MASS-TRANSFER PARAMETERS OF CAPILLARY-POROUS BODY IN REGIONS OF ADSORPTION, CAPILLARY, AND OSMOTIC MOISTURE

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A thermodynamic method is proposed for the calculation of the specific isothermal mass capacity and thermal-gradient coefficient of a colloidal capillary-porous body in a hygroscopic region, taking into account adsorption, capillary, and osmotic moisture.

By determining the mass-transfer parameters c_m and δ_p of a capillary-porous body as a function of the moisture content (for T = const), the form of binding of the moisture with the material can be analyzed and the material can be classified according to its colloidal-physical properties.

The dependence $c_m(u)_T$ and $\delta_p(u)_T$ can be determined from sorption and desorption isotherms, but this involves graphical differentiation of the curves of $u(\mu)_T$ and $\mu(T)_u$, which is laborious and insufficiently accurate.

TABLE 1. Specific Isothermal Mass Capacity and Thermal-Gradient Coefficients for Wood and Cellular Concrete According to the BET Equation in the Adsorption-Moisture Region

Material	T, °K	u, kg/kg	$c_m \cdot 10^6$, moles/J	$\delta_p \cdot 10^3$, 1/°K
Wood	253	0,05	10,2	0,216
		0,06	11,4	0,234
		0,08	20,9	0,23
		0,1	38	0,22
	273	0,038	8,8	0,216
		0,05	11,6	0,246
		0,06	14,9	0,25
		0,07	20	0,262
		0,08	26	0,23
	293	0,03	6,25	0,181
		0,053	14,1	0,278
		0,063	19	0,282
		0,08	31,4	0,362
	333	0,02	5,77	0,179
		0,05	16,4	0,294
		0,06	24,8	0,358
		0,08	38,9	0,506
Cellular concrete	253	0,021	3,03	0,091
		0,025	5,65	0,12
		0,027	6,9	0,118
		0,03	9,55	0,115
		0,032	11,3	
	273	0,018	3,44	0,114
		0,021	5,06	0,132
		0,025	8,1	0,140
		0,027	9,7	0,152
	293	0,015	3,34	0,136
		0,018	4,87	0,150
		0,021	6,45	0,153
		0,025	9,7	0,157
	313	0,015	4,18	0,153
		0,018	5,1	0,159
		0,021	7,9	0,168

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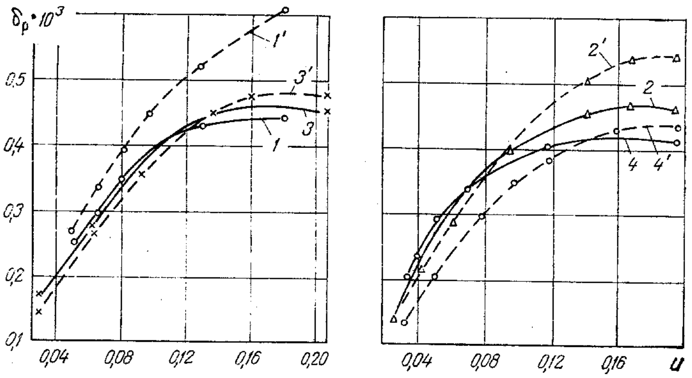

Fig. 1. Dependence of thermal-gradient coefficient δ_p, $(°K)^{-1}$, on the specific moisture content u, kg/kg, of wood at various temperatures, °K: 1, 1') T = 253.16; 2, 2') 273.16; 3, 3') 293.16; 4, 4') 313.16.

