CONDITIONS OF SORPTION EQUILIBRIUM AND THEIR ANALYSIS

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On the basis of the conditions of minimum Gibbs energy, relations are obtained for capillary-porous and colloidal capillary-porous bodies describing sorption equilibrium. An analysis of these relationships is given.

The intensity of drying and moistening processes depends on the deviation in moisture content of a material from its equilibrium value; this also determines the importance of studying the mechanism of sorption equilibrium of hygroscopic materials.

To find the conditions of equilibrium, the thermodynamic approach was used in the present work. Therefore, though the sorption of water vapor will be chiefly discussed, the obtained results can be extended without loss of generality to other sorbed substances. The examined sorbents will be capillary-porous and colloidal capillary-porous bodies.

The equation describing adsorption equilibrium with a view to capillary and wedging pressures is contained in [1]. Other factors affecting the state of equilibrium will be discussed below.

In the region of medium and high air humidity φ, which is of practical importance, the moisture sorbed by the material may be viewed as a continuous liquid phase. This makes it possible to find the equilibrium conditions with the aid of the well-known principle of the minimum isobaric–isothermal potential (Gibbs energy) Φ.

The complex mechanism of moisture absorption in the general case includes processes of adsorption, absorption, capillary condensation, and it is accompanied by a change in the dimensions of the bodies (swelling). The state of a sorbed liquid differs from the state of a bulk liquid on account of the effects accompanying these processes. Therefore the Gibbs energy of the system can be determined as the sum of the isobaric–isothermal potentials of the vapor $N_2(f_2 + p_2 v_2^*)$, of the bulk liquid $N_1(f_1 + pv_1)$, and of additional components determined by the respective effects.

Part of them manifest themselves because of the finite thickness of the liquid layer adsorbed on the surface of a solid (including the surface of the pores). The interphase liquid–vapor and liquid–solid interfaces contribute in the form of free energies of the interfaces $\sigma_{12}s_{12}$ and $\sigma_{13}s_{13}$, respectively. Here the specific surface energies σ_{12} and σ_{13} are referred to a liquid layer of infinite thickness, and the finite thickness of the layer is taken into account by the term $f_0 s_{13}$ representing the residue of free energy of the layer due to the interaction of the molecules of the liquid with each other and with the molecules of the solid. When the thickness of the layer increases, f_0 tends toward zero.

The absorption processes characterize such bodies whose structural elements are situated sufficiently freely so that the molecules of the sorbed substance can diffuse within the material or into its surface layers. Such processes are most characteristic of a number of polymer materials and are accompanied by a change in volume, the swelling of polymers.

The process of limited swelling of polymers may also be viewed as a process of dissolution, of mixing a high-molecular substance with a low-molecular one, or as a process of osmotic absorption of a low-molecular substance in which the polymer plays the part of a semipermeable baffle and osmotic cell [2]. On the question of which substance plays the part of solvent, there exist contradictory views: the low molecular substance [3] as well as the polymer [2] are considered the solvent. Viewing the former opinion as correct, we concretize it; we will view absorption as a process of mixing n active sites of the solid with N_1 molecules of the sorbent. In such a process, the free Gibbs energy can be found as [4]

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$$\Delta\Phi = nkT \ln \frac{n}{eN_1} + n\psi(p,\ T) + \frac{n^2}{2N_1}\beta(p,T).$$

Penetration of the low-molecular substance between the elements of the structure of macromolecules of the polymer causes its swelling and gives rise to mechanical stresses in it.

Assuming that swelling is accompanied by three-dimensional expansion of the solid, we can represent the work of deformation, and consequently also the increase in free energy, as an increase in excess pressure due to the swelling multiplied by the increase in volume of the solid. This excess pressure in fact represents the swelling pressure, and on the assumption that the liquid and solid phases are incompressible, the increase in volume of the solid coincides with V_1 because $\Delta\Phi = p_{sw}V_1$.

