A THERMODYNAMIC INTERPRETATION OF A MODEL FOR THE
EQUILIBRIUM STATES OF WATER PHASES IN POROUS MATERIALS

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A thermodynamic explanation is given for the empirical coefficients in a model for the equilibrium state of water in a porous material.

A model has been set up [1] for various materials to describe the thermodynamic equilibrium state of water in the pores in the form

$$u_2 = b_0 + b_1 u + \frac{b_2 + b_3 u}{t} \quad \text{for} \quad t \leqslant t_{\text{sf}},$$ (1)

where

$$t_{\text{sf}} = \frac{b_2 + b_3 u}{u(1 - b_1) - b_0}.$$ (2)

In spite of the practical value of the model of (1), it is only empirical and has a deficiency inherent in such a model, i.e., the physical significance of the coefficients has not been established, and they have to be determined for each particular material.

Here we provide a physical interpretation of the empirical coefficients from the corresponding thermodynamic relations.

The water in the pores of a porous building material is usually a solution of dissociated components, and these may consist not only of water-soluble components from the skeleton but also various additives responsible for the structuring (air-entraining additives, foam and gas producers, etc.), as well as additives to hinder freezing in concrete during winter operations, and aerosols from salts, acids, and bases, which deposit on industrial buildings such as those in chemical plants, and which then dissolve and migrate into the material. If the solution is unsaturated, the solid formed at temperatures less than the eutectic value T_e consists of pure ice.

The isobaric equilibrium state in a two-phase n-component system is described via the following equation [2] when one phase contains only component n:

$$\frac{d \ln (x_n \gamma_n)}{dT} = - \frac{\Delta H_n}{RT^2}.$$ (3)

Expression (3) is thermodynamically rigorous if one can neglect the effects of external factors such as electrical and gravitational fields together with surface phenomena at the phase boundaries. The latter must be considered in the thermodynamic description of water-phase equilibrium in a porous or powdered material of high specific surface.

We integrate (3) from $x_n = 1$ to x_n, which corresponds to the temperature range from the freezing point of the pure solvent T_0 up to $T < T_e$ and we use the fact that $\ln(x_n \gamma_n) = 0$ in accordance with the choice of the standard state for $x_n = 1$ and $\gamma_n = 1$, and we restrict ourselves to terms in the expansion containing $\Delta T = T - T_0$ to the first power, which corresponds to the model of (1), and this gives

$$\ln (x_n \gamma_n) = - \frac{\Delta H_0}{RT_0^2} \Delta T.$$ (4)

Also, for an electrolyte solution [3]

$$\ln (x_n \gamma_n) = - \Phi \sum_{j=1}^{n-1} m_j \frac{M_n}{1000} , \tag{5}$$

so (4) can be put as

$$\Delta T = K\Phi \sum_{j=1}^{n-1} m_j. \tag{6}$$

In the particular case of an electrolyte with one dissolved component, we have [4]

$$\Delta T = Kim. \tag{7}$$

The constant $K = RT_0^2 M_n/1000\Delta H_0$ in (6) and (7) is dependent only on the properties of the pure solvent, and $K = 1.856$ for water. When there is no chemical interaction between the components, the reduction in the freezing point ΔT in (6) is made up of the freezing-point depressions due to each dissolved component separately. Then one can write $\Phi = \sum_{j=1}^{n-1} i_j m_j / \sum_{j=1}^{n-1} m_j$, and

the latter enables one to use handbook data on the solubilities or freezing-point depressions for individual solutions with single dissolved components to calculate the freezing point T of a multicomponent solution. For this purpose we write (6) as follows:

$$\Delta T = K \sum_{j=1}^{n-1} i_j m_j = \frac{K}{100} \sum_{j=1}^{n-1} \left(\frac{i}{M}\right)_j C_j = \frac{K}{100} \left(\frac{i}{M}\right)_{av} C_{vol} . \tag{8}$$

where $(i/M)_{av} = \left[\sum_{j=1}^{n-1} (i/M)_j C_j\right]/C_{vol}$ and $C_{vol} = \sum_{j=1}^{n-1} C_j$. An expression in the form of (8) is par-

ticularly convenient in the computational sense for a multicomponent solution when the composition is constant, as is the mass ratio of the dissolved components.

If the solid phase is formed as a solid solution (ice plus hydrated salt), then (3) applies when the thermodynamic features are incorporated appropriately.

