rivatives of the corresponding functions with respect to the density; ρ''_{tr}, ρ'_{tr}, vapor and gas density at triple point; $\delta c_V = (c_V^{calc} - c_V^{exp})/c_V^{exp}$; $\delta\rho = (\rho^{calc} - \rho^{exp})/\rho^{exp}$; φ_I, φ_{1R}, φ_{2R}, ρ_0, A_i, D_i, E_i, $B_i^{\pm}$, $C_i^{\pm}$, constants corresponding to the cases $\rho \geqslant \rho_C$ (+) and $\rho < \rho_C$ (−).

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DIFFUSIONAL EXTRACTION OF MATERIAL FROM MODEL POROUS BODIES

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The solution and diffusional extraction of solid materials from porous membranes is investigated theoretically and experimentally.

The extraction of materials from porous bodies is widespread in commercial technology and in nature: the separation of inorganic and organic products in porous catalysts, the leaching out of mineral salts, the extraction of oil from cells of plant origin, hydrometallurgical treatment, etc. Similar subjects were investigated, e.g., in [1-3]. However, in describing these processes, mass transfer in a single capillary is most often considered, with a specified density of the solute at the exit, or the mass transfer in the solution and diffusional extraction in a porous body and outside it is not investigated in a consistent formulation. In the present work, results are given of experimental and theoretical investigations of the successive processes of solution of a solid material and its diffusional extraction from model porous membranes, the capillaries of which are entirely filled with material in the form of a solid phase or solution. A mathematical model of the above-noted processes is proposed in the form of a refined version of that described in [4].

As follows from [5], reflective spectroscopy, based on the phenomenon of attenuation of

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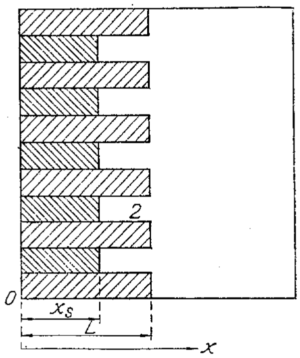

Fig. 1. Coordinate system.

the total internal reflection [6], allows the mass transfer in a porous membrane to be traced in the evaporation of liquid from the capillaries. In [5], thermal membranes of thickness 16, 15.5, and 12.5 μm and pore diameter d = 0.2, 0.5, and 1 μm, respectively, were used. In the present work, with the same experimental procedure and in analogous membranes, it proved possible to measure the absorption of radiation in a certain layer of material on solution in a porous membrane. The height of this layer coincides with the so-called penetration depth δ of the IR radiation employed [6].

The required contact between the porous membrane and the optical prism was achieved by means of an elastic metallic lattice pressed to the membrane by a shallow ($\sim 3 \cdot 10^{-3}$ m) cylindrical polyethylene bath of diameter h (see Fig. 2 in [5]). The filling of pores with material was accomplished in such a way as to avoid gas bubbles. Otherwise, the mechanism of extraction of the material from the porous body becomes significantly different [2, 7].

The extraction curve, i.e., the dependence of the reflected-radiation intensity I on the time t, was plotted at constant wavelength on a UR-20 spectrometer made by K. Zeiss-Jena (German Democratic Republic), with the appropriate attachment from the same manufacturer; recording began simultaneously with filling of the bath with solvent. Using this attachment, multiple reflection at the walls of the KRS-5 prism was achieved. The dependence I(t) was converted to the function E(t), in which E = log (I_0/I) is related to the molar concentration c* of the material as follows [8]

$$E = \lg \frac{I_0}{I} = \varepsilon c^* \delta. \tag{1}$$

The absorption coefficient ε was determined in a separate experiment using an expression analogous to Eq. (1), with the passage (and not the reflection) of beams through a layer of solution with a known concentration and thickness. The penetration depth was determined from the formula [9]

$$\delta = \frac{\cos \varphi_0}{c^* N \varepsilon} \frac{I_0 - I}{I_0} .$$

In the experiment a solution of cocoa butter in chloroform ($CHCl_3$) was investigated. The diffusion coefficient D was determined by the method proposed in [9].

In the mathematical description of the given process, two problems must be distinguished: 1) the solution of the solid material, taking account of the motion of the phase interface; 2) diffusional extraction of the solute from the membrane capillaries. In both cases a one-dimensional model is used.

