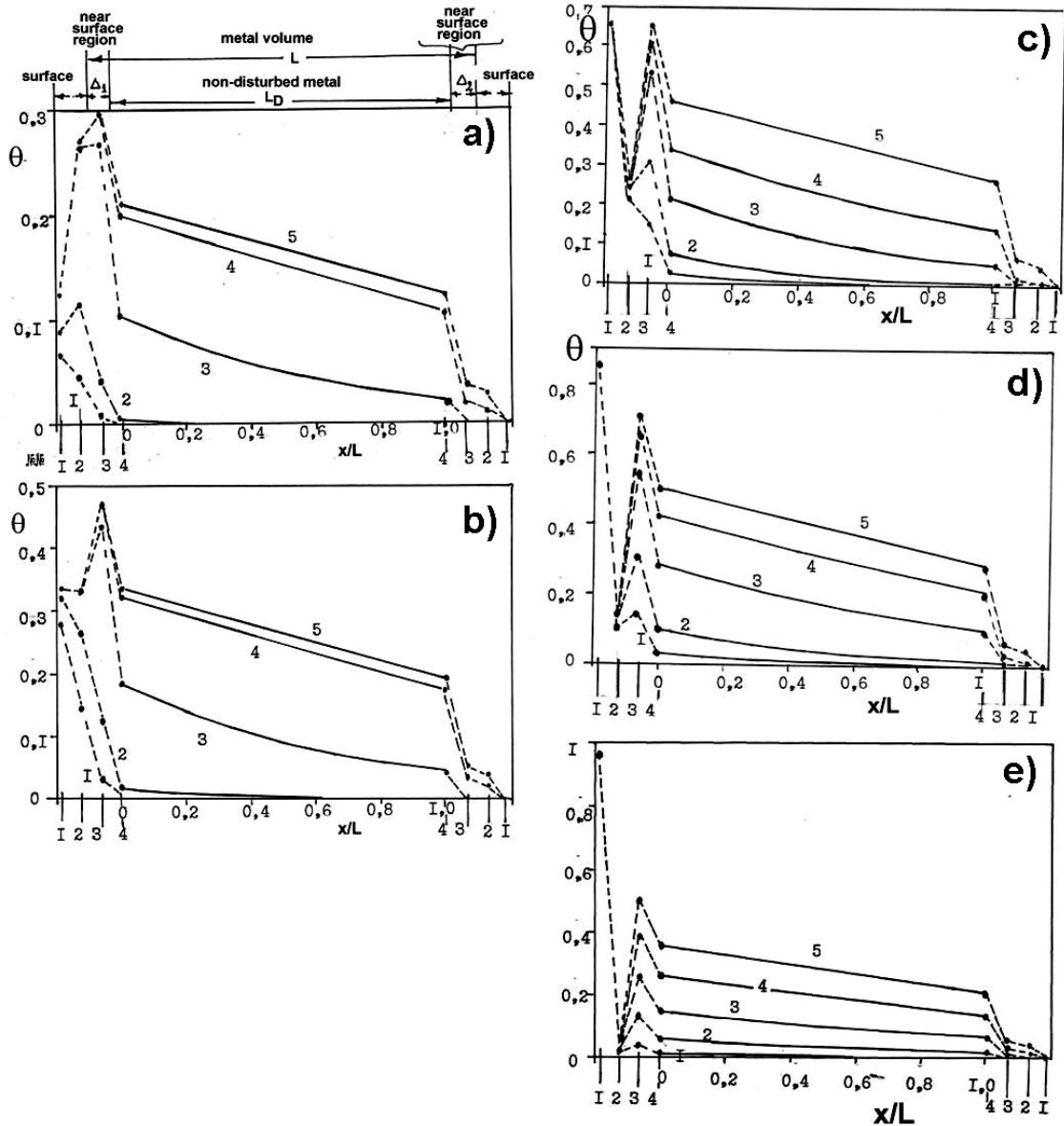


Fig. 4. The influence of partial hydrogen pressure at the membrane input on non-stationary concentration profiles of hydrogen. (Parameters as Fig.2). a – $p_0 = 0,2$ mmHg; $\tau = \frac{Dt}{L^2} = 0,0625$ (1); 0,125(2); 0,625(3); 3,125(4); 10(5). b – $p_0 = 1$ mmHg; $\tau = 0,125$ (1); 0,25(2); 0,625(3); 3,125(4); 10(5); c – p_0 , $\tau = 0,125$ (1); 0,25(2); 0,625(3); 1,25(4); 8,75 (5); d – $p_0 = 32$ mm Hg; $\tau = 0,25$ (1); 0,5(2); 1,25(3); 2,5(4); 17,5(5) e – $p_0 = 512$ mm Hg; $\tau = 0,5$ (1); 1,25(2); 2,5(2); 5(4); 40(5).