If we sum the above components of Gibbs energy, we obtain the expression

$$\Phi = N_1(f_1 + pv_1) + N_2(f_2 + pv_2^*) + \sigma_{12}s_{12} + \sigma_{13}s_{13} + f_0 s_{13} + nkT\ln\frac{n}{eN_1} + n\psi(p,T) + \frac{n^2}{2N_1}\beta(p,\ T) + p_{sw}V_1. \tag{1}$$

After simple transformations we obtain from the condition of minimum $\partial\Phi/\partial v_1 = 0$ the pressure p_1 in the liquid phase:

$$p_1 = p + \sigma_{12}\frac{\partial s_{12}}{\partial V_1} + s_{13}\frac{\partial f_0}{\partial V_1} + p_{sw}. \tag{2}$$

Here it is taken that $p_1 = -\partial f_1/\partial V_1$ and $V_1 = v_1N_1$.

The derivative $\partial s_{12}/\partial V_1$ in expression (2) is equal to the curvature of the surface of the liquid [5] so that the second term in (2) represents the capillary Laplace pressure p_c whose sign is determined by the sign of the curvature K:

$$p_c = \sigma_{12}\frac{\partial s_{12}}{\partial V_1} = \sigma_{12}K = \sigma_{12}\left(\frac{1}{r_a} + \frac{1}{r_b}\right). \tag{3}$$

The third term in (2) is the wedging pressure [6]

$$p_w = -s_{13}\frac{\partial f_0}{\partial V_1}. \tag{4}$$

For a plane layer with thickness h, expression (4) assumes the form $p_w = \partial f_0/\partial h$, which was used by B. V. Deryagin for determining the wedging pressure [7]. Thus, the pressure in the liquid phase is determined by the barometric pressure p, capillary pressure p_c, wedging pressure p_w, and swelling pressure p_{sw}:

$$p_1 = p + p_c - p_w + p_{sw} \tag{5}$$

The partial pressure of water vapor in the air can be easily calculated on the basis of Dalton's law if we view humid air as an ideal gas:

$$p_2v_2 = p_2v_2^*. \tag{6}$$

We obtain the main condition of sorption equilibrium from the condition of minimum Gibbs energy $\partial\Phi/\partial N_1 = 0$ which after simple transformations assumes the form

$$f_2 + p_2v_2 = \left\{f_1 + v_1\left(p + \sigma_{12}\frac{\partial s_{12}}{\partial V_1} + s_{13}\frac{\partial f_0}{\partial V_1} + p_{sw}\right)\right\} - \frac{nkT}{N_1} - \frac{n^2}{2N_1^2}\beta(p,\ T). \tag{7}$$

Here Eq. (6) was taken into account and also the fact that $dN_2 = -dN_1$ and $V_1 = v_1N_1$. The left-hand part of (7) represents the chemical potential of the vapor μ_2 taken with p_2, and the expression in the braces represents the chemical potential of the liquid μ_1 which is under pressure p_1, determined by the relationships (2) and (5). Thus, the condition of equilibrium (7) is transformed to the form

$$\mu_2(p_2) = \mu_1(p_1) - \frac{nkT}{N_1} - \frac{n^2}{2N_1^2}\beta(p,\ T). \tag{8}$$

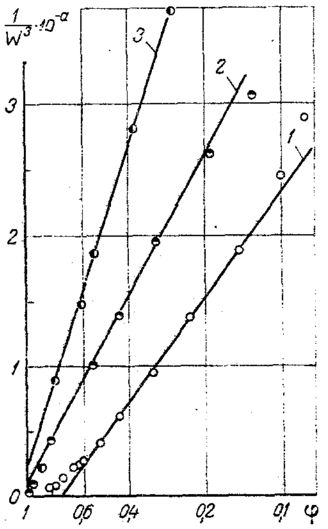

Fig. 1

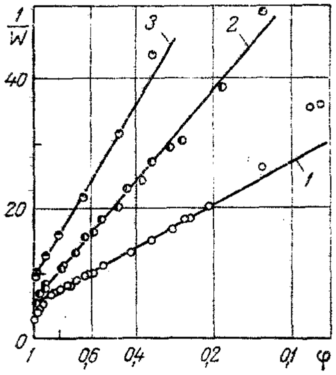

Fig. 2

Fig. 1. Adsorption isotherms of nitrogen vapors on different adsorbents: 1) $a = 2$, alumosilica gel with large pores [12]; 2) $a = 5$, montmorillonite [13]; 3) $a = 5$, iron catalyst [10].