We integrate (3) with limits from T_0 to $T_{e_1} \leqslant T \leqslant T_{e_2}$ and concentrations from x_n to x_n^* correspondingly, and we perform transformations analogous to the above on the basis that component 1 enters the solid phase at $T = T_{e_1}$, which gives

$$\Delta T = K \sum_{j=2}^{n-1} i_j m_j = \frac{K}{100} \sum_{j=2}^{n-1} \left(\frac{i}{M}\right)_j C_j = \frac{K}{100} \left(\frac{i}{M}\right)_{av} C_{vol}. \tag{9}$$

where $(i/M)_{av} = \left[\sum_{j=2}^{n-1} (i/M)_j C_j\right] C_{vol}$ and $C_{vol} = \sum_{j=2}^{n-1} C_j$. On comparing (8) and (9) we see that

they can be extended to describe the equilibrium state of a multicomponent two-phase system on sequential increase in ΔT, which involves passage through the eutectic temperatures and correspondingly the elimination of solutes $j = 1, \ldots, n - 1$ from the liquid phase, with the latter going over completely to the solid at $T = T_{e(n-1)}$.

These equations are based on the thermodynamic expression (3), which describes the equilibrium state of the phases without allowance for the surface phenomena.

Two essentially different treatments are used [5, 6] for surface phenomena in heterogeneous systems. In the first, which was proposed by Gibbs [5], the actual two-phase system is replaced by a set of two phases with a clear geometrical boundary between them, to which one symbolically refers the excess amounts of energy, entropy, mass, and other extensive parameters. In the second treatment [6], one distinguishes the homogeneous phases and surface layers, the latter being assigned a finite thickness. By surface-layer thickness is meant the effective thickness outside which the local deviations in properties from the bulk values become unimportant. This is possible because the radii of action of the intermolecular forces

are small, which means that the effect of one phase on any other adjacent one decreases fairly rapidly. As the effective thickness is determined by the particular property, it may vary from one property to another. The concept of a surface layer of finite thickness has proved extremely fruitful in interpreting surface phenomena, since the thermodynamic relations apply for the residual unbound phase without constraint on the surface phenomena, while the excess values of the extensive parameters are predetermined by the effective thickness and by the area of effective volume of the surface layer.

We now describe the phase equilibrium in a dissociating interstitial solution in a porous material, and (8) and (9) are used with allowance for the water bound by surface forces in the form

$$t = \frac{K}{100}\left(\frac{i}{M}\right)_{av} C_{vol} = \frac{K}{100}\left(\frac{i}{M}\right)_{av} \frac{\omega_{vol}}{(u_2 - u_b)} = \frac{K}{100}\left(\frac{i}{M}\right)_{av} \frac{(u - u_b)C}{(u_2 - u_b)} , \qquad (10)$$

where $u - u_b$ is the initial amount of free interstitial solution and C is the concentration. Expression (10) is convenient for interpreting the phase equilibrium in a dissociated interstitial solution when one measures or monitors any of the parameters u, C, and ω_{vol}.

A study has been made [7] of the cryogenic phase transformations in specimens made of foam concrete and clay brick, which were saturated under vacuum with especially prepared solutions having various concentrations of sodium and potassium chlorides. The experiments were performed in the temperature range outside the eutectic temperatures of the solutions. Statistical analysis showed that the depression for a solution given by (10) was statistically equivalent to the corresponding part of the model of (1) at the level $\alpha = 0.95$.

Also, complete chemical analyses were performed on these two building materials in a fashion similar to [8, 9], which gave the quantitative and qualitative compositions of the water-soluble components. Table 1 gives the analysis results.

Table 1 shows the water-soluble components as follows: the first four columns are taken by sparingly soluble components, whose effects in producing the freezing temperature can be neglected, while the other are arranged in order of decreasing eutectic temperature (for Na_2SO_4; K_2SO_4; Na_2CO_3; K_2CO_3; $CaCl$ $t_e = 1.2$; -1.55; -2.1; -36.5; -49.8 correspondingly) [10].

Table 2 gives values of the empirical coefficients appearing in (1) and sample standard deviations for the same materials.

A statistical analysis was applied to the sets of corresponding values of u_2, which relate to the experimental data, the values u'_2 predicted by the model of (1), and u''_2 calculated from (10); in particular, the F test showed that the variances $S^2_{u'_2}$ and $S^2_{u''_2}$ were homogeneous, these characterizing the deviations of the calculated u'_2 and u''_2 from the experimental u_2, and this showed that (10) is an adequate representation of the experimental data for foam concrete at the level $\alpha = 0.90$ or for clay brick for $\alpha = 0.95$. We also estimated the discrepancies between the values $u'_{2_i} - u''_{2_i} = \Delta u_{2_i}$, $i = 1, \ldots, m$, by means of the $\hat{t}$ test [11], the value being given by

$$\hat{t} = \frac{(\Delta u_2)_{av}}{S_{\Delta u_2}} = \frac{(\Sigma \Delta u_{2_i})/m}{\sqrt{\dfrac{\Sigma(\Delta u_{2_i})^2 - (\Sigma \Delta u_{2_i})^2/m}{m(m-1)}}} .$$

We compared the calculated value of $\hat{t}$ with the tabulated value $\hat{t}_{tab}$ for $\nu = m - 1$ degrees of freedom, which showed that the mean differences were not statistically significant for foam concrete at $\alpha = 0.80$ and for clay brick at $\alpha = 0.90$.

