THERMODYNAMICS OF THE HYGROSCOPIC STATE OF DISPERSE MATERIALS

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Expressions of the analytical dependences of the specific isothermal mass capacity and thermal gradient coefficient on moisture content and temperature for disperse materials in a hygroscopic state are found on the basis of the expression of the chemical potential and B. A. Posnov's formula.

The main properties of capillary-porous colloidal materials are determined by the content and forms of bonds between moisture and material [1-3, 9]. The classification of the forms of bonds between moisture and material, according to P. A. Rebinder's scheme [3], is constructed on the basis of the magnitude of the bond energy – free energy of dehydration. In connection with this, four forms of the bond between water and disperse systems are recognized:

1. Chemically bound water.
2. Adsorption-bound water, represented mainly by a monomolecular layer on the inner and outer surfaces of the disperse material.
3. Capillary-bound water enclosed in capillaries and bounded by free meniscuses.
4. Osmotically bound water. The bond energy of osmotic moisture is characterized by the entropy of the system, and therefore such water is considered entropy-bound.

In the region of the hygroscopic state of disperse bodies the moisture is bound with the material by adsorption, capillary, and diffusion-osmotic forces.

TABLE 1. Values of the Coefficients $|B|$, u_S, and n_1, n_2 at Different Temperatures for Disperse Materials

Type of material	$\|B\|$	u_S	T, °K	n_1	n_2
Wood (γ_0 = 300 kg/m^3)	3,33	0,25	253,16	2,5	—0,58
	4	0,238	273,16		
	4,67	0,228	293,16		
	5,62	0,222	313,16		
	6,65	0,213	333,16		
Heat-insulating aerated concrete (γ_0 = 300 kg/m^3)	16,7	0,108	233,16	3	—1,125
	21,4	0,098	253,16		
	26,5	0,09	273,16		
	33,3	0,0834	293,16		
	40,5	0,0768	313,16		
Clay	18,8	0,154	308,16	3,09	—2,58
	22,2	0,133	328,16		
	26,4	0,115	350,16		
	30,9	0,1	363,16		
Clay (mixture of 80% Chasov-Yar clay and 20% fireclay)	23,6	0,125	293,16	1,95	—2,25
	27,5	0,098	328,16		
	30,9	0,085	348,16		
	36,3	0,077	363,16		
Gelatin	6,35	1,25	298,16		

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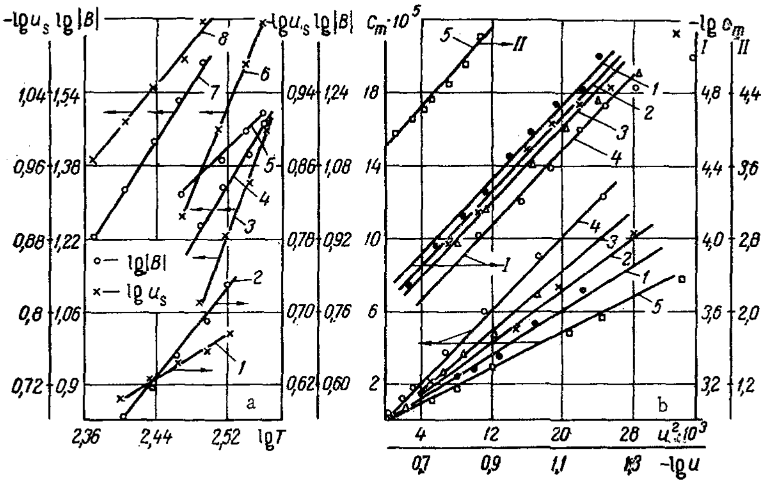

Fig. 1. Functional dependences: a) log |B| and log u_s vs log T for wood (1, 2), clay (3, 4), mixture of 80% Chasov-Yar clay and 20% fireclay (5, 6), and aerated concrete (7, 8); b) c_m (mole /J) vs u^2 and log c_m vs u for wood (1-4) and gelatin (5) at different temperatures; 1) T = 253.16°K; 2) 273.16; 3) 293.16; 4) 333.16; 5) 298.16.

As the moisture transport potential in the hygroscopic region we will use in the first approximation the chemical potential μ, which is a function of the moisture content and temperature of the material and is expressed in the form [4, 5]

$$\mu = RT \ln \varphi, \tag{1}$$

where $\varphi = P/P_s$.