In [4], analytical expressions for the coefficients c_m and δ_p were obtained in the form of functional dependences on the specific moisture content and temperature:

$$c_m = \frac{B_0 T^{n_1-1}}{R} u^2, \tag{1}$$

$$\delta_p = -\frac{1-n_1}{T} u + \frac{1-n_1-n_2}{u_{c0} T^{n_2+1}} u^2 = \alpha u - \beta u^2, \tag{2}$$

where

$$\alpha = \frac{n_1-1}{T}, \quad \beta = \frac{n_1+n_2-1}{u_{c0} T^{n_2+1}}. \tag{3}$$

The starting point for the derivation of Eqs. (1)-(3) is Posnov's empirical formula [3]

$$\frac{1}{u} = \frac{1}{u_c} + B \ln \varphi, \tag{4}$$

corresponding to a smooth isotherm $u(\varphi)_T$, characteristic for a colloidal capillary-porous body in the presence of polymolecular-adsorption, capillary, and osmotic moisture. Graphical dependences of δ_p on u, constructed in accordance with Eq. (2) and on the basis of experimental adsorption isotherms of wood and cellular concrete [2], are shown in Figs. 1 and 2.

In Figs. 1 and 2, the curves of $\delta_p(u)_T$ obtained by graphical treatment of experimental desorption isotherms are shown as continuous lines, while those calculated from Eq. (2) are shown as dashed lines.

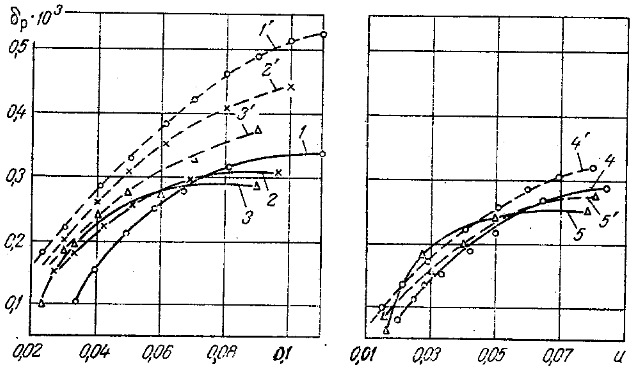

Fig. 2. Dependence of thermal-gradient coefficient δ_p, $(°K)^{-1}$, on the specific moisture content, u, kg/kg, of cellular concrete at various temperatures, °K: 1, 1') T = 233.16; 2, 2') 253.16; 3, 3') 273.16; 4, 4') 293.16; 5, 5') 313.16.

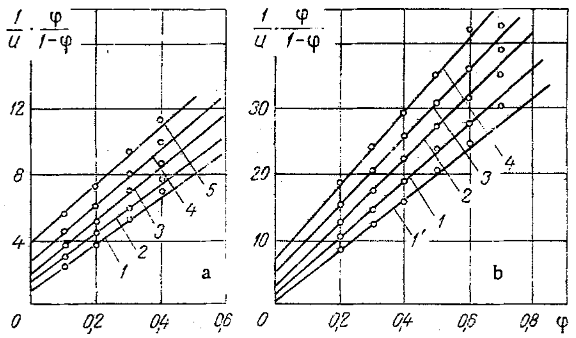

Fig. 3

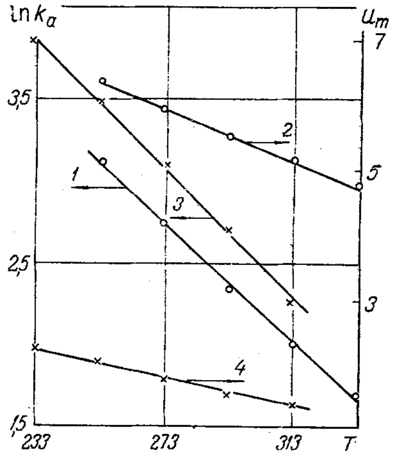

Fig. 4

Fig. 3. Dependence of $(1/u)[\varphi/(1-\varphi)]$ on φ for wood (a) and cellular concrete (b) at different temperatures, °K: 1') 233.16; 1) 253.16; 2) 273.16; 3) 293.16; 4) 313.16; 5) 333.16.

