SORPTION OF WATER VAPOR BY CAPILLARY-POROUS SUBSTANCES IN RELATION TO TEMPERATURE

V. P. Dushchenko, M. S. Panchenko,
and S. F. D'yachenko

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Sorption of water vapor by typical capillary-porous substances in relation to temperature is examined. The data are used to calculate the temperature dependence of the chemical potential and some coefficients of mass transfer for the hygroscopic state of these substances.

It is known that the equilibrium moisture content of a substance depends on the relative humidity and temperature of the air and on the method by which equilibrium is attained. Published data on the temperature dependence of the equilibrium moisture content of capillary-porous substances of the same chemical composition, but different porous structure, are extremely sparse. If such experimental data are available, valuable information can be obtained about the temperature coefficient of the chemical potential $(\partial\mu/\partial T)_W$ and the isothermic mass capacity C_m, and about the thermogradient coefficient δ for the hygroscopic state of the material [1, 2].

As typical capillary-porous substances we took four samples of sorbents of globular structure: the silica gels KSK-2 (homogeneous large-pored), KSS-4 (homogeneous medium-pored), KSM-5 (homogeneous small-pored), and 5-a (homogeneous ultrafine-pored), which represent fairly fully the main structural types of silica gels [3].

The isotherms for sorption and desorption of water vapor by these silica gels were recorded on a thermostated vacuum sorption apparatus. The sorption apparatus was enclosed in a still-air chamber made of heat-insulating material. The sorption tubes were encased in cylindrical sheaths of sheet brass covered with asbestos and with the heater wires wound on them. The surface temperature of the sorption tubes was kept constant to within ±0.3°C by means of an electronic thermoregulator. The batching tube containing the distilled water was also surrounded by a heater, the output of which was controlled by a thermoregulator so that the water temperature throughout the experiment was a little lower (by 1-2°C) than the temperature of the samples. This ensured that there was no condensation of water vapor on the samples. The temperature in the sorption tubes and hatching tube was measured by means of thermocouples embedded in the sorption tubes and by calorimetric thermometers.

The sorption and desorption isotherms (Fig. 1) give a complete picture of the qualitative and quantitative changes in the sorption of the silica gels with increase in temperature.

In the temperature range 293-313°K the moisture content due to monomolecular adsorption, calculated by using the BET polymolecular adsorption equation, was practically constant for all the investigated silica gels, whereas the moisture content of the polymolecular layers (start of sorption hysteresis loop) decreased.

In the region of capillary condensation the moisture contents, including the maximum hygroscopic content, of all the silica gels decreased with increase in temperature and φ constant. This is perfectly consistent with Lykov's ideas [4]. The volume V of moisture condensed in the capillaries of the substance as a result of sorption is equal to the total pore volume

$$V = \int_{r_1}^{r_2} f(r)\,dr. \tag{1}$$

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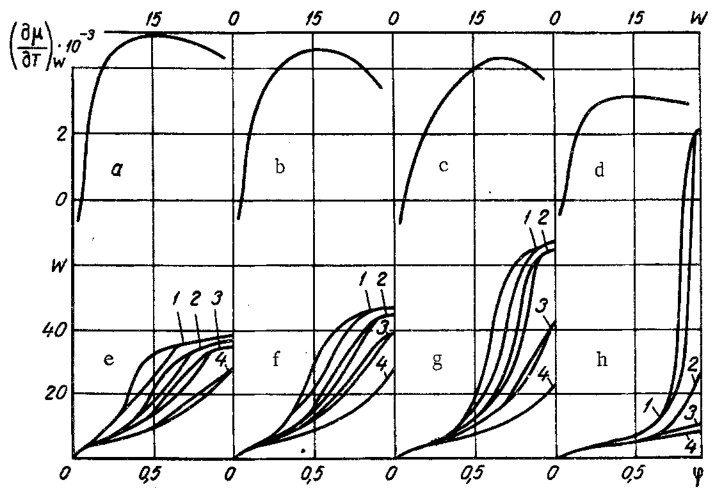

Fig. 1. Temperature coefficient of chemical potential of mass transfer $(\partial\mu/\partial T)_W$, J/kg·deg as function of moisture content W, % of silica gels: a) 5-a; b) KSM-5; c) KSS-4; d) KSK-2 and water-vapor sorption isotherms [at temperatures: 1) 293; 2) 301.5; 3) 308; 4) 313°C] for silica gels [e) 5 A; f) KSM-5; g) KSS-4; h) KSK-2].