We can thus say that the variable component compositions incorporated via $\dfrac{K}{100}\left(\dfrac{i}{M}\right)_{av}\omega_{vol}$ in (10) are equivalent in the model of (1) to the expression $b_2 + b_3 u$, and also b_2 becomes lacking in statistical significance when the composition is constant, as has been shown in [7].

We now use the model of (1) to determine the amount of bound water in terms of the layer thickness and area of the binding surface; before that, however, we note that the area relates not only to the porous material but also to the product from the cryogenic phase transformations (the ice), because the most stable thermodynamic state corresponds [12] to a thin

layer of liquid at the surface of the ice, as the free energy of the system is then reduced. In that paper, an attempt was also made to relate the film thickness to temperature. NMR measurements [13] confirm that there is an unfrozen film on the ice and the general behavior of the film thickness (reduction as the temperature is reduced). The same form of relationship for the film thickness or specific unfrozen volume has been obtained for various other materials by independent methods [13, 14]. In [15, 16] there are data on the effects of solute concentrations, including dissociated ones, on the nondissolving volume. It should be mentioned that the nondissolving volume is to be understood not in the literal sense of the word but as some effective value. As a rule, the surface of a porous material has an electrical potential and is in contact with a solution of ionic type, so one gets a double electrical layer, with specifically adsorbed ions at the surface of the material. However, much of the surface is occupied by water molecules, so the adsorbed-ion concentration is fairly small even for a highly charged surface [17]. The corresponding solvated counter ions lie in the diffuse part of a double electrical layer by virtue of the electrical neutrality. The effective thickness is dependent on a particular property and may vary from one to another. However, the available data indicate that the effective thicknesses related to various properties are either almost equal [14] or show a definite relation.

Within the model of (1), the amount of bound water is

$$u_b = b_0 + b_1 u = b_0 + b_1 (u_2 + u_3) = b_0 [1 + \beta (u_2 + u_3)],$$

which corresponds to the above concepts and to the experimental evidence if one assumes that b_0 is the amount of bound water (nondissolving and nonfreezing) having high binding energy, while $b_1 u_2$ is the indirect effect from the concentration of the dissolved components C_{vol} in the solution, since C_{vol} is correlated with u_2, and $b_1 u_3$ is the effect from the surface of the ice, so the last two terms inexplicitly represent the effects of temperature on the total amount of bound water. While b_0 can be expressed in terms of the thickness h_b of the bound film and the specific binding surface s_b, the coefficient b_1 and consequently β will describe a more complicated and so far inexplicit relationship, and therefore the values of β have been measured for building materials and are given in Table 3.

De Boer's method [18] was used to determine the specific surfaces of foam concrete and clay brick, which is based on the dependence of the adsorbed-layer thickness on the relative vapor pressure of the adsorbant. The working formula for the adsorption of water vapor takes a simple form $s = u_{ad}/h_{ad}$, where u_{ad} and h_{ad} are dependent on the relative vapor pressure of the adsorbant and are given with dimensions kg/kg and Å, while s is in m^2/g. The $h_{ad}(P/P_{max})$ relationship has been tabulated for the adsorption of nitrogen [18]. For the adsorption of water, the data have to be multiplied by the conversion factor $2.84/3.54 = 0.80$, where 2.84 and 3.54 Å are the thicknesses of statistical monolayers for water and nitrogen correspondingly. It has been shown that this approach is justified for various building materials. For these materials, which are based on cement as bonding agent, there was good agreement between the specific surfaces calculated by the BET method and given by de Boer's method with the use of the conversion factor. The justification for this needs experimental tests for other materials. The $u_{ad}(P/P_{max})$ relationships have been found by experiment for these materials, and to eliminate the effects of water-soluble components on u_{ad}, the materials were carefully washed before use. Table 4 gives the values of the specific surface together with the confidence ranges for $\alpha = 0.80$ derived from these experiments and calculations, together with the thickness of the layer of bound water having high binding energy as derived only on the basis of the specific surface, together with the corresponding confidence ranges. The thicknesses

TABLE 1. Quantitative and Qualitative Compositions of Water-Soluble Components in Building Materials