Fig. 4. Dependence of $\ln k_a$ and u_m, kg/kg, on T, °K, for wood (1, 2) and cellular concrete (3, 4).

As already noted in [4], there are several discrepancies between $\delta_{p\,calc}$ and $\delta_{p\,graph}$, most notably in the region of high moisture content corresponding to φ close to 1 and in the temperature range T ~ 233-237°K. This indicates that the different forms of binding of moisture have a considerable effect on the coefficients c_m and δ_p, and this effect cannot be completely taken into account by the single empirical relation in Eq. (4), which is valid only in the limited region $0.1 < \varphi < 1$.

Therefore, it is of interest to determine analytical dependences $c_m(u, T)$ and $\delta_p(u, T)$ by differentiation, taking into account the forms of binding of the moisture with the material.

In the region of adsorption moisture, the isotherm of polymolecular adsorption is often described by the BET equation [6]

$$\frac{1}{u} \cdot \frac{\varphi}{1-\varphi} = \frac{1}{k_a u_m} + \frac{k_a - 1}{k_a u_m} \varphi, \tag{5}$$

where $k_a = \exp[(Q_a - Q_0)/RT]$.

On the basis of Eq. (5) and the expression for the chemical potential

$$\mu = RT \ln \varphi, \tag{6}$$

the coefficients $\delta_p(u, T)$ and $c_m(u, T)$ can be determined in the adsorption-moisture region.

After appropriate rearrangements, Eq. (5) gives

$$\frac{1}{u} = \frac{1-\varphi}{k_a u_m} \left(\frac{1}{\varphi} + k_a - 1 \right), \tag{7}$$

$$2u \frac{1}{\varphi} = 2u + k_a u_m - k_0 u + \sqrt{k_a^2 (u - u_m)^2 + 4 k_a u u_m}. \tag{8}$$

On the basis of Eqs. (6), (7), and (8), expressions can be written for the specific isothermal mass capacity c_m, the temperature coefficient $(d\mu/dT)_u$, and the thermal-gradient coefficient δ_p:

$$c_m = \left(\frac{\partial u}{\partial \mu} \right)_T = \frac{u}{RT k_a u_m} \Gamma, \tag{9}$$

$$\left(\frac{\partial \mu}{\partial T} \right)_u = -R \ln \frac{2u + k_a u_m - k_a u + \Gamma}{2u} + RT \frac{k_a u - k_a u_m + 2u_m - \Gamma}{2(k_a - 1)} \cdot \frac{dk_a}{dT} - \frac{k_a}{\Gamma} \cdot \frac{du_m}{dT}, \tag{10}$$

$$\delta_p = -\frac{u}{k_a T u_m}\,\Gamma \ln \frac{2u + k_a u_m - k_a u + \Gamma}{2u} + \frac{u}{k_a u_m}\cdot\frac{k_a u - k_a u_m + 2u_m - \Gamma}{2(k_a - 1)}\cdot\frac{dk_a}{dT} - \frac{u}{u_m}\cdot\frac{du_m}{dT}, \tag{11}$$

where

$$\Gamma = \sqrt{k_a^2 (u - u_m)^2 + 4k_a u u_m}\,.$$

Thus, Eqs. (9) and (11) are functional dependences of the specific isothermal mass capacity and the thermal-gradient coefficient on the moisture content and temperature in the region of polymolecular-adsorption moisture. As follows from Eq. (11), the dependence $\delta_p(T)_u$ is mainly determined by the temperature dependences $k_a(T)$ and $u_m(T)$.

In order to use Eqs. (9) and (11) for the materials studied in [4] (wood and cellular concrete), it is necessary to verify that the BET equation is valid for their isotherm $u(\varphi)_T$. According to the BET equation, the dependence of $(1/u)[\varphi/(1-\varphi)]$ on φ is a straight line.