5. Corollaries of the phenomenological theory of diatomic gas permeability under reversible non-linear, non-stationary boundary conditions of the 3-rd kind.

Within the framework of a theory considered here we managed to explain such well-known experimental facts, as leveling of the dependence of stationary flow J_∞ on $1/L$, a very strong influence of a membrane surface state on the permeability a sharp decrease of permeability at low pressures, the change of activation energy of a hydrogen penetration process with changing of its regime (in different versions of the permeability method this

energy is expressed in different manner in terms of activation energies of elementary processes), the non-coincidence of kinetic curves, obtained in a sorption version, with those measured in a desorption version of the permeability method, the dependence of a stationary flow value on the direction of gas flow through the membrane, the dependence of effective diffusion coefficient on a partial pressure of hydrogen at the membrane input, etc.

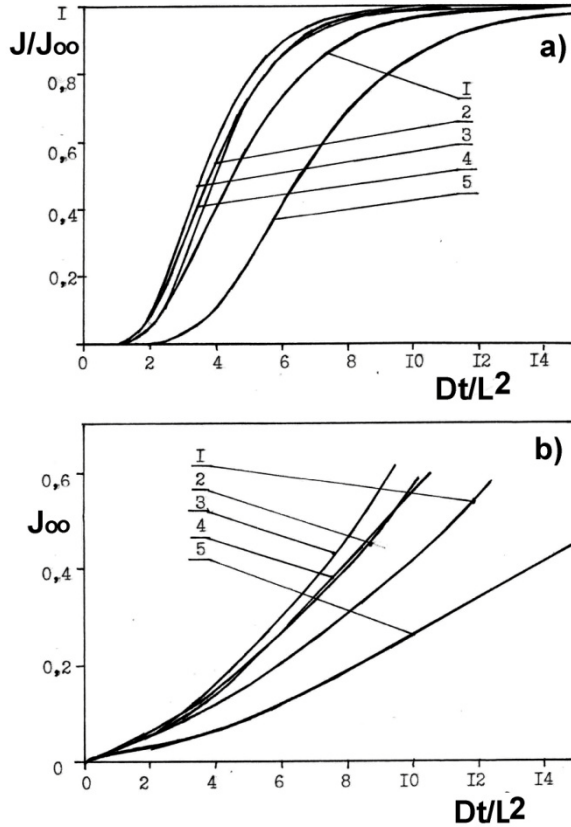


Fig. 5. The influence of partial hydrogen pressure on the shape of kinetic curves of non-stationary hydrogen permeability of a plate (Parameters as in Fig. 2). a - usual scale; b - functional scale.

Note that, if one neglects the specific property of a near-surface layer, the system of equations we have proposed transfers into the system considered in paper [6], which takes into account the molecular hydrogen adsorption processes, hydrogen dissociation recombination reactions and atomic hydrogen absorption at the membrane surface. If the molecular hydrogen adsorption can be neglected, then we arrive at the case of non-linear, non-stationary boundary conditions of the 3-rd kind considered in paper [2], and if one can neglect, besides, the atomic hydrogen adsorption, then one gets stationary nonlinear boundary conditions of the 3-rd kind [3]. And, finally, if one neglects the atomization-recombination reaction, then one should take into account the presence of extra barrier when hydrogen transfers from the metal surface to the volume – the linear boundary of the 3-rd kind [5].

The presence of additional resistances of hydrogen migration at membrane boundaries (the linear boundary conditions of the 3-rd kind) results (when the surface process rate constant decreases) in increasing time of reaching stationary state of diffusion and in decreasing values of effective diffusion coefficient and stationary permeability flow. The solution of the problem in the dimensionless form does not depend on partial hydrogen pressure at the membrane input. Hence, kinetic curves and concentration profiles, obtained at different pressures, differ only in a constant factor

proportional to pressure. The effective diffusion coefficient does not depend on hydrogen pressure at the membrane input. The linear boundary conditions of the 3-rd kind can not be transformed into the boundary conditions of the 1-st kind by changing the hydrogen pressure.