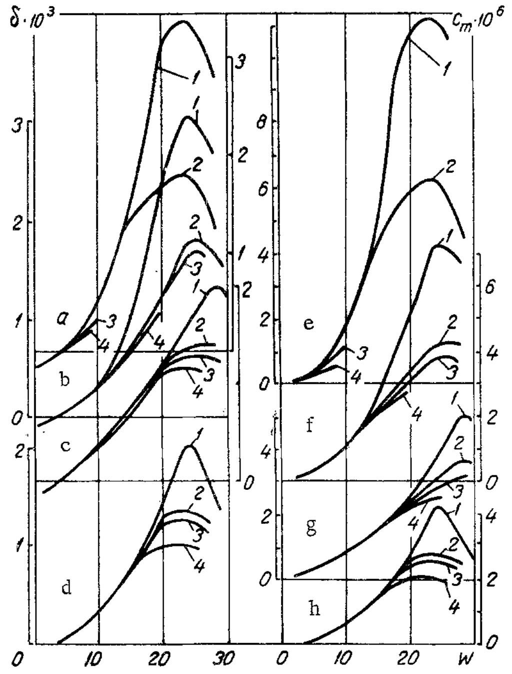

Fig. 2. Thermogradient coefficient δ (deg^{-1}) and specific isothermic mass capacity C_m (kg/J) as functions of moisture content W(%) of silica gels at temperatures: 1) 293; 2) 301.5; 3) 308; 4) 313°K. a,e) KSK-2; b,f) KSS-4; c,g) KSM-5; d,h) 5-a.

The effective pore sizes are given by the well-known expression [4]

$$r = \frac{2\sigma\rho_v \cos\alpha}{\rho_l P_s \ln\left(\frac{1}{\varphi}\right)}. \tag{2}$$

With increase in temperature, as (2) indicates, r decreases, which leads to a reduction of the equilibrium moisture content of the silica gels. This reduction is greatest for capillary condensation moisture.

The maximum hygroscopic moisture content decreased with increase in temperature, slowly at first and then more rapidly, which corresponds to a considerable increase in the pressure of the saturating water vapor. The larger the pores, the greater was the reduction of W_{mh} with temperature increase. The start of the sorption hysteresis loop or, in other words, the start of capillary condensation, was shifted towards higher relative moisture contents.

All the types of silica gels were characterized by a narrowing of the sorption hysteresis loop with temperature increase. We give a possible explanation of this experimental fact.

If we regard the sorption hysteresis as due to incomplete wetting of the surface of the substance by the liquid owing to the presence of adsorbed air on it [this is allowed for by the factor cos α in (2)], then it is clear that with increase in temperature removal of air from the sample is improved and for vapor sorption $\cos\alpha \to 1$, which leads to convergence of the sorption and desorption branches of the isotherm.

Sorption hysteresis may also be due to the presence in the capillary-porous substance of globular pores and bottle-shaped pores or cavities with narrow constrictions, as well as cylindrical pores open at both ends. The latter are only an approximation to the real shapes of the pores.

Capillary condensation, according to current ideas [5], cannot begin until there is a continuous film of adsorbed liquid of a particular thickness filling all the irregularities, depressions, and cracks in the pores.

Increase in temperature adversely affects the linking-up of the individual adsorption formations, particularly the saddle-shaped menisci. There is also a reduction of the polymolecular film thickness, which is a characteristic parameter in the equation of capillary condensation [5]. This can lead, particularly in the case of large-pored silica gels, to the almost complete absence of capillary condensation as a result of only a slight rise in temperature. This was observed in the case of KSK-2 silica gel (Fig. 1h) which has almost cylindrical pores. This conclusion can be derived from the shape of the sorption hysteresis loop [6]. KSK-2 silica gel has the lowest density of packing of the spherical particles.

The pores of silica gel 5-a, where the spherical particles are most densely packed, correspond most closely to the bottle-shaped type, as is indicated by the shape of the sorption hysteresis loop on the 293°K isotherm (Fig. 1e).