From the given desorption isotherms of wood and cellular concrete, graphical dependences of $(1/u)\cdot[\varphi/(1-\varphi)]$ on φ are drawn (Fig. 3a, b). These graphs are straight lines, and hence it is obvious that the BET equation is satisfied for the investigated materials in the range $\varphi \sim 0.1$-0.4. The coefficients k_a and u_m are determined graphically at different temperatures.

As shown in Fig. 4, the temperature dependences of $\ln k_a(T)$ and $u_m(T)$ are given by

$$\ln k_a = A_0 - \alpha_0 T, \tag{12}$$

$$u_m = B_0 - \beta_0 T. \tag{13}$$

The derivatives dk_a/dT and du_m/dT appearing in Eq. (11) may be determined from Eqs. (12) and (13):

$$\frac{dk_a}{dT} = -\alpha_0 k_a, \tag{14}$$

$$\frac{du_m}{dT} = -\beta_0. \tag{15}$$

The values of α_0 and β_0 are determined graphically from Fig. 4:

$$\alpha_{0\,\mathrm{wood}} = 0.0183;\quad \alpha_{0\,\mathrm{c.conc}} = 0.0196;$$

$$\beta_{0\,\mathrm{wood}} = 0.0002;\quad \beta_{0\,\mathrm{c.conc}} = 0.00011.$$

Taking into account Eqs. (14) and (15), Eq. (11) for the thermal-gradient coefficient takes the form

$$\delta_p = -\frac{u}{k_a T u_m}\,\Gamma \ln \frac{2u + k_a u_m - k_a u + \Gamma}{2u} - \frac{u}{k_a u_m}\cdot\frac{k_a u - k_a u_m + 2u_m - \Gamma}{2(k_a - 1)}\,\alpha_0 - \frac{u}{u_m}\,\beta_0. \tag{16}$$

From Eqs. (9) and (16), values of c_m and δ_p were determined for wood and cellular concrete in the region of polymolecular-adsorption water at various temperatures. The results obtained are shown in Table 1.

As is evident from Table 1, Eqs. (9) and (16) predict that, in the region of polymolecular-adsorption moisture, the specific isothermal mass capacity and the thermal-gradient coefficient of wood and cellular concrete will increase with increase in moisture content and temperature. However, calculation according to Eq. (2) indicates principally an insignificant increase in $\delta_p(T)_u$. Hence, Posnov's equation [3], on the basis of which Eq. (2) was derived, is not entirely reliable in the region of small u, φ. However, it should be noted that the temperature variation $\delta_p(T)_u$ is small, and the use of Eq. (2) for approximate estimates of the mean value of δ_p is acceptable. Since the BET equation is not correct for $\varphi \geq 0.4$ for the investigated materials, Eq. (16) may only be used when u is small.

In the capillary-moisture region, the moisture content of the body may be determined from the formula [1] (for a nonswelling capillary-porous body)

$$u = \frac{\gamma_l}{\gamma_0}\int_{r_0}^{r_m} f_v(r)\,dr = \frac{\gamma_l}{\gamma_0}\,\overline{f_v(r)}\,\bar{r}. \tag{17}$$

The mean pore radius may be expressed by the Thompson formula

$$\bar{r} = \frac{2v_m \sigma \cos\theta}{RT \ln \frac{1}{\varphi}}. \tag{18}$$

Then Eqs. (17) and (18) give

$$u = -\frac{2M\overline{f_v(r)}\, \sigma \cos\theta}{\gamma_0 RT \ln \varphi} \tag{19}$$

or taking into account Eq. (6)

$$u = -\frac{2Mf_v(r)\, \sigma \cos\theta}{\gamma_0 \mu} \tag{20}$$

and hence

$$\mu = -\frac{2Mf_v(r)\, \sigma \cos\theta}{\gamma_0 u}. \tag{21}$$

On the basis of Eq. (21), the specific isothermal mass capacity of the body in the capillary-moisture region is determined:

$$c_m = \left(\frac{\partial u}{\partial \mu}\right)_T = \frac{\gamma_0}{2M\sigma f_v(r) \cos\theta}\, u^2 = K_{\mathrm{cap}} u^2. \tag{22}$$

According to Eq. (22), the temperature dependence of c_m is determined by the temperature dependence of the surface tension σ, which (in the first approximation) decreases linearly with increase in T:

$$\sigma = \sigma_0 - \alpha_n T. \tag{23}$$

Thus, in the capillary-moisture region, the specific isothermal mass capacity rises with increase in temperature, which agrees with Eq. (1).