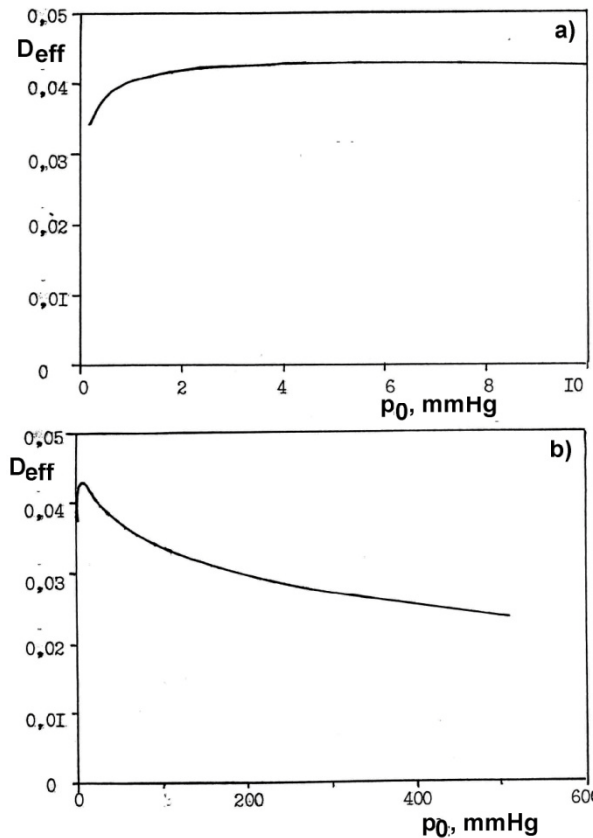


Fig. 6. The effective diffusion coefficient as a function of partial hydrogen pressure at the membrane input (Parameters as in Fig2). a - low pressures; b - wide range of pressures.

6. Conclusion

Thus, the mathematic formalism of diatomic dissociating gas diffusion through a plane plate we have proposed in this paper allows to take into account the whole succession of solution -outgassing processes occurring at the membrane input and output. Whether all these processes will influence the hydrogen permeability kinetics of metals, or only one particular process will be critical, - this depends on the experiment temperature, on the element composition of a surface layer, on the presence, type and concentration of surface impurities, on partial hydrogen pressure, on the membrane thickness and on the other factors.

Because the majority of constants in equation (6) experimentally increase with temperature, one can expect that the processes at membrane surfaces, considered in this paper, will essentially decelerate the rate of hydrogen permeability of metal foils at low temperatures, partial hydrogen pressures and membrane thicknesses. Note that by increasing partial hydrogen pressure at the membrane input one can eliminate limiting effect of practically all stages of hydrogen penetration through the phase interface, with the exception of a potential barrier arising due to the difference in the composition and structure of near-surface layer from the metal volume. The growth of temperature completely transforms all stages of generalized boundary conditions of the 3-rd kind into conventional conditions of the 1-st kind.

The presence of impurities at the membrane surface increases the time of reaching stationary state of diffusion and decrease the stationary flow value due to increasing height of potential barrier at the membrane input, changes the adsorption capacity with respect to molecular or atomic hydrogen, stimulates processes of activation or inhibition of catalytic dissociation-recombination reaction. (The change of energy diagram in the presence of "catalytic poison" at the surface is marked in this case by dash-dotted line in Fig. 1). The conclusions drawn above emphasize the importance of monitoring the element composition of the surface (by the Ouger-spectroscopy method, for instance [8]) in the course of hydrogen permeability process. On the other hand, by monitoring the surface purity one can control the metal membrane productivity.

Naturally, the use of atomic hydrogen beams produced by the external atomizer eliminates the stages of molecular hydrogen adsorption and dissociation-recombination reactions at the membrane input (those stages remain unchanged at the membrane output). The presence of potential barriers at membrane surfaces, caused by the difference between near-surface and volume properties of material, is essential for atomic hydrogen adsorption. The increase of height of these barriers (due to surface "poisoning", for instance) results, in case of irradiating the input membrane surface by atomic hydrogen, in the "superpermeability" effect [9]. The formalism of diatomic gas permeability through the metal partition, considered within the framework of this paper, is included into the bank of models of automatized system for processing the data of diffusion experiments. This formalism is used for simulating, processing and interpreting the experiments on studying gas diffusion in construction materials applied in vacuum technology.

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