Fig. 2. Isotherms of sorption of water vapor by textile fibers [11]: 1) silk; 2) cotton; 3) nylon.

Viewing vapor as an ideal gas, we can represent $\mu_2(p_2)$ in the form

$$\mu_2(p_2) = \mu'' + kT \ln \frac{p_2}{p_s} = \mu'' + kT \ln \varphi. \tag{9}$$

If we expand the chemical potential of the liquid $\mu_1(p_1)$ into a series in the vicinity of the point $p = p_s$ and take into account that $v = \partial\mu/\partial p$, we obtain

$$\mu_1(p_1) = \mu' + v_1(p - p_s) + v_1(p_c - p_w + p_{sw}). \tag{10}$$

If we solve Eqs. (8)-(10) jointly, we obtain the condition of sorption equilibrium

$$RT \ln \varphi = (p - p_s)/\rho_1 + (p_c - p_w + p_{sw})/\rho_1 - \frac{RTn_0 m}{W} - \frac{N_0 n_0^2 m^2}{2W^2}\,\beta(p,\ T). \tag{11}$$

Equations (7), (8), and (11) do not change if we view absorption not as a process of mixing but as osmotic absorption. In this case the last two terms multiplied by ρ_1 determine the osmotic pressure. In accordance with Eqs. (7) and (8), the osmotic pressure is determined by the difference of the chemical potentials, which agrees with the tenets of [2].

If the dependence of the wedging and capillary pressures, and also of the swelling pressure on the moisture content of the body is known, the condition of equilibrium (11) yields the equation of the sorption isotherm.

In capillary-porous solids of homogeneous chemical composition, where sorption is effected by the entire surface of the body, dissolution of the active sites apparently does not take place, and we may put $n_0 = 0$ in (11). Swelling is also small, the swelling pressure may be neglected, and Eq. (11) is therefore simplified:

$$RT \ln \varphi = (p - p_s)/\rho_1 + (\sigma K - p_w)/\rho_1. \tag{12}$$

For values of φ that are not very close to unity, $(1-\varphi) \gg (p-p_s)/(RT\rho_1)$; for humid air at room temperature this corresponds to $(1 - \varphi) \gg 10^{-3}$, the first term on the right-hand side of (12) may be neglected, and it is transformed to the known [1] condition of equilibrium

$$RT \ln \varphi = (\sigma K - p_w)/\rho_1. \tag{13}$$

TABLE 1. Values of Specific Surface Calculated by Adsorption of Vapors of Nitrogen N_2

System	s_{sp}, m^2/g	
	by (17)	by BET
N_2—alumosilica gel	312	240
N_2—montmorillonite	24	28
N_2—iron catalyst	38	—

It follows from (13) that specifying relative humidity of vapors determines unambiguously only the sum of the wedging and capillary pressures but not the separate terms of this sum. And since in general the dependences of p_c and p_w on the moisture content are different, a change of the individual components, with their sum remaining constant, also leads to a change in moisture content. Thus, the correlation between relative humidity of the vapors and the moisture content of the material will not be single-valued any more. This thermodynamic explanation of capillary hysteresis complements the motions explained in [8].

If the curvature of the surface of the solid and the thickness of the liquid layer on it are small, so that the liquid film may be considered plane, then the wedging pressure due to the van der Waals interaction is calculated by the thickness of the film [9]

$$p_w = A/h^3, \tag{14}$$

and its correlation with the moisture content is expressed by the formula

$$p_w = A(s_{sp}\rho_1)^3/W^3. \tag{15}$$

When the curvature of the surface of the solid is small, the following regularities may be expected to manifest themselves: if the layer of adsorbed liquid is sufficiently thin, then during the process of adsorption the curvature of the surface of the layer copies the curvature of the surface of the solid so that in some interval of change in φ the capillary pressure will not change. In this case, in accordance with (13) and (15), the equation of the adsorption isotherm has the form