To study the problem of binding of water with disperse media it is very important to investigate the equilibrium state of the capillary-porous materials with the ambient moist air. On the basis of the curves obtained for the relation between the relative humidity φ and the specific moisture content u of the material at a constant temperature (isotherm of sorption and desorption) we determine the thermodynamic parameters of the material – the specific isothermal mass capacity c_m and the thermal gradient coefficient δ_p, which are represented in the form of the relations [1, 2]:

$$c_m = \left(\frac{\partial u}{\partial \mu}\right)_T, \tag{2}$$

$$\delta_p = c_m \left(\frac{\partial \mu}{\partial T}\right)_u. \tag{3}$$

As shown in [1, 2, 4, 7-9], different forms of the bond between moisture and material can be determined from the curves $c_m = f(u)_T$ and $\delta_p = f(u)_T$.

For the majority of materials the thermal gradient coefficient changes depending on the moisture content according to a certain curve having a maximum [2, 4, 7, 8]. This maximum for capillary-porous colloidal materials corresponds mainly to the transition limit of adsorption-bound moisture to capillary [2]. A decrease of the thermal gradient coefficient with increase of the specific moisture content of the material can be explained by the presence of entrapped air in the pores of the material, expansion of which causes the liquid to move in the direction of the heat flux. In the case of complete saturation with liquid (all capillaries of the material are filled) the thermal gradient coefficient is equal to zero (the entrapped air is completely displaced by the liquid). For colloidal materials the quantity of adsorption-bound moisture gradually decreases with an increase of the specific moisture content in comparison with osmotically bound moisture. Accordingly, the thermal gradient coefficient also decreases, and at some specific moisture content becomes equal to zero. Thereafter the quantity of the liquid being absorbed is bound only by osmotic forces.

The specific moisture content corresponding to the zero value of the thermal gradient coefficient is the approximate limit of adsorption- and osmotically-bound moisture in the material [2]. The curves

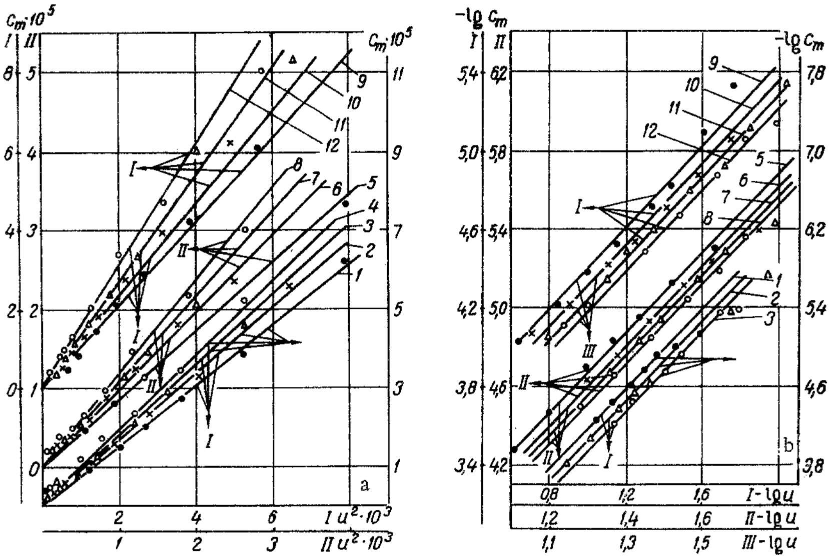

Fig. 2. Functional relations: a) specific mass capacity c_m (mole /J) vs square of the specific moisture content u^2; b) $\log c_m$ vs log u for clay (1-4), mixture of 80% Chasov-Yar clay and 20% fireclay (5-8), and aerated concrete (9-12) at different temperatures: 1) T = 308.16°K; 2) 328.16; 3) 350.16; 4) 363.16; 5) 293.16; 6) 328.16; 7) 348.16; 8) 363.16; 9) 253.16; 10) 273.16; 11) 293.16; 12) 313.16.

$\delta_p = f(u)_T$ can serve, consequently, as the initial data for determining different forms of the bond between moisture and material.

From this viewpoint it is of interest to obtain the analytical expression of the coefficients c_m and δ_p in the form of a functional dependence on the specific moisture content and temperature. For this purpose the initial relation is the empirical relation obtained by B. A. Posnov [6] on the basis of various experimental data, which expresses the relation between the equilibrium specific moisture content of wood and the relative humidity:

$$\frac{1}{u} = \frac{1}{u_s} + B \ln \varphi. \tag{4}$$

Equation (4) is valid in the hygroscopic region in the interval $0.1 < \varphi < 1$.