Material	Water-soluble component in % by mass								
	$CaCO_3$	$Ca(COC_2)H_2O$	$Ca(OH)_2$	$CaSO_4$	Na_2SO_4	K_2SO_4	Na_2CO_3	K_2CO_3	$CaCl$
Clay brick ($\gamma' = 1550$ kg/m³)	1,67	0,80	1,31	0,53	—	0,22	—	—	0,11
Foam concrete ($\gamma' = 850$ kg/m³)	0,64	—	2,61	3,76	1,32	0,99	1,32	0,99	—

TABLE 2. Values of the Empirical Coefficients Appearing in the Model of (1) and Sample Standard Deviations

Material	Coeff. in (1)				$S_{u_2} \cdot 10^2$
	$b_0 \cdot 10^2$	b_1	$b_2 \cdot 10^2$, °C	b_3, °C	
Clay brick ($\gamma' = 1550$ kg/m³)	0,151	0,023	—3,717	—0,321	0,08
Foam concrete ($\gamma' = 850$ kg/m³)	2,353	0,242	—7,670	—1,135	0,18

TABLE 3. Values of β

Material	β	Material	β
Cement stone ($\gamma' = 2300$ kg/m³)	11,2	Ceramsite concrete ($\gamma' = 1430$ kg/m³)	2,9
Cement—sand 1·1 slurry ($\gamma' = 2120$ kg/m³)	12,7	Foamed solution ($\gamma' = 1320$ kg/m³)	4,3
Cement—sand 1:4 slurry ($\gamma' = 1725$ kg/m³)	11,8	Clay brick ($\gamma' = 1530$ kg/m³)	15,2
Foam concrete ($\gamma' = 850$ kg/m³)	10,3	Foam glass ($\gamma' = 170$ kg/m³)	14,7

TABLE 4. Values for the Specific Surface, Firmly Bound Water Thickness, and Corresponding Confidence Ranges for $\alpha = 0.80$

Material	s, m²/g	$\pm t_\alpha S_s$, m²/g	h_b, Å	$\pm t_\alpha S_{h_b}$, Å
Clay brick ($\gamma' = 1550$ kg/m³)	2,6	0,3	5,8	0,7
Foam concrete ($\gamma' = 850$ kg/m³)	43,0	4,0	5,5	0,5

of these bound water layers on clay brick and foam concrete are virtually equal, and as the thickness of a molecular layer of water corresponds to 2.84 Å, they correspond to two molecular layers.

This physical treatment of the coefficients in (1) increases its practical value, since firstly one can design a new building material or item from the start with improved or even optimal properties; secondly, various measures can be applied in projected or existing buildings to influence the thermophysical or strength characteristics of the material, since these properties are substantially predetermined by the cryogenic phase transitions, which enables one to reduce the heat losses and increase the working life.

NOTATION

b_0, b_1, ..., b_k, empirical coefficients in (1); ΔH_n, molar enthalpy difference for the solvent in the liquid and solid states; ΔH_0, molar heat of solvent phase transition (melting); R, universal gas constant; K, cryoscopic constant; T, t, Kelvin and Celsius temperatures, respectively; x, molar fraction; γ, Φ, i, activity, osmotic, and Van't Hoff coefficients, respectively; m, C, ω, molar and mass concentrations and amount of components dissolved in water; u_1, u_2, u_3, total (initial) water content and amounts of liquid and ice, respectively; s, specific surface; h, film thickness; S, standard deviation; γ', volumetric mass (density); t, Student coefficient; α, reliability. Subscripts (not mentioned): j = 1, ..., (n — 1), components dissolved in water; n, solvent (water); av, vol, average and volume, respectively; b-ad, bound adsorbed liquid (water); sf, start of freezing.

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MODEL OF HEAT AND MASS TRANSFER IN THE DRYING PROCESS WITH THE
REMOVAL OF MULTICOMPONENT LIQUID SYSTEMS

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A mathematical model of heat and mass transfer is proposed on the basis of the assumption of thermodynamic equilibrium between the liquid and the vapor removed in the course of drying.

It is often necessary to calculate the drying of a material containing a multicomponent liquid system (MLS), taking account of the change in moisture content of the material for each component, in performing many technological processes. This is a consequence, on the one hand, of stiffening of the requirements on the dried products — the final specific mass contents of each component are specified — and, on the other, of a tendency to optimize drying processes, which requires detailed study of the kinetics of MLS removal from the products.

In [1], under the assumption of thermodynamic equilibrium of the liquid and the vapor removed, the surface mass transfer in convective drying of bodies including MLS was investigated. In [2], it was shown that the values of the transfer coefficients for the MLS differ from their values for the individual liquids, which confirms the urgency of research into the drying process. In [3], a model of the drying process with removal of a binary ideal

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