$$\rho_1 RT \ln\varphi = \sigma K - A(s_{sp}\rho_1)^3/W^3 \tag{16}$$

and in coordinates $1/W^3 = f(-\log\varphi)$ it has to be represented by a straight line. As an example, Fig. 1 shows three adsorption isotherms of nitrogen vapors; each of the isotherms has a straight section. From the tangent of the angle of slope of the straight line in these coordinates, the specific surface of the solid can be determined. A comparison of the values of s_{sp}, calculated that way for $A = 10^{-21}$ J and found by the BET method, is given in Table 1. The satisfactory agreement of the values of s_{sp} for the first two systems confirms the correctness of using (16) for describing the adsorption isotherms under the above conditions. For the nitrogen—iron system catalyst, the constant of the BET equation [10], expressed by an exponential curve, assumes a negative value; this has no physical meaning and does not make it possible to find s_{sp}.

When the curvature of the surface of the solid is large, which is most characteristic of bodies with small pores, than the probability of the appearance of a rectilinear section in the adsorption isotherm is much smaller because in this case, the wedging and capillary pressures change simultaneously.

We will examine adsorption equilibrium for $\varphi = 1$ and when the system does not contain any nonadsorbed gases. Then in (12) $p = p_s$, and the condition of equilibrium assumes the form

$$\sigma K - p_w = 0. \tag{17}$$

Equation (17) may be fulfilled at different states of the system. If the state $\varphi = 1$ is attained as a result of the adsorption of liquid by the body that was originally in the dry state, then the amount of sorbed liquid is the minimally possible amount under these conditions, and it may be expected that $p_w \neq 0$. In that case, the pores of a capillary-porous body will not be completely filled.

The state of the system is different if in the vapors above the liquid there is a body previously wetted in this liquid. The moisture content of such a body will be the maximally possible amount because all pores will be filled (dehydration of the body under the effect of the force of gravity is not considered here), and the thickness of the layer of liquid is sufficiently great so that $p_w = 0$, and the surface of the liquid is practically plane ($K = 0$).

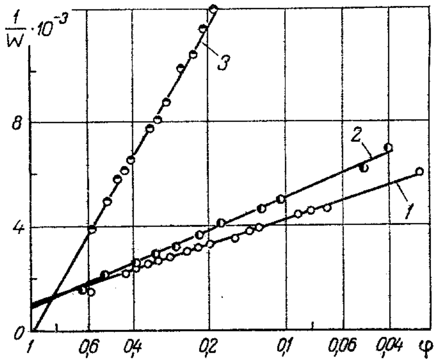

Fig. 3

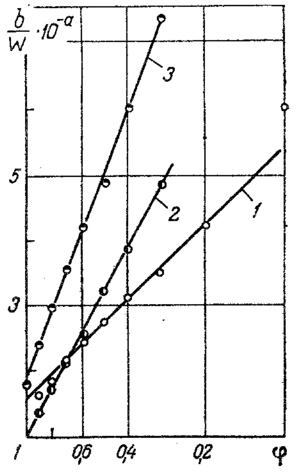

Fig. 4

Fig. 3. Isotherms of sorption of nitrogen by textile fibers [11]: 1) viscose; 2) wool; 3) nylon.

Fig. 4. Isotherms of sorption of vapors on different adsorbents [14]: 1) $a = 1$, b = 2, clay; 2) $a = 2$, b = 1, silicate brick; 3) $a = 1$, b = 2, culm.

If a specimen with maximum moisture content is subjected to partial desorption and then again to adsorption up to the value $\varphi = 1$, then the final moisture of the specimen is already lower because of hysteresis. This process can be carried out in such a way that in the final state the layer of liquid is sufficiently thick so that $p_W = 0$. However, because of the lower moisture content, the surface of the liquid then is not plane. This surface has to be saddle-shaped (of the type of bonding, sealing liquid [8]), and the mean values of the principal radii of curvature of this surface, having different signs, must have the same modulus so that the curvature $K = 0$.