Experimental data of the values of the equilibrium specific moisture content as a function of φ for different materials are given in [4]. On the basis of these data we determined by means of (4) the coefficient B and the maximum sorption moisture content u_s (Table 1) at different temperatures for some disperse materials (wood with γ_0 = 300 kg/m^3, heat-insulating aerated concrete with γ_0 = 300 kg/m^3, gelatin, clay, and a mixture of 80% Chasov-Yar clay and 20% fireclay). According to a preliminary check, Posnov's formula (4) proved to be valid for the selected materials.

Using the values of B and u_s obtained for different temperatures, we plotted $\log |B|$ and $\log u_s$ against $\log T$ (Fig. 1a).

On the basis of these graphs we can represent the temperature dependence of the values of $|B|$ and u_s in the form of relations

$$\lg|B| = \lg B_0 + n_1 \lg T, \quad \text{or} \quad |B| = B_0 T^{n_1}, \tag{5}$$

$$\lg u_s = \lg u_{s0} + n_2 \lg T, \quad \text{or} \quad u_s = u_{s0} T^{n_2}, \tag{6}$$

where B_0, u_{s0}, n_1, n_2 are coefficients independent of temperature. We see from relations (5) and (6) that the coefficients B_0, u_{s0}, n_1, n_2 are easily determined from the appropriate graphs (Fig. 1a).

The value of $\ln \varphi$ from Eq. (4) after substituting into Eq. (1) takes the form

$$\mu = \frac{RT}{B}\left(\frac{1}{u} - \frac{1}{u_s}\right). \tag{7}$$

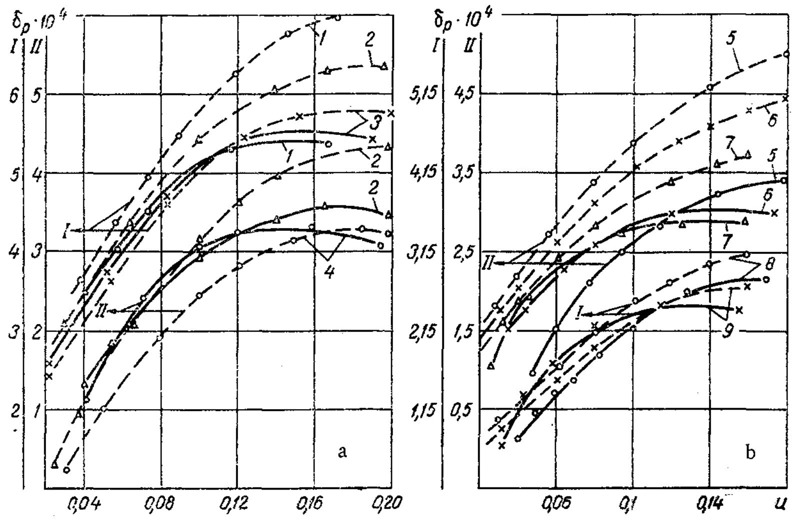

Fig. 3. Functional relations: a) thermal gradient coefficient δ_p (1/°K) vs specific moisture content u (kg/kg) for wood (1-4); b) for aerated concrete (5-9) at temperatures: 1, 6) T = 253.16; 2, 7) 273.16; 3, 8) 293.16; 4, 9) 313.16; 5) 233.16. Solid lines: δ_p experimental; dashed lines: calculated.

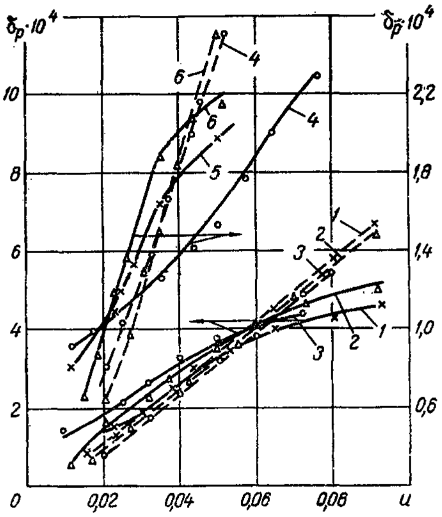

Fig. 4. Thermal gradient coefficient δ_p (1/°K) vs specific moisture content u (kg/kg) for clay (1-3) and mixture of 80% Chasov-Yar clay and 20% fire-clay (4-6) at temperatures: 1, 5) T = 328.16°K; 2) 350.16; 3, 6) 363.16; 4) 293.16. Solid lines: δ_p experimental; dashed lines: calculated.