Similarly, differentiating μ in Eq. (21) with respect to T with u = const, for σ as in Eq. (23), gives the temperature coefficient

$$\left(\frac{\partial \mu}{\partial T}\right)_u = \frac{2\alpha_n M f_v(r) \cos\theta}{\gamma_0 u}. \tag{24}$$

On the basis of Eqs. (22) and (24), the value of the thermal-gradient coefficient in the capillary-moisture region is written in the form

$$\delta_p = \frac{\alpha_n u}{\sigma}. \tag{25}$$

From Eq. (25), it follows that for a fixed value of the moisture content, in the capillary-moisture region, the value of δ_p should rise with increase in T.

It remains to complete the analysis by a similar consideration of the osmotic-moisture region.

The body, as it absorbs liquid, has a swelling pressure similar to the osmotic pressure of a dissolved material [5, 7]:

$$P_{\mathrm{swel}} = \frac{c_d}{M} RT + A_d c_d^2, \tag{26}$$

where c_d is the concentration of dry material in the liquid, the inverse of the moisture content of the body:

$$c_l = \frac{\gamma_d}{u}, \tag{27}$$

and A_d is a coefficient depending on the nature of the solvent.

In [1], on the basis of the usual thermodynamic equations, a relation was established between the swelling pressure and the relative vapor pressure of the given liquid in the form

$$P_{\text{swel}} = -\frac{RT}{M}\gamma_l \ln\varphi. \tag{28}$$

In the hygroscopic region, Eqs. (6) and (28) give

$$\mu = -\frac{RT}{u} - A_l\frac{RTM\gamma_d}{u^2}. \tag{29}$$

Substituting Eq. (27) into Eq. (29) and performing the appropriate differentiation gives the specific isothermal mass capacity of the body and the temperature coefficient in the osmotic-moisture region:

$$c_m = \frac{u^3}{RT\left(u - Mu\gamma_l\frac{\partial A_d}{\partial u} + 2A_dM\gamma_l\right)}, \tag{30}$$

$$\left(\frac{\partial\mu}{\partial T}\right)_u = -\frac{R}{u} - \frac{A_dRM\gamma_l}{u^2} - \frac{RTM\gamma_l}{u^2}\cdot\frac{\partial A_d}{\partial T}. \tag{31}$$

Thus, starting from Eqs. (30) and (31), the thermal-gradient coefficient in the osmotic-moisture region can be written in the form

$$\delta_p = \frac{u\left(Ru + A_dRM\gamma_l + RTM\gamma_l\frac{\partial A_d}{\partial T}\right)}{RT\left(uM\gamma_l\frac{\partial A_d}{\partial u} - 2A_dM\gamma_l - u\right)}. \tag{32}$$

From Eq. (32) it follows that for u = const the thermal-gradient coefficient decreases in absolute value with increase in temperature.

In a colloidal capillary-porous body, all of the considered forms of binding moisture are present.

The temperature dependence $\delta_p(T)_u$ in Eq. (2), obtained on the basis of Posnov's equation [3], is in the main characteristic of osmotic moisture. This is because the dependence $\delta_p(T)_u$ was determined on the basis of empirical dependences $u_c(T)$ and B(T) for the considered body, and the value of u_c corresponds to $\varphi = 1$, i.e., to the osmotic-moisture region. Therefore, once again, there are discrepancies between the curves of $\delta_p(u, T)$ obtained from Eq. (2) and those obtained by graphical treatment of isotherms.