The first term in the right-hand part of Eq. (14) takes into account the effect of additional pressure on the equilibrium exerted on the liquid from the side of the inert nonadsorbing gases. This pressure becomes considerable when φ is close to unity: in order of magnitude $(1-\varphi) \approx (p-p_s)/(RT\rho_1)$. The additional pressure of the inert gas has the effect that the vapor above the surface of an infinitely thick layer is supersaturated. For water vapor mixed with air above the plane surface of a bulk liquid at room temperature, the degree of supersaturation corresponds to $\varphi = 1.001$. In accordance with that, it should be expected that the presence of inert gases affects adsorption when φ is close to unity (at room temperature at $\varphi > 0.999$). When $\varphi < 0.99$, the presence of air need not affect the adsorption of water vapor; this is confirmed by experimental data [10].

The presence of moisture absorption by polymer materials include in the general case both adsorption of vapor by the surface and absorption of vapor by the internal layers of the material. Evaluating calculations showed that the contribution of adsorption on the surface of textile fibers to the overall moisture content is negligibly small when φ is 0.8-0.9. The effect of absorption on equilibrium is taken into account chiefly by the term RTn_0m/W in Eq. (11). The isotherms of sorption of nitrogen and water vapors by textile fibers are shown in Figs. 2 and 3 in coordinates $1/W = f(-\log\varphi)$.

For all these isotherms it is characteristic that they contain a rectilinear section. The sorption isotherms of formic acid on nylon and keratin, a component of fibers of animal origin, plotted from data of [11], have the same shape. The validity of the same regularities in sorption of vapors of different liquids (both polar and nonpolar) by the given material confirms the assumption made at the beginning of the article, that the absorption process taking place under the given conditions can be thermodynamically described as a mixing process.

In accordance with Eq. (11), within the limits of the rectilinear section of the dependence $1/W = f(-\log\varphi)$, the term characterizing the swelling pressure has to remain constant (we neglect the term with the virial coefficient). This constancy is obviously due to elastic deformation of the polymer. Assuming that the swelling pressure is constant over the cross section of the fiber, we can estimate its order of magnitude on the rectilinear section of the dependence $1/W = f(-\log\varphi)$ by determining the size of the segment up to the intercept of

TABLE 2. Numbers of Active Sites Calculated by the Absorption of Nitrogen and Water Vapors

Sorbent	n_0, 10^{-5} kmole/kg		Sorbent	n_0, 10^{-5} kmole/kg	
	nitrogen	water		nitrogen	water
Viscose	2,56	508	Cotton	1,26	277
Wool	2,00	650	Acetate	0,49	207
Silk	1,39	576	Nylon	0,49	188

the straight line with the axis of ordinates. Unfortunately, it is impossible to compare the obtained values ($\sim 10^7$ Pa) with the experimental values of the swelling pressure because experimentally, the swelling pressure was measured with only constant volume.

From the tangent of the angle of slope of the straight line in coordinates $1/W = f(-\log\varphi)$ it is not difficult to find, in accordance with (11), the number of active sites n_0. The values of n_0 for the isotherms shown in Figs. 2 and 3 are presented in Table 2.

Water molecules are polar, therefore it must be expected that they, in the first place, will be sorbed by polar groups of polymers. According to [11], the number of polar groups for silk is $220 \cdot 10^{-5}$, and for wool approximately $330 \cdot 10^{-5}$ kcal/kg, which in order of magnitude agrees with the values n_0 for water given in Table 2.

The lower values of n_0 for the sorption of nitrogen vapors are apparently due to the fact that nitrogen molecules are nonpolar. Therefore, not all groups that served as active sites in the sorption of water vapor will also be active sites for nitrogen molecules. Besides that, the permeability of the material may be different for different sorbed substances, and the process of nitrogen absorption may be confined to the surface layers, the most porous layers of the fiber material.

Equation (11) has a term containing the virial coefficient β. This term can be important only for large values of n_0/W, i.e., in the region of low moisture contents. Analysis of the experimental data showed that for materials with such low hygroscopicity as nylon and acetate, taking into account this term together with RTn_0m/W makes it possible to broaden the range of applicability of Eq. (11) toward low values of φ.

