ON THE THERMODYNAMICS OF MOISTURE RETAINED
IN MODELS OF CAPILLARY-POROUS MODELS

M. S. Panchenko, A. L. Panasyuk,
and A. S. Mosievich

UDC 541.183:536.24

The thermodynamic differential functions of moisture retained in silica gel models of capillary-porous bodies are shown here as function of moisture content, temperature, and porosity structure.

The general laws governing the mechanism of moisture absorption in colloidal dispersions can be established and the state of the retained moisture can be determined by the methods of thermodynamic analysis in conjunction with a set of physicochemical research techniques.

Moisture absorbed by a colloidal dispersion is retained in it by forces of various origins and magnitudes [1], the effect of these forces possibly varying with the moisture content level, with temperature, and with the porosity structure of the medium. In order to describe the thermodynamic state of such moisture in a colloidal dispersion under these conditions, one needs the entire set of thermodynamic differential functions, namely: the internal energy ΔU, the free energy ΔF, and the bound energy $T\Delta S$ of the bond at any given moisture content u and temperature T in model specimens of different porosity structures.

Four grades of silica gel of the same chemical composition $SiO_2 \cdot nH_2O$ were chosen as model specimens rather adequately representing the structural types of such sorbents: KSK-2 (uniformly coarse porosity), KSS-4 (uniformly medium porosity), KSM-5 (uniformly fine porosity), and 5-A (uniformly ultrafine porosity) according to the classification given in [2, 3, 4]. Their structural-sorptive characteristics and their structure geometry have been described in [5].

The said problem was solved using a sorption apparatus with thermostatic control and vacuum [6] along with an isothermal electrocalorimeter for measuring the specific heat of evaporation of the moisture and of the colloidal dispersions [7].

The free energy ΔF of the bond between moisture and silica gel was determined from the desorption branches of isotherms for various temperatures and moisture content levels, on the basis of conventional physicochemical thermodynamic relations. The result of calculations is shown in Fig. 1A.

The internal energy ΔU of the bond between moisture and a specimen was determined as the difference between the specific heat of isothermal evaporation of moisture and that of free water at the same temperature. These quantities are shown in Fig. 1B as functions of moisture content and temperature.

The bound energy $T\Delta S$ of the bond was found from the well-known relation

$$T\Delta S = \Delta U - \Delta F.$$

The authors deemed it more appropriate to analyze the relations $T\Delta S/\Delta U$ (u, T). These have been plotted in Fig. 2.

The dashed lines on all graphs indicate the average position of the boundary between adsorbed moisture and moisture contained within the microcapillaries.

According to Fig. 1A, the free energy ΔF of a bond between moisture and silica gel is generally a function of the temperature and of the moisture content, decreasing as the latter both increase. Least moisture is retained in coarse-porosity KSK-2 polymolecular layers. A slight temperature rise may result in
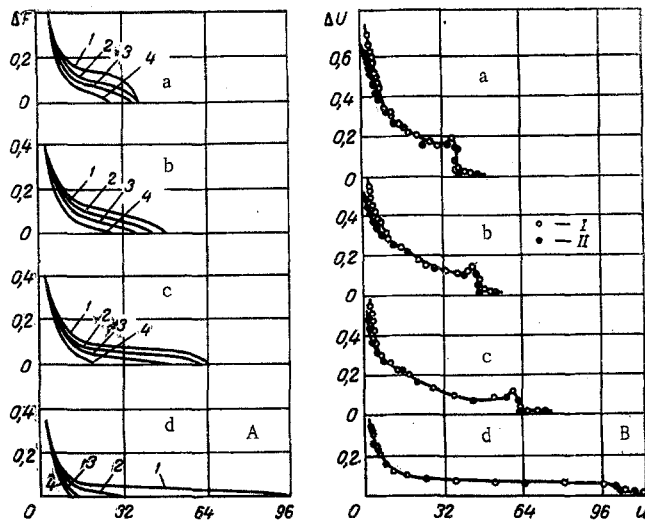
Fig.1