After appropriate differentiation of (7) the value of the specific isothermal mass capacity will be

$$c_m = \frac{|B|}{RT}u^2. \tag{8}$$

After logarithmic operation Eq. (8) takes the form

$$\lg c_m = \lg\frac{|B|}{RT} + 2\lg u. \tag{9}$$

By substituting (5) into (9) the value of c_m is expressed as a functional dependence on the specific moisture content and temperature:

$$c_m = \frac{B_0 T^{n_1-1}}{R}u^2. \tag{10}$$

Equations (9) and (10) were checked by experimental data [4].

The graphic dependences $c_m = f(u^2)_T$ and $\log c_m = f(\log u)_T$ (Fig. 1b and Fig. 2) at different temperatures for the selected materials are plotted as straight lines according to Eqs. (10) and (9). The corresponding values of c_m and $\log c_m$ from experimental data [4] are plotted as circles on these same graphs. Thus, Fig. 1b and Fig. 2 show mainly the sufficiently close agreement of the experimental values of c_m and those calculated by Eqs. (10) and (9). The maximum divergence is obtained in the region of φ close to 1 and φ close to 0.1.

The value of the temperature coefficient $(\partial\mu/\partial T)_u$ is obtained by appropriate differentiation of Eq. (7) after substituting (5) and (6) into it:

$$\left(\frac{\partial\mu}{\partial T}\right)_u = -\frac{R(1-n_1)}{B_0 u T^{n_1}} + \frac{R(1-n_1-n_2)}{B_0 u_{s0} T^{n_1+n_2}}. \tag{11}$$

On the basis of Eqs. (3), (10), and (11) the thermal gradient coefficient δ_p has the form

$$\delta_p = -\frac{1-n_1}{T}u + \frac{1-n_1-n_2}{\mu_{s0}\,T^{n_2+1}}u^2 = \alpha u - \beta u^2, \tag{12}$$

where

$$\alpha = \frac{n_1 - 1}{T}; \ \beta = \frac{n_1 + n_2 - 1}{\mu_{s0}\, T^{n_2+1}} = \frac{n_1 + n_2 - 1}{u_s T}.$$

Equation (12) represents an equation of a parabola, for which

$$u_{\max} = \alpha/2\beta. \tag{13}$$

The graphic dependences of δ_p on u at different temperatures for the selected materials, plotted according to Eq. (12) and the experimental data [4], are presented in Figs. 3 and 4. The calculated and experimental curves are analogous with respect to the character of the dependence $\delta_p(u)$. The maximum divergence is observed in the region of moisture contents corresponding to φ close to 1 owing to inaccuracy of initial Eq. (4). The positions of the maxima on the calculated and experimental curves coincide for the most part.

Thus, Eqs. (10) and (12) permit determining dependences $c_m(u, T)$ and $\delta_p(u, T)$ and analyzing the forms of the bond between moisture and material for disperse bodies in the hygroscopic region.

It is known [2] that the thermodynamic analogy between swelling and dissolution permits regarding the process of wetting of a colloidal body as a process of formation of a solid solution. In this case the quantity inverse to the moisture content of the material $\omega = 1/u$, which represents the content of dry matter in the liquid, is important. The specific isothermal mass content here will be expressed so:

$$c_m = \left(\frac{\partial u}{\partial \mu}\right)_T = -\left(\frac{\partial \omega}{\partial \mu}\right)_T u^2. \tag{14}$$

The quantity $(\partial\omega/\partial\mu) = c'_m$ represents the specific isothermal mass content of moisture with respect to dry matter. On the basis of Eqs. (8) and (14) the value

$$c'_m = -\frac{B}{RT}. \tag{15}$$

Equation (15) shows that c'_m depends on the temperature and is independent of the moisture content. Thus, a moist colloidal body can be regarded as a solid solution.

NOTATION

μ	is the chemical potential;
R	is the universal gas constant;
T	is the absolute temperature;
φ	is the relative humidity;
P	is the partial pressure of water vapor in air;
P_s	is the saturated vapor pressure;
u	is the specific moisture content;
u_s	is the maximum hygroscopic moisture content;
c_m	is the specific isothermal mass capacity;
δ_p	is the thermal gradient coefficient;
γ_0	is the density of dry matter;
c'_m	is the specific isothermal mass capacity of moisture with respect to dry matter.

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