CHEMICAL POTENTIAL OF MASS TRANSFER IN COLLOIDAL BODIES

V. M. Kazanskii

The chemical potential of moisture absorbed by any kind of colloidal body in the moist state is shown to be equal to that of free water.

A series of investigations [1–5] have been devoted to the determination of the relation between the mass transfer potential (chemical potential) of the moisture absorbed by a disperse body and the moisture content of the latter. In most of these researches, however, only the moisture content region at which the relative water vapor pressure is less than unity (body in a hygroscopic state) is considered. Only [4,5] are devoted to the determination of the chemical potential of moisture in the so-called moist state (i. e., at a relative vapor pressure equal to unity), and we cannot accept the results for reasons given below.

At the same time, knowledge of the chemical potential of moisture in the region of moist states, is of great interest, since colloidal and capillary-porous colloidal bodies are able to absorb considerable quantities of moisture in these conditions.

The chemical potential of moisture for bodies in the moist state can be found in the following manner.

By definition [6], the moist state is the level of moisture in a disperse body at which the equilibrium vapor pressure P over the body is equal to the equilibrium vapor pressure over a plane surface of pure water at the same temperature Ps (P/Ps = 1). Since the specific free energy (i. e., chemical potential) of the vapor is determined only by its temperature and pressure, it follows, therefore, directly from the definition given above, that for the moist state region the chemical potential of the vapor over the body is equal to the chemical potential of the vapor over free water. What has been said concerning the equilibrium vapor pressure applies also to the chemical potential of the moisture in the body in the moist state, which should be equal to the chemical potential of free water. If the chemical potential of free water is taken as zero for a given temperature, as it has been in most investigations [1–5], then the chemical potential of moisture contained in the disperse body in the moist state will always be equal to zero.

By analogous considerations, the reverse can easily also be proved: each departure from zero of the chemical potential is always related to the deviation from unity of the relative vapor pressure over the body, i. e., with transition of the body from moist to the hygroscopic state.

The above considerations make it impossible to agree with the formula for calculation of the chemical potential of moisture in the moist state (in particular, the osmotic pressure) derived in [4,5]:

$$\mu = \mu_0(T) + RT \ln \omega. \tag{1}$$

This formula is obtained by regarding a colloidal body as a single-phase molecular-colloidal solution.

First of all, formula (1) relates essentially to the hygroscopic state of the colloidal body, since the solution of any nonvolatile in water (in this particular instance, gelatin) is always associated with a certain decrease in the equilibrium vapor pressure above the solution. Moreover, formula (1) is imprecise. Indeed, according to Raoult's law, the depression in equilibrium vapor pressure above a solution is equal to the mole ratio of water in the solution [5,7]:

$$P/P_s = n_0. \tag{2}$$

Substituting expression (2) in the usual equation for chemical potential of moisture absorbed by a body [1,3,7]

$$\mu = \mu_0(T) + RT \ln (P/P_s), \tag{3}$$

we obtain

$$\mu = \mu_0(T) + RT \ln n_0. \tag{4}$$

Formula (4) differs from (1) only in the use of the mole, and not the weight, fraction of water in solution (molar and not gravimetric "moisture"). The micellar weight of colloidal bodies can exceed the molecular weight of water by several hundreds, so that the difference between formulas (1) and (4) becomes very substantial.

This, so it would seem to us, explains the reason for the discrepancy between the chemical potential curves for gelatin in Figs. 1 and 2 reported by Nikitin [5]. Both curves are calculated for the same temperature and have the same zero readings equal to the chemical potential of free water (at a moisture content $\omega = 1$ and P/Ps = 1). At the same time, the curve in Fig. 1, calculated from the standard formula (3) in chemical thermodynamics, decreases as the moisture increases, and, moreover, at a moisture content 0.5 kg per kg of dry substance (corresponding to a moisture content of 0.33 kg per kg of moist material), the chemical potential is equal to 0.

The curve in Fig. 2, calculated from formula (1), gives a value of 1.5 M joule/mole for the chemical potential at a much higher moisture content—0.5 kg per kg of moist material (moisture content 1.0 kg per kg of dry substance.)

Thus it follows from the general principles of thermodynamics that for disperse bodies of any kind in the moist state range, the chemical potential of absorbed moisture equals 0. Consequently, any attempt

to establish formulas for calculating the chemical potential of bodies in the moist state range is doomed to failure.

NOTATION

μ—chemical potential of moisture absorbed by the disperse body; μ_0—chemical potential of free water at a given temperature; R—universal gas content; T—absolute temperature; ω—moisture in body (mass of absorbed moisture as a ratio of unit mass of body); n_0—mole fraction of water in solution; P—equilibrium water vapor pressure over the body at a given moisture content; P_s—equilibrium water vapor pressure over free water.

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