From curves of $\delta_p(u, T)$ obtained by graphical treatment of desorption isotherms of the investigated body, it is evident that for u = const the change in δ_p with change in temperature is insignificant. This is because capillary moisture and osmotic moisture have opposite effects on the temperature dependence of the thermal-gradient coefficient, as is apparent in Eqs. (25) and (32). Therefore, when both capillary and osmotic moisture are present in the colloidal body, both increase and decrease of $\delta_p(T)_u$ in this region are possible, and a clearly expressed temperature dependence $\delta_p(T)_u$ indicates a predominance of either capillary or osmotic moisture in the body. Thus, Eqs. (30) and (32) may be used to explain the effects of different forms of binding of moisture in modifying the dependence of the mass-transfer coefficients on temperature and moisture content.

NOTATION

μ, chemical potential; R, universal gas content; T, absolute temperature; φ, relative humidity of air; u, specific moisture content; u_c, maximum hygroscopic moisture content; B_0, u_{c0}, n_1, n_2, coefficients independent of temperature; u_m, moisture content of body at total monolayer filling; Q_a, heat of adsorption of first layer; Q_0, latent heat of vaporization of liquid-phase adsorbing material; c_m, specific isothermal mass capacity; δ_p, thermal-gradient coefficient; $f_V(r)$, differential curve of radial pore distribution; r_0, r_m, $\bar{r}$, minimum, maximum, and mean pore radius; M, molecular mass of material.

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EXPERIMENTAL DETERMINATION OF PARAMETERS OF A PLASMA JET

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Experimental results from the diagnostics of argon plasma flows used for an ablation investigation of materials in the range of Mach numbers $M \leq 3.5$ and deceleration enthalpy up to 7,000 kcal/kg are presented. A schematic diagram of the equipment and the procedure of measurements are given.

Ablation investigations of different materials under the action of high-energy flows, in particular, plasma jets, have been extensively used in research practice [1, 2]. In all the cases it is very important to organize plasma flows (of a high-enthalpy gas) with uniform distributions of pressure and temperature (enthalpy) over the cross section of the flow in the zone of its action on the sample, and to determine the region of the flow for placing the sample. This information can so far be obtained only from experiment.

In the present work we give the results of such measurements obtained during the study of the behavior of samples in high-enthalpy supersonic flows.

In [3, 5] results of thermal and electrical measurements are presented; these measurements were carried out on plasmotrons with a segmented channel operating with argon and intended for creating high-energy flows.

The overall scheme of the gasdynamic bench is shown in Fig. 1. After heating in the plasmotron channel and passing through the damping chamber the operating gas flow enters the nozzle device (8) and flows out of the nozzle in the form of a supersonic plasma jet (10) into the operating vacuum chamber (1). The required pressure in the operating chamber is maintained with the use of a VN-300 vacuum pump (3).

The damping chamber with 50 mm diameter and 70 mm height is placed immediately after the discharge channel of the plasmotron; its diameter is 20 mm and it is water-cooled just as the section of the plasmotron channel. The use of the damping chamber makes it possible to ensure mixing of the flow at the entrance into the nozzle and to obtain a plasma flow with sufficiently uniform distribution of the parameters along its section in the operating vacuum chamber behind the nozzle. The diameter of the critical section of the operating

TABLE 1. Operating Regimes of the Plasmotron

Regime number	I, A	N, kW	η, %	p_0', torr	G, g/sec	q_0, kcal/m·sec	$\bar{I}_0$, kcal/kg	i_0, kcal/kg
1	170	8	41	32	0,8	630	1000	2100
2	300	16	35	23	0,8	1400	1700	3000
3	400	24	34	23	0,85	2000	2300	3900
4	500	33	32	24	0,85	2800	3000	4900
5	600	43	32	28	0;9	3300	4000	5900
6	700	54	32	29	0,9	4000	4300	7100

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