DETERMINATION OF THE THERMODYNAMIC FUNCTIONS OF THE MOISTURE ABSORBED BY A DISPERSE BODY FROM ITS SPECIFIC HEAT OF EVAPORATION

V. M. Kazanskii

Thermodynamic functions have been calculated from measured data on the specific heat of evaporation of the moisture absorbed by typical and colloidal capillary-porous bodies. It is shown that the relationships between the thermodynamic functions for adsorbed and capillary moisture are different, this being the result of the different nature of the forces holding the moisture in the body.

The moisture absorbed by disperse bodies is retained by different forces. Therefore, a recent classification of moisture according to the nature of the bond[1] is based on differences in both the magnitude and the nature of the bond energy. In this case, one thermodynamic function is insufficient; it is necessary to take into consideration both the heat effect (internal energy) and the free energy and entropy of the bond. Thus, the author has been led to measure and calculate the moisture-content dependence of the internal and free energy and the entropy of the bond between moisture and typical disperse bodies and to examine the relation between them.

The experimental materials were typical capillary-porous bodies: KSM silica gel and activated charcoal, and typical colloidal capillary-porous bodies: bentonite and Chasov Yar clay.

The quantity measured directly was the internal energy of the moisture-solid bond (heat effect of the bond) ΔL, defined as the difference between the specific heat of evaporation of moisture from the solid L, at a given moisture content, and the heat of evaporation of free water L_0. The method, and some results of the measurements, were given in [2, 3]. The measurements were made at 61.5°C. The results are plotted as curves 1 in the figure.
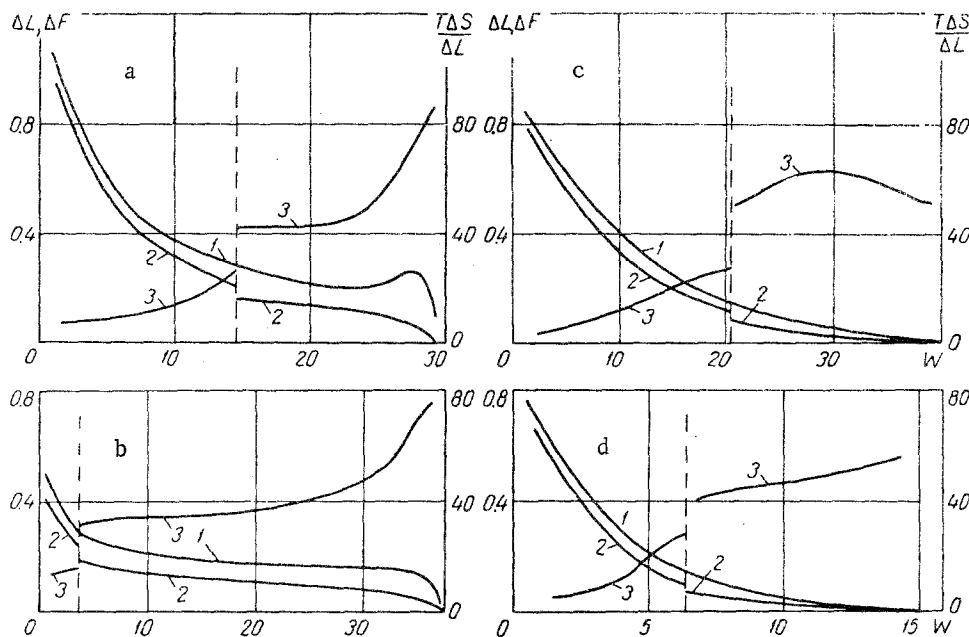
Dependence of (1) the internal bond energy ΔL, kJ/g, (2) the free bond energy ΔF, kJ/g, and (3) the ratio of bound to internal energy $T\Delta S/\Delta L$, %, on the moisture content W% of (a) KSM silica gel, (b) activated charcoal, (c) bentonite, and (d) Chasov Yar clay (broken lines mark boundary between adsorbed and capillary moisture).

From the measured data, the free energy ΔF and entropy ΔS of the moisture bonds were calculated. The calculation of the free energy from the specific heat of evaporation in the moisture content region corresponding to moisture bound by adsorption forces (moisture content region from zero to the vertical broken line in the figure) was based on the formulas derived in [4].