Fig.2

Fig.1. A) Free energy differential (ΔF MJ/kg) of moisture retained in silica gel at the follow-
ing temperatures: 1) 293°K; 2) 301.5°K; 3) 308°K; and 4) 313°K. B) Internal energy differential
(ΔU MJ/kg) of moisture retained in silica gel at the temperature [I) 303°K and II) 333°K] as a
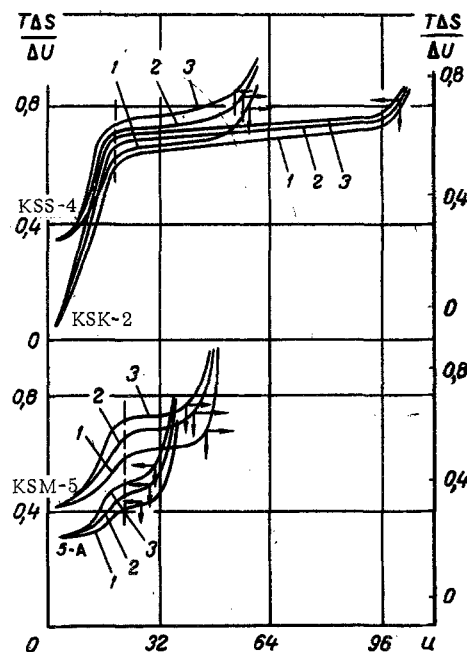function of moisture content (u, %): a) 5-A; b) KSM-5; c) KSS-4; and d) KSK-2.

Fig.2. Ratio of bound energy to internal energy differentials (TΔS/ΔU) of a moisture bond as
a function of the moisture content in silica gel: 1) 293°K; 2) 301.5°K; and 3) 308°K.

an intensive breakup of the moisture polylayers, which makes it possible that no capillary condensation will
occur during the adsorption of water vapor [6].

Comparing the values of ΔF for moisture retained in silica gel at various fixed temperatures and
moisture content levels, we can see that the ΔF(u) curves converge at higher temperatures in the region of
low moisture content. This is an indication that the moisture molecules interact above all with the most
active adsorption centers only, the latter being the free hydroxy groups on the silica gel surface. It is also
evident from Fig. 1A that the ΔF(u) curves for fine-porosity silica gels at different temperatures lie above
the corresponding curves for coarser-porosity silica gels. This is confirmed by the existence of a stronger
adsorptive force field in the microcapillary-porosity silica gels.

Thus, for silica gels the quantity of retained moisture and the free energy of a bond both vary with
temperature while the magnitude of these variations is determined by the porosity structure of the speci-
mens.

The quantity of adsorptively bonded moisture decreases, according to [8], because the kinetic energy
of adsorbed molecules due to their thermal agitation increases with rising temperature. The stresses in
the adsorption field, on the other hand, vary insignificantly, if at all, as a result of temperature changes.

By virtue of the fact that the surface tension of moisture decreases with rising temperature, the bond
energy of moisture in microcapillaries should also decrease.

An analysis of experimental results on the effect of temperature on the magnitude of ΔU at different
moisture content levels reveals a pronounced temperature dependence mainly in the case of fine-porosity
silica gels KSM-5 and 5-A (Fig.1B). Moreover, the systematic deviations of ΔU values at higher tempera-
tures from the values at 303°K have to do with the overall decrease in these ΔU values. It has also been
discovered in [9] that, in the case of fine-porosity silica gel KSM-5, a rising temperature is accompanied
by a decreasing ΔU. A comparison of our test results with the data in [9] shows that the ΔU values for
coarser-porosity silica gels (KSK-2 and KSS-4) do not depend on temperature, while there is a weak tem-
perature dependence for the finer-porosity grades (KSM-5 and 5-A).

For a moisture bond, therefore, the values of internal energy as well as their dependence on temperature are determined by the porosity structure of the specimens. Some decrease in ΔU at a constant moisture content, in the case of adsorptively bonded moisture in fine-porosity specimens of silica gel, can probably be explained by the endothermal effect of structural transformations in the dispersion lattice.

According to [10], if a wettable colloidal dispersion undergoes structural changes during a rise of temperature, then this will, indeed, alter the heat of wetting and, consequently, also the internal energy of the moisture bond.