For this gel the great separation of the desorption branch of the isotherm from the adsorption branch at the start of the desorption process can be attributed to the difficulty of removing the liquid in the narrow throat of the pore, which traps the liquid contained in the broad part of the pore. As distinct from cylindrical pores φ must be greatly reduced to obtain the same moisture content.

With increase in temperature the surface tension of the "throat" liquid is reduced. The removal of this liquid becomes easier and, hence, the desorption branch of the isotherm comes closer to the adsorption branch.

For KSM-5 and KSS-4 silica gels, where the effective pore size is larger and the pores are more nearly cylindrical, the variation of sorption with temperature is of an intermediate nature (Fig. 1f, g).

Figure 1 also shows the relationships $(\partial\mu/\partial T)_W = f(W)$, calculated from the desorption branches of the isotherms, for the investigated silica gels. The values of $(\partial\mu/\partial T)_W$ are greater, the smaller the pores of the silica gels. The greatest increase in $(\partial\mu/\partial T)_W$ for all the silica gels is in the region of monomolecular adsorption. This can probably be attributed to the energetic inhomogeneity of the adsorption centers of the silica gel surface. At moisture contents corresponding approximately to polymolecular adsorption the temperature coefficient of the chemical moisture potential becomes almost constant and subsequently begins to decrease. This indicates that mass transfer has less effect on the internal heat transfer of capillary-porous substances in the region of capillary condensation of moisture. In fact, in this region of moisture contents the fraction of the total diffusive transfer due to transfer of moisture in liquid form increases and this is responsible for the reduction of the total diffusive transfer of moisture.

If we know the relationships $(\partial\mu/\partial T)_W = f(W)$ and $(\partial W/\partial\mu)_T = \psi(W)$ and take into account that $\theta \equiv \mu$ for the hygroscopic region [7] we can calculate the coefficients C_m and δ for different moisture contents. Similar calculations for other materials are given in [2]. The relationships $C_m(W)$ and $\delta(W)$ were calculated on the basis of the formula

$$\delta = \left(\frac{\partial W}{\partial \theta}\right)_T \left(\frac{\partial \theta}{\partial T}\right)_W = C_m \left(\frac{\partial \theta}{\partial T}\right)_W, \tag{3}$$

which does not include the Soret thermal diffusion coefficient. This simplification is perfectly valid for many cases of unsteady mass and heat transfer [1]. We note also the lack of reliable data for the Soret coefficient.

Figure 2 shows the relationships $\delta(W)$ and $C_m(W)$ for different temperatures. In the region of monomolecular adsorption the thermogradient coefficient becomes negative, which corresponds to moisture transfer to the "hot" end of the body, obviously by vapor effusion [8] and thermoosmotic creep [9]. With increase in moisture content of the material the coefficient δ increases, reaching a maximum value at moisture contents which correspond approximately to the borderline between adsorption-bound water and microcapillary moisture. The thermogradient coefficient then decreases, which can be attributed to the presence of trapped air in the micropores of the substance [8]. The expansion of this air leads to movement of the capillary moisture in the direction of the heat flow. This effect is more pronounced in silica gels with fine pores.

Increase in temperature shifts the maximum of the curves $\delta(W)$ towards lower moisture contents and also reduces δ_{max}. The latter result is due to reduction of C_m with temperature increase.

The relationships $C_m(W)$, which are used for the calculation of δ, depend in a similar way on the total moisture content of the material, the forms of moisture binding, and the temperature of the material. In the region of monomolecular adsorption the values do not become negative, of course.

The results presented above confirm once again that it is worthwhile to extend sorption research over a wide temperature range for the solution of several important theoretical and practical problems of internal mass and heat transfer in capillary-porous substances.

NOTATION

φ is the relative humidity of air;
W_{mh} is the maximum hygroscopic moisture content;
r is the effective size of capillaries;
$f(r)$ is the volume characteristic of effective size distribution of pores;
σ is the surface tension of water;
ρ_v, ρ_l are the densities of moisture in vapor and liquid form;
α is the contact wetting angle;
P_s is the saturated vapor pressure;
θ is the experimental mass-transfer potential.

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