THE EQUILIBRIUM HUMIDITY OF DISPERSED SOLIDS AT DIFFERENT TEMPERATURES

V. M. Kazanskii

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The use of the free energy of water vapor as a unique characteristic of saturated air permits the level of dehydration of dispersed solids to be determined unambiguously. The moist air diagram is computed for compensation of the moisture fluctuation of the surrounding air, corresponding to a change of the temperature of drying.

The equilibrium moisture content of a dispersed solid is defined by two independent parameters – the temperature of the surrounding air and its humidity. However, in the practice of thermophysical and physicochemical investigations usually only the temperature is specified and the effect of the air humidity is neglected. A typical example is the determination of the relative dry-weight of dispersed solids when dried up to 105°C without stating the humidity of the air. This, as shown below, leads to considerable fluctuations of the relative dry-weight and sharply reduces the accuracy and feasibility of comparing data on the very different properties of moist dispersed solids as a function of their moisture content.

It is shown in this present paper how, based on thermodynamics mechanisms, it is possible to fix almost unambiguously the level of dehydration of dispersed solids by means of a single parameter – the free energy of the water vapor in the drying air and thus to compensate the variations of humidity of the air, in the laboratory corresponding to the drying temperature.

We shall consider the equilibrium thermodynamics of a moist dispersed solid with the surrounding air. It is well known [1] that equilibrium is reached when at the same temperatures the free energy of the water vapor in the air is equal to the free energy of the water bond in the dispersed solid:

$$T_1 = T_2;\ \Delta F_1(T_1, p_1) = \Delta F_2(T_2, W). \tag{1}$$

The quantity ΔF_1 is determined by the formula [2]

$$\Delta F_1 = \frac{RT_1}{M} \ln \frac{p_s}{p_1} \tag{2}$$

and depends on the temperature and moisture content of the air (water vapor pressure). The dependence of ΔF_2 on the moisture content and temperature is determined further by the individual properties of the dispersed solid [2]. Thus, ΔF_1 and ΔF_2 in different ways depend on the temperature and moisture content and therefore, in order to obtain an identical degree of desiccation of the dispersed solid W, as can be seen from Eq. (1) it is necessary on the whole to maintain constant two parameters of the drying air – its temperature and moisture content, which is frequently found to be difficult. This difficulty can be avoided by taking into account that for the weakly bound water ΔF_2 depends on the temperature of the solid, so that to a first approximation this dependence can be neglected.

Actually, according to the Gibbs–Helmholtz equation

$$\Delta L_2 = \Delta F_2 - T_2 \left(\frac{\partial \Delta F_2}{\partial T_2} \right)_W; \tag{3}$$

$\partial \Delta F_2 / \partial T_2$ can be estimated if ΔF_2 and ΔL_2 are known provisionally. For weakly bound water, i.e., water evaporated from a dispersed solid at atmospheric pressure up to a temperature of 105-110°C approximately,

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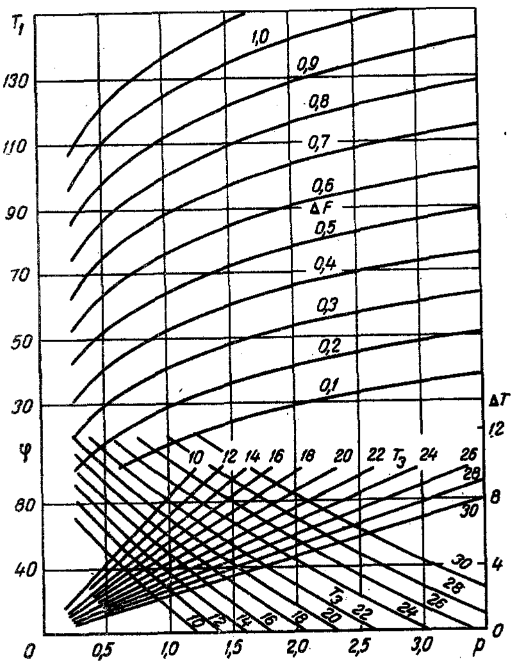

Fig. 1. Air-humidity diagram (ΔF is the free energy kJ/g; p is the absolute humidity of the air, N/m^2; ΔT is the difference between the dry and wet thermometers in the laboratory, ℃).

ΔL_2 does not exceed 1.0 kJ/g and ΔF_2 falls within the limits $0.5 \leq \Delta F_2/\Delta L_2 \leq 1.0$ [3, 4, 5]. Under these conditions a calculation by Eq. (3) shows that the relative dependence of ΔF_2 on the temperature $1/\Delta F \cdot \partial \Delta F/\partial T$ cannot be greater than 0.3% $\cdot \text{deg}^{-1}$, and usually it is several times less. This conclusion, obtained for weakly bound water of any kind and for any dispersed solids, is confirmed also by direct experiments with silica gel [6] and cement stones [7], for which the dependence of ΔF_2 on temperature is also found to be very small. Consequently, to a first approximation, it can be assumed that for small temperature intervals ΔF_2 is independent of temperature.

The condition for equilibrium is then written as:

$$\Delta F_1 (T_1, p_1) \approx \Delta F_2 (W). \tag{4}$$

It can be seen from Eq. (4) that, taking account of the approximation made, the equilibrium moisture content of a dispersed solid is determined only by the magnitude of the free energy of the water in the surrounding air ΔF_1, independently of the temperature for which the given value of ΔF_2 is obtained.

Consequently, instead of two independent parameters T_1 and p_1, defining the equilibrium of a dispersed solid with the drying air, it is sufficient to hold only one parameter constant – ΔF_1, and thus to obtain an almost identical degree of desiccation W of the dispersed solid. In other words, moisture variations in the air in the laboratory can be compensated by a corresponding change of the drying temperature.

In order to find ΔF_1 of the air rapidly at a specified temperature and humidity, the diagram in Fig. 1 has been constructed. In contrast from the other well-known diagrams of air humidity [8], the free energy ΔF_1 and not the enthalpy is plotted in T–p coordinates. The calculation was carried out by formula (2) based on the tables in [9]. Knowing the absolute humidity of the air in the laboratory (and, consequently also, in the ventilated desiccator), from the graph of Fig. 1 it is easy to determine the drying temperature at which a specified value of ΔF_1 is attained. For convenience of usage, diagrams are given in the lower part of Fig. 1 which enable the absolute humidity of the air p to be found rapidly, if its relative humidity q and the temperature, or the dry (T_3) and wet (T_4) thermometer temperature are known.

The curves of Fig. 1 show that variations of the drying temperature, compensating changes of humidity of the air in the laboratory, can be extremely important especially in those cases when it is necessary to compare the results of experiments carried out at different times of the year and in different climatic conditions. Thus, by changing the relative humidity of the air in the laboratory from 30% at 18℃ in winter to 70% at 26℃ in summer, ΔF_1 in the ventilated desiccator heated to 105℃ changes from 0.90 to 0.68 kJ/g, which corresponds to a change of temperature from 93 to 121℃ with constant air humidity.

Correspondingly also, samples of a dispersed solid dried at a temperature of 105℃ and different ambient