THE TEMPERATURE DEPENDENCE OF THE TRANSPORT POTENTIAL OF MOISTURE IN CAPILLARY-POROUS SOLIDS

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Inzhenerno-Fizicheskii Zhurnal, Vol. 8, No. 2, pp. 211-215, 1965

The author gives a thermodynamic derivation of formulas for the temperature dependence of the chemical potential and thermogradient coefficient of free, adsorbed and capillary water in a porous solid.

The kinetics of moisture migration in a capillary-porous solid is determined by different mass transport potentials at different points in the solid. Direct measurement of the mass transport potential (chemical potential) of moisture absorbed in the solid is difficult, so it is of special interest to relate the chemical potential of the absorbed moisture to readily determinable parameters, in the first place to the moisture content of the solid and the temperature.

Earlier studies [1, 2] have dealt with the dependence of the chemical potential on the moisture content of the solid. It is important to establish the temperature dependence of the chemical potential, since mass transfer frequently occurs simultaneously with heat transfer and the temperature inside the solid can not be considered constant, even to a first approximation. In this paper I shall atempt to calculate the temperature dependence of the chemical potential and the thermogradient coefficient of free, capillary and adsorbed moisture in a capillary-porous solid.

The chemical potential of moisture absorbed in a capillary-porous solid is given by the sum of two terms [1, 2]

$$\mu = \mu_0(T) + \mu_1(T, W). \tag{1}$$

Accordingly, the temperature dependence of the chemical potential can also be given as a sum

$$\left(\frac{\partial \mu}{\partial T}\right)_W = \frac{d\mu_0}{dT} + \left(\frac{\partial \mu_1}{dT}\right)_W. \tag{2}$$

The first term on the right-hand side of Eq. (1) is the chemical potential of pure water. It depends only on the temperature and the properties of water. Therefore the temperature dependence of the first term will be the same for any solid. The second term in Eq. (1) gives the free energy of water absorbed in the solid; it depends on the moisture content and the properties of the porous solid. Because of the second term, Eq. (2) will be different for different types of porous solid and for different types of interaction between the solid and the absorbed moisture.

Values of the chemical potential of pure water μ_0 at various temperatures, and hence its temperature dependence, are readily obtained from tables of thermodynamic properties of water, e.g., [3].

The temperature dependence of the chemical potential of adsorbed moisture will be different for different adsorbents. However, analysis of experimental data has shown that many capillary-porous solids conform to the principal postulate of the potential theory of adsorption (the Polanyi postulate), i.e., the adsorption potential and the chemical potential are independent of temperature for constant surface coverage [4]. In this case, the temperature dependence of the chemical potential of adsorbed moisture can be calculated from the curve $\mu_1 = \mu_1(W)$ at a single temperature.

Consider two temperatures T' and T", separated by a small interval; the dependence of chemical potential on moisture content is given by the equations

$$\mu_1' = \mu_1'(W), \quad \mu_1'' = \mu_1''(W). \tag{3}$$

Then the temperature dependence of chemical potential is given by

$$\left(\frac{\partial \mu_1}{\partial T}\right)_W = \lim_{\Delta T \to 0} \frac{\mu_1''(W') - \mu_1'(W')}{T'' - T'}. \tag{4}$$

It follows from the Polanyi postulate that [5]

$$\mu''(W') = \mu'(W'v'/v''). \tag{5}$$

Substituting (5) in (4) and passing to the limit, we obtain

$$\left(\frac{\partial \mu_1}{\partial T}\right)_W = -\left(\frac{\partial \mu_1}{\partial W}\right)_T \frac{W}{v}\frac{dv}{dT}. \tag{6}$$

In Eq. (6), $(1/v)(dv/dT)$ is the coefficient of thermal expansion of adsorbed moisture α_2. Usually it is taken as 20-40% less than the coefficient of expansion of free water at the same temperature [6]. Then,

$$\left(\frac{\partial \mu_1}{\partial T}\right)_W = -W\alpha_2\left(\frac{\partial \mu_1}{\partial W}\right)_T. \tag{7}$$

Formula (7) permits calculation of the temperature dependence of the chemical potential of water adsorbed on any adsorbent for which the Polyani postulate is valid.

The chemical potential of the water contained in the micro-capillary pores of the solid is determined [1] by the equation

$$\mu_1 = -2v\sigma/r. \tag{8}$$

Differentiation of Eq. (8) gives the temperature dependence of the chemical potential in the form

$$\left(\frac{\partial \mu_1}{\partial T}\right)_W = \mu_1\left[\frac{1}{\sigma}\frac{d\sigma}{dT} + \frac{1}{v}\frac{dv}{dT} - \frac{1}{r}\left(\frac{\partial r}{\partial T}\right)_W\right]. \tag{9}$$

We can assume, to a first approximation, that the porous skeleton of the solid does not change in size with temperature. This assumption is supported by the known fact that the coefficient of thermal expansion of the majority of porous solids is approximately an order of magnitude less than the coefficient of expansion of liquids; hence it can be neglected in comparison with the temperature variation of the specific volume of water. Thus, the variation of the radius of curvature of the meniscus r depends only on the thermal expansion of water:

$$\frac{1}{r}\left(\frac{\partial r}{\partial T}\right)_W = \frac{1}{rv}\frac{dr}{dW}\frac{dv}{dT} = \frac{\alpha_1}{r}\frac{dr}{dW}, \tag{10}$$

from which

$$\left(\frac{\partial \mu_1}{\partial T}\right)_W = \frac{\mu_1}{\sigma}\frac{d\sigma}{dT} + \mu_1\alpha_1\left(1 - \frac{d\ln r}{dW}\right). \tag{11}$$