In the preceding part of the work, most attention was given to sorption of vapors by textile fibers. However, isotherms similar to those shown in Fig. 2 can also be found for other colloidal capillary-porous bodies of vegetable and animal origin such as leather, soap, gelatin, tobacco, potatoes, flour, wheat, rice, etc. Besides, isotherms of the same type are also found for a number of bodies that are not polymers. The sorption isotherms of some of them are shown in Fig. 4. Similar dependences are found for limestone, cellular concrete, sandstone, blast-furnace slag, bentonite, hydrated coal, etc. Apparently, these bodies also contain together with fairly large pores, pores of molecular dimensions so that the introduction of molecules of the sorbed substance into such pores may be viewed as a process of mixing, and it can be described by the corresponding term of Eq. (11). It should then be expected that the chief regularities examined with respect to textile fibers are also correct for such capillary-porous bodies.

NOTATION

A	is the Hamacker constant;
f	is the free energy of a molecule in the bulk phase;
f_0	is the excess free energy of a molecule in a thin film on the surface of a solid body;
h	is the thickness film;
k	is the Boltzmann constant;
K	is the surface curvature;
m	is the molecular mass;
n	is the number of active sites in a solid;
n_0	is the same in kilomoles per kilogram of solid;
N	is the number of molecules in the given phase;
N_e	is the Avogadro number;
p	is the pressure;
r_a, r_b	are the principal radii of curvature of the surface;
R	is the gas constant;

s	is the surface area;
T	is the absolute temperature;
v	is the molecular volume;
V	is the phase volume;
W	is the mass of adsorbed substance in a solid of unit mass, moisture content;
β, ψ	are the virial coefficients;
μ	is the chemical potential;
ρ	is the density;
σ	is the surface tension;
$\varphi = p_2/p_s$	is the relative vapor tension, relative air humidity;
Φ	is the Gibbs energy.

Indices

1, 2, 3	denote the liquid, vapor, and solid phases, respectively;
s	is the state of saturation;
' and "	are the liquid and vapor, respectively, in a state of saturation;
w	is the wedging pressure;
c	is the capillary pressure;
sw	is the swelling pressure.

LITERATURE CITED

1. N. V. Churaev, "The effect of film motion on the evaporation of moisture from capillaries," Kolloidn. Zh., 27, No. 6 (1965).
2. A. A. Tager, Polymer Physicochemistry [Russian translation], Khimiya, Moscow (1978).
3. S. S. Voyutskii, Course of Colloid Chemistry [in Russian], Khimiya, Moscow (1978).
4. L. D. Landau and E. M. Livshits, Statistical Physics [in Russian], Nauka, Moscow (1964).
5. R. Kubo, Thermodynamics, Elsevier (1968).
6. B. V. Deryagin, "Determination of the concept of wedging pressure and its role in the statics and kinetics of thin layers of a liquid," Kolloidn. Zh., 17, No. 3 (1955).
7. B. V. Deryagin and N. V. Churaev, "Polymolecular adsorption and capillary condensation in narrow slitlike pores," Kolloidn. Zh., 38, No. 6 (1976).
8. A. V. Lykov, Theory of Drying [in Russian], Énergiya, Moscow (1968).
9. B. V. Deryagin, S. V. Nerpin, and N. V. Churaev, "Theory of evaporation of liquids from capillaries," Kolloidn. Zh., 26, No. 3 (1964).
10. S. Brunauer, Adsorption of Gases and Vapors [Russian translation], IL, Moscow (1948).
11. Harris (editor), Handbook of Textile Fibers, Washington (1954).
12. V. P. Dreving, A. V. Kiselev, and O. A. Likhacheva, "Absolute isotherms of adsorption on silica gel, alumosilica gel, and barium sulfate," Dokl. Akad. Nauk SSSR, 82, No. 2 (1952).
13. S. Greg and K. Sing, Adsorption, Specific Surface, Porosity [Russian translation], Mir, Moscow (1970).
14. L. M. Nikitina, Thermodynamic Parameters and Coefficients of Transfer in Moist Materials [in Russian], Énergiya, Moscow (1968).