The $\Delta U(u)$ curve provides factual data on how the state variables of moisture retained in silica gel relatively to the state variables of free water change with temperature. Since ΔU changes little with temperature, one may say that on both accounts there is an almost equal change in state variables due to rising temperature. This agrees with the observation that extremely hydroxylized silica gel surfaces interact with water molecules, this interaction being based essentially on the hydrogen-bond mechanism. Such an interaction within the bulk of free water is also based principally on a similar mechanism. Therefore, changes in the bond energy of moisture molecules due to changes in temperature are of the same order of magnitude in both cases.

According to Fig. 2, moisture retained in silica gel specimens of different porosity structures is not only characterized — as in the general case — by an increasing fraction of bound energy at higher moisture content levels, but also by the peculiar property that this fraction of bound energy in the first samples of adsorbed moisture is greater in fine-porosity specimens than in coarse-porosity ones. This property can be explained, considering that the bound energy is proportional to the entropy differential ΔS of a bond. The greatest change in ΔS is observed in the finest-porosity specimens [5] and this, consequently, makes for the largest fraction of bound energy in fine-porosity specimens within the range of adsorptively bonded moisture.

It also follows from Fig. 2 that, unlike the energy bond in mono- and polymolecular moisture layers, the fraction of entropy bond increases where moisture is formed by capillary condensation. This confirms the statement in [1] that not only the magnitude of retaining forces which retain moisture in a colloidal dispersion but also their nature must be considered. Indeed, both test and calculation data show that the trend of the $T\Delta S/\Delta U(u)$ curves indicates more clearly than the trend of the $\Delta F(u)$ and the $\Delta U(u)$ curves a transition from one form of moisture bond to another, i.e., that the energy fraction differential is more sensitive to a change of forces (adsorptive into capillary) which retain moisture in a colloidal dispersion. The absence of sudden jumps on this curve where transition from one kind of bond to another occurs is an indication that the nature of the forces changes gradually and that the transitions occur over some ranges rather than at discrete values of moisture content. This is in agreement with the concepts which have been developed in [11].

Thus, our studies have revealed how, from the thermodynamic viewpoint, the differentials of thermodynamic functions and the relations between them which characterize the processes of silica gel moistening and drying are affected by the form of the moisture bond, by the porosity structure, and by the temperature.

NOTATION

ΔU is the differential of internal energy of a moisture bond;
ΔF is the differential of free energy of a moisture bond;
$T\Delta S$ is the differential of bound energy of a moisture bond;
u is the moisture content in silica gel;
T is the temperature.

LITERATURE CITED

1.   P. A. Rebinder, in: All-Union Conference on the Process Intensification and the Material Quality Improvement in Drying in Basic Industry and Agriculture [in Russian], Profizdat, Moscow (1958).
2.   A. V. Kiselev, Zh. Fiz. Khim., 23, No. 4 (1949).
3.   A. V. Kiselev, Vestnik Moskov. Gosud. Univ. Ser. Fiz. Matem. i Estestv. Nauk, 11 (1949).
4.   O. M. Dzhigit, A. V. Kiselev, and I. E. Neimark, Zh. Fiz. Khim., 28, No. 10 (1954).
5.   V. P. Dushchenko, M. S. Panchenko, I. A. Romanovskii, and I. B. Slinyakova, Inzh. Fiz. Zh., 15, No. 4 (1968).

6. V. P. Dushchenko, M. S. Panchenko, and S. F. D'yachenko, Inzh. Fiz. Zh., 16, No. 1 (1969).

7. V. P. Dushchenko, M. S. Panchenko, and V. V. Bel'dii, Izv. VUZov, Pishchevaya Tekhnologiya, 5 (1966).

8. N. N. Edlefsen and A. B. S. Anderson, in: Thermodynamics of Ground Moisture [Russian translation], Gidrometizdat, Leningrad (1968).

9. M. F. Kazanskii, R. V. Lutsik, and V. M. Kazanskii, Inzh. Fiz. Zh., 11, No. 5 (1966).

10. F. D. Ovcharenko, Hygroscopy of Clays and Argillaceous Minerals [in Russian], Izd. AN UkrSSR, Kiev (1960).

11. V. M. Kazanskii, in: Heat and Mass Transfer [in Russian], Naukova Dumka, Kiev (1968).