For the first boundary problem the following system of equations is written (Fig. 1):

$$\frac{\partial c_1}{\partial t} + \Pi v_2 \frac{\partial c_1}{\partial x} = D \frac{\partial^2 c_1}{\partial x^2}, \quad L < x < \infty, \ t > 0, \tag{2}$$

$$\frac{\partial c_2}{\partial t} + v_2 \frac{\partial c_2}{\partial x} = D \frac{\partial^2 c_2}{\partial x^2}, \quad x_s(t) < x < L, \ t > 0, \tag{3}$$

with the boundary conditions

$$x = x_s,\ c_2 = c_s, \tag{4}$$

$$\frac{dx_s}{dt} = \frac{D}{\rho_{\text{T}}\left(1 - \frac{c_s}{\rho_s}\right)} \frac{dc_2}{dx}, \tag{5}$$

$$x = L,\ c_1 = c_2, \tag{6}$$

$$\frac{\partial c_1}{\partial x} = \Pi \frac{\partial c_2}{\partial x}, \tag{7}$$

$$x = \infty,\ c_1 = 0 \tag{8}$$

and the initial conditions

$$t = 0,\ c_1 = 0,\ c_2 = c_s,\ x_s = L, \tag{9}$$

where c_i is the mass concentration (g/cm^3) of the solute in the bath (i = 1) and in the membrane (i = 2).

The problem in Eqs. (2)-(8) is a conjugate problem of mass transfer with boundaries $x_S(t)$ between the media that are moving and unknown prior to solution. Therefore, the boundary condition in Eq. (5) and the relation between the velocity of motion of the solution v_2 and dx_S/dt are obtained as the matching conditions at the interface, using the laws of conservation of the dissolved component and the whole mixture [10, 11]. Then

$$v_2 = \frac{dx_s}{dt}\left(1 - \frac{\rho_{\mathrm{S}}}{\rho_s}\right).$$

The additional condition in Eq. (4) at $x = x_S$ reflects the equilibrium nature of the solution process. Using the same conservation laws at the boundary x = L, the result obtained, in a one-dimensional formulation, consists of Eq. (7) and the relation $v_1 = \Pi v_2$, which is taken into account in writing Eq. (2). At the same time, it is assumed that Eq. (6) holds, although, generally speaking, this condition may not be satisfied in the case of vary narrow capillaries.

It may readily be shown that the problem formulated in Eqs. (2)-(9) admits of the self-similar variable

$$\eta = \frac{\bar{x} - 1}{2\sqrt{\tau}},$$

by means of which the solution of the problem is written in the form

$$\bar{c}_2(\bar{x}, \tau) = 1 - \alpha A \sqrt{\pi} \frac{\operatorname{erf}\{\eta + \alpha B\} + \operatorname{erf}\{\alpha(1 - B)\}}{\exp\{-[\alpha(1 - B)]^2\}}, \tag{10}$$

$$\bar{c}_1(\bar{x}, \tau) = \left[1 - \alpha A \sqrt{\pi} \frac{\operatorname{erf}\{\alpha B\} + \operatorname{erf}\{\alpha(1 - B)\}}{\exp\{-[\alpha(1 - B)]^2\}}\right] \frac{\operatorname{erfc}\{\eta + \alpha \Pi B\}}{\operatorname{erfc}\{\alpha \Pi B\}}, \tag{11}$$

where α is the constant in the expression for the law of motion of the solution front ($1 - \bar{x}_S = 2\alpha\sqrt{t}$), determined from the transcendental equation

$$\operatorname{erf}\{\alpha B\} + \operatorname{erf}\{\alpha(1 - B)\} - \frac{\exp\{-[\alpha(1 - B)]^2\}}{\alpha A \sqrt{\pi}} + \Pi \operatorname{erfc}\{\alpha \Pi B\} \frac{\exp\{(\alpha \Pi B)^2\}}{\exp\{(\alpha B)^2\}} = 0,$$

$$A = \frac{\rho_{\mathrm{S}}}{c_s - c_\infty}\left(1 - \frac{c_s}{\rho_s}\right),\ B = 1 - \frac{\rho_{\mathrm{S}}}{\rho_s}. \tag{12}$$

(Note that in [4] it must be assumed that $x_S = \alpha\sqrt{t}$, i.e., α has a different value.)