Formulas for the moisture contained in the micro-capillaries of the disperse body (the moisture content region to

the right of the vertical broken line in the figure) were also derived in [4]. However, they are applicable only to capillary-porous solids with a rigid, undeformable skeleton. As shown in [5], for moisture contained in rigid micro-capillaries the dependence of the specific heat of evaporation on the radius of curvature of the meniscus is expressed by

$$
\begin{aligned}
\Delta L = &- \left(T\alpha_2 + \frac{2\sigma\beta_2}{r} \right) \frac{2v_2\sigma}{r} + (1 - T\gamma) \frac{2v_2\sigma}{r} + \\
&+ \left(T\alpha_2 + \frac{2\sigma\beta_2}{r} \right) \frac{2v_2\sigma(W - W_a)}{r^2} \frac{dr}{dW} + \\
&+ \left(T\alpha_3 + \frac{2\sigma\beta_3}{r} \right) \frac{2v_3\sigma(W - W_a)}{W_h r^2} \frac{dr}{dW},
\end{aligned}
\tag{1}
$$

which differs from the corresponding formula for brittle gels [6] only in respect of the last term, which takes account of deformation of the solid phase. Substituting for the radius of curvature of the meniscus in (1) an expression for the free bond energy in the form

$$
\Delta F = -2v_2\sigma/r
\tag{2}
$$

and carrying out calculations analogous to those in [4], we obtain the following relation between the free bond energy and the heat of evaporation of capillary moisture

$$
\Delta F = \sum_{k=0}^{n} \frac{a_k(W - W_a)^k}{A(k+1) + Ck - B},
\tag{3}
$$

if

$$
\Delta L = \sum_{k=0}^{n} a_k(W - W_a)^k,
\tag{4}
$$

where

$$
\begin{aligned}
A &= T\alpha_2 - \beta_2\Delta F^0/v_2, \quad B = 1 - T\gamma, \\
C &= (T\alpha_3 - \beta_3\Delta F^0/v_2)\, v_3/v_2 W_h.
\end{aligned}
\tag{5}
$$

The notation in (1)–(5) is the same as in [4–6].

The entropy of the moisture bond was calculated from data on the internal and free bond energies using the usual relation

$$
\Delta S = (\Delta L - \Delta F)T^{-1}.
\tag{6}
$$

Results of the calculation of the free bond energy are given as curves 2 in the figure. The parts of the curves 2 separated by the vertical broken lines were calculated using different formulas applicable only to adsorbed, or only to capillary moisture. Therefore at the boundary curves 2 exhibit discontinuities, corresponding to the gradual change-over from one form of moisture bond to the other.

Comparison of curves 1 and 2 shows that for all samples the relation between the internal and free bond energies is different for capillary and adsorbed moisture, not only in magnitude but also in the form of the dependence on moisture content. This difference, connected with the different characters of the moisture-retaining forces, together with the magnitude of these forces, is important in dividing the moisture retained in a disperse body according to the type of bond.

The difference between the internal and free bond energies is the so-called bound energy $T\Delta S$, which is proportional to the entropy of the bond ΔS. Curves 3 in the figure show the proportion of the internal energy comprised by bound energy.

It is interesting that for both capillary-porous and colloidal capillary-porous solids the proportion of bound energy increases continuously with increase in moisture content, the most noticeable increase being found in the region of transition from adsorbed to capillary moisture. The entropy term plays a comparatively small part (10–20%) in the case of adsorbed moisture and a significantly greater part (50–70%) in the case of moisture in micro-capillaries. This makes it possible to detail the division of bound moisture proposed in [1] into energy and entropy components.

Thus the results of measurements and calculation of the thermodynamic functions of the moisture absorbed by typical capillary-porous and colloidal capillary-porous solids show that the relation between the internal, free, and bound energies is different for adsorbed and capillary moisture, and this is caused by a difference in the nature of the moisture-retaining forces.

NOTATION

ΔL—increment of specific heat of evaporation of moisture from solid; ΔF—free bond energy; ΔS—entropy of moisture bond; W—moisture content; T—temperature; α_2—coefficient of expansion of water; α_3—coefficient of expansion of solid phase; β_2—isothermal compressibility of water; β_3—isothermal compressibility of solid; σ—surface tension; γ—temperature coefficient of surface tension; v_2—specific volume of water; v_3—specific volume of solid; r—radius of curvature of water meniscus in pores of solid; W_a and W_h—maximum quantity of water in adsorbed monolayer and hygroscopic state of solid, respectively.

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Higher Engineering-Aviation Military College, Kiev