From a knowledge of the temperature dependence of the chemical potential of free, adsorbed and capillary water, it is possible to calculate the thermogradient coefficient, the fundamental quantity characterizing non-isothermal transport of water in a solid. By definition [7], the thermogradient coefficient

$$\delta = \left(\frac{\partial W}{\partial \theta}\right)_T\left(\frac{\partial \theta}{\partial T}\right)_W = s_t\left(\frac{\partial \theta}{\partial T}\right)_W. \tag{12}$$

If it is accepted that the mass transport potential in the region of hygroscopic moisture content of the solid is the chemical potential of absorbed moisture, i.e., that $\theta \equiv \mu$ [2], then after substitution of (7) and (11) in (12) we obtain the final formula in the form

$$\delta = \delta_0 + \delta_1, \tag{13}$$

where

$$\delta_0 = \left(\frac{\partial W}{\partial \mu}\right)_T\frac{d\mu_2}{dT}, \tag{14}$$

$$\delta_1 = -\alpha_2 W \tag{15}$$

for adsorbed water, and

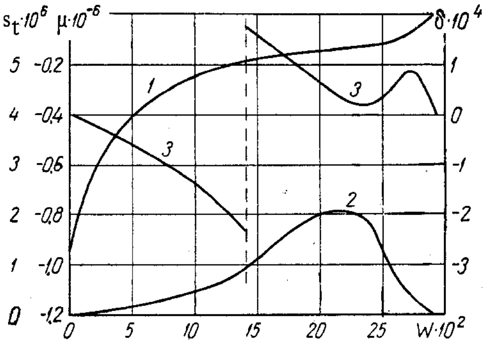
$$\delta_1 = \mu_1\left(\frac{\partial W}{\partial \mu}\right)_T\left[\frac{1}{\sigma}\frac{d\sigma}{dT} + \alpha_1\left(1 - \frac{a\ln r}{dW}\right)\right] \tag{16}$$

for capillary water.

As an illustration, we calculated δ for silica gel KSM, a typical porous solid.

Clearly, from formulas (13)-(16) the calculation of δ for the entire hygroscopic region only requires a knowledge of the dependence of chemical potential on moisture content at a single temperature. This dependence is readily obtained from the adsorption isotherm measured at one temperature, or from data on the heat of vaporization of moisture from the solid [1]. In our case we used the adsorption isotherm of water vapor on silica gel at 20°C, previously given in [8].

As shown in [1], there is a well-defined dependence of the chemical potential of water on the moisture content of capillary-porous solids only in cases of monotonic variation of the moisture content of the solid. In our case the dependence of the chemical potential on moisture content was calculated from the desorption branch of the isotherm, that is, for moisture content decreasing from the saturated level. The results were calculated by the usual method [1] and are shown as curve 1 in the figure. By graphical differentiation of curve 1 the specific isothermal mass-capacity of silica gel was obtained (curve 2).



Dependence of (1) μ, Joule/kg, (2) s_t, kg/Joule, and (3) δ, deg^{-1}, of silica gel KSM on W. The vertical broken line marks the boundary of removal of adsorbed and capillary water.

The thermogradient coefficient δ for a silica gel moisture content from 0-14% was calculated from Eqs. (14) and (15), which are accurate only for adsorbed moisture. For moisture contents from 14-29.3% δ was calculated from formulas (14) and (16), which are applicable to capillary moisture. Curve 3 in the figure represents the dependence of the thermogradient coefficient on moisture content for silica gel KSM, as obtained from these calculations.

The figure shows that the thermogradient coefficient of adsorbed moisture is a negative quantity. Thus, for adsorbed moisture, δ_1 does not depend on the properties of the adsorbent, which is to be expected from Eq. (15). Furthermore, δ_1 is approximately two orders of magnitude less than δ_0 and therefore has practically no influence on the trend of the thermogradient coefficient. In the region of moisture content corresponding to capillary moisture conditions are different. The term δ_1, given by Eq. (16), then becomes bigger than δ_0. Therefore the total thermogradient coefficient is a positive quantity and nonisothermal flow of moisture to colder parts of the solid occurs.

At a silica gel moisture content of 14% curve 3 shows a discontinuity which divides the curve into two parts; these two parts were calculated from different equations valid for adsorbed or for capillary moisture only. In a real solid, however, the binding energy of adsorbed moisture in a multilayer is comparable with the binding energy in very fine microcapillaries, so that a sharp boundary between regions of different forms of binding is not possible. Therefore the real thermogradient coefficient will obviously be expressed by a smooth curve.

In concluding, it should be remarked that calculations of the thermogradient coefficient based on the simplified Eq. (12) do not take into account the Soret coefficient. The Soret coefficient can be included by adding a further term to Eq. (13) [9]

$$\delta_2 = \left(\frac{\partial W}{\partial \mu}\right)_T S_T. \tag{17}$$

It is regrettable that the published data on the value of the Soret coefficient and its dependence on the moisture content of a disperse solid [10-12] are extremely inconsistent, so that it is not possible to calculate the term δ_2 for silica gel quantitatively and evaluate the influence of this term on the relation between the thermogradient coefficient and the moisture content of the solid.

NOMENCLATURE

μ – chemical potential; T – temperature; W – moisture content; v – specific volume of water; α_1 – coefficient of thermal expansion of pure water; α_2 – coefficient of thermal expansion of adsorbed water; σ – surface tension; r – radius of curvature of liquid meniscus in capillaries of solid; S_T – Soret coefficient; s_t – specific isothermal mass capacity of solid; δ – thermogradient coefficient.

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17 January 1964

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