Afer termination of the process, i.e., after the solution front reaches the membrane boundary x = 0, diffusion of the dissolved component from the capillaries into the volume of the solution occurs. This stage of extraction is described by the following system of equations and boundary conditions:

TABLE 1. Time Dependence of E

$t-t_p$, sec	E			
	experimental data	calculation		
0	0,2566	0,2560	0,2560	0,2560
15	0,1975	0,1790	0,1801	0,1765
30	0,1478	0,1474	0,1439	0,1415
60	0,0876	0,1110	0,0949	0,0919
90	0,0532	0,0910	0,0642	0,0598
120	0,0330	0,0785	0,0443	0,0389
150	0,0214	0,0699	0,0312	0,0253
180	0,0153	0,0636	0,0224	0,0164

$$\frac{\partial \bar{c}_2}{\partial \tau} = \frac{\partial^2 \bar{c}_2}{\partial \bar{x}^2}, \quad 0 < \bar{x} < 1, \quad \tau > \tau_p, \tag{13}$$

$$\frac{\partial \bar{c}_1}{\partial \tau} = \frac{\partial^2 \bar{c}_1}{\partial \bar{x}^2}, \quad \bar{x} > 1, \quad \tau > \tau_p, \tag{14}$$

$$\bar{x} = 0, \quad \frac{\partial \bar{c}_2}{\partial \bar{x}} = 0, \tag{15}$$

$$\bar{x} = 1, \quad \bar{c}_1 = \bar{c}_2, \quad \frac{\partial \bar{c}_1}{\partial \bar{x}} = \Pi \frac{\partial \bar{c}_2}{\partial \bar{x}}, \tag{16}$$

$$\bar{x} \to \infty, \quad \bar{c}_1 = 0. \tag{17}$$

The most natural initial conditions for the system in Eqs. (13)-(17) are

$$\bar{c}_1(\bar{x}, \tau_p) = \psi(\bar{x}), \tag{18}$$

$$\bar{c}_2(\bar{x}, \tau_p) = \varphi(\bar{x}), \tag{19}$$

where the concentration profiles $\varphi(\bar{x})$ and $\psi(\bar{x})$ are obtained from the solution of Eqs. (10)-(12) of the preceding problem up to the moment τ_p at which solution ends. This formulation of the problem takes no account of the influence of free convection on the mass transfer; this process is a consequence of the dependence of the solution density on the concentration. Its influence, as shown by estimates, may become significant in the region outside the capillaries. In the given one-dimensional model, free convection in the quasisteady approximation may be taken into account using the corresponding solution for the case of a vertical plate obtained in [12]. If the mean diffusional flux over the membrane height at $\bar{x} = 1$ is calculated from this solution for the given problem, it is found that

$$\frac{\partial \bar{c}_1}{\partial \bar{x}} = -0.66L \left[\frac{g(\rho_0 - \rho_1)}{\mu D h} \right]^{1/4} \bar{c}_1. \tag{20}$$

The conditions in Eq. (16) must be used in order to write Eq. (20) in the form of the boundary condition for Eq. (13). Then

$$\frac{\partial \bar{c}_2}{\partial \bar{x}} = -0.66 \frac{L}{\Pi} \left[\frac{g(\rho_0 - \rho_1)}{\mu D h} \right]^{1/4} \bar{c}_2 \equiv -\beta \bar{c}_2, \quad \bar{x} = 1. \tag{21}$$

Thus, the problem of the diffusion of the dissolved component, taking free convection into account, reduces to solving Eq. (13), with the boundary conditions in Eqs. (15)-(21) and the initial condition in Eq. (19).

If the function $\rho_1(\bar{c}_2)$ in Eq. (21) is approximately replaced by some fixed value ρ_1^* known a priori, the solution of the problem is written in series form [13]

$$\bar{c}_2(\bar{x}, \tau) = \sum_{n=1}^{\infty} \frac{2\cos(\gamma_n \bar{x})}{\sin^2 \gamma_n} \cdot \frac{\beta^2 F(\gamma_n)}{\gamma_n^2 + \beta^2 + \beta} \exp\{-\gamma_n^2 (\tau - \tau_p)\}, \tag{22}$$

where

$$F(\gamma_n)=\int_0^1 \cos(\gamma_n \bar{x})\,\varphi(\bar{x})\,d\bar{x},$$

and γ_n are the positive roots of the equation $\gamma \tan \gamma = \beta$.

The numerical values of the quantities used in the present work were as follows: ρ_S = 1.145 g/cm³; c_S = 0.6 g/cm³; ρ_S = 0.975 g/cm³; ρ_0 = 1.498 g/cm³; μ = 0.0051P; D = $2.17\cdot10^{-6}$ cm²/sec; δ = $3.46\cdot10^{-4}$ cm; ε = 1064 liter/mole·cm; h = 2 cm; Π = 0.4; L = $12.5\cdot10^{-4}$ cm; M = 860. Comparison with experimental data involves calculating the quantity

$$E=\varepsilon\frac{1000}{M}c_s L\int_0^{\delta/L}\bar{c}_2(\bar{x},\ \tau)\,d\bar{x}. \tag{23}$$

Table 1 compares the experimental — $E = \log(I_0/I)$ — and calculated values of E. In the third and fourth columns, the results of numerical solution of the problem of solute diffusion when free convection, respectively, is not — Eqs. (13)-(19) — and is taken into account are given. In the fifth column, E is calculated on the basis of the solution in Eq. (22), with ρ_1^* chosen in the form

$$\rho_1^*=\rho_0-(\rho_0-\rho_s)\frac{\Pi}{1+\Pi},$$

since it is assumed that the density of the solution depends linearly on the concentration [12] and that $c_1(L)/c_s \approx \Pi/(1+\Pi)$. It is evident from Table 1 that taking free convection into account significantly improves the agreement between calculation and experiment. At the same time, comparison with [4] shows that the approximate expressions in Eq. (14) or even (15) of [4], obtained from the solution of the problem in Eqs. (13)-(19) when $\psi = 0$, $\varphi = 1$, may be used for initial estimates at $t<\left[\frac{\mu D h}{g(\rho_0-\rho_1^*)}\right]^{1/2}\frac{1}{2\Pi^2\pi D}$.

NOTATION

x, coordinate; L, membrane thickness; x_S, coordinate of solution front; Π, porosity; c_S, mass concentration of material in saturated solution; ρ_S, density of solid material; ρ_S, density of saturated solution; $\bar{c}_i=\frac{c_i-c_\infty}{c_s-c_\infty}$ $(i=1,\ 2)$; $\bar{x}=\frac{x}{L}$; $\tau=\frac{Dt}{L^2}$; ρ_0, density of solvent; ρ_1, density of solution at $\bar{x}$ = 1; h, membrane height; g, acceleration due to gravity; μ, dynamic viscosity of the solvent; M, molecular weight of the solute; $\operatorname{erf} z=\frac{2}{\sqrt{\pi}}\int_0^z \exp(-z_1^2)\,dz_1$, erfc z = 1—erf z.

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MOVING DYNAMIC THERMOCOUPLE

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It is shown theoretically that the temperature measured by a dynamic thermocouple corresponds to the mean mass temperature of the junction. A method of a moving dynamic thermocouple is proposed.

Among contact methods of the diagnostics of thermal plasma, the dynamic thermocouple occupies a special place, since it allows local values of the plasma temperature, heat flux, and heat-transfer coefficient in the thermocouple to be obtained from the result of a single measurement. In the measurements, the change in heating temperature of the thermocouple junction in a regular cycle is measured as a function of the time. However, it remains unclear what temperature of the thermocouple is meant here, since a temperature difference is established over the radius of the thermocouple in regular conditions.

To simplify the solution of the given problem, consider that a cylindrical thermocouple is used, i.e., a butt-welded thermocouple. For the calculations it is assumed that the temperature is zero on the thermocouple axis and changes linearly over the radius

$$T_p(r) = k_1 r_p. \tag{1}$$

Then the emf (E) on a rectilinear section of the curve $E = f(T)$ will be of analogous form

$$E_p(r) = k k_1 r_p. \tag{2}$$

Since calculation shows that in a plasma jet with $T \approx 4000$°K and $v \approx 100$ m/sec, for a junction with $r_{pc} \approx 0.5 \cdot 10^{-3}$ m, the temperature drop over the radius is no more than 200°K, while the temperature coefficient of resistivity $\alpha_0 = 2.6 \cdot 10^{-4}$ deg^{-1} is small, the change in resistivity over the thermocouple radius may be neglected. Then, dividing the cross section of the thermocouple junction into concentric rings of equal area, they may be regarded as independent sources of emf, with equal internal resistance, connected in parallel. In this case the effective emf may be expressed as

$$E_e = \frac{1}{n} \sum_{i=0}^{n-1} E_i. \tag{3}$$

In view of Eq. (2), Eq. (3) may be rewritten in the form

$$E_e = \frac{k_1 k_2}{n} \sum_{i=0}^{n-1} r_{pi}. \tag{4}$$

The value of r_{pi} may be obtained from the condition that the concentric rings into which the thermocouple cross section is divided are of equal area

$$r_{pi} = r_{pc} \sqrt{\frac{n-1}{n}}. \tag{5}$$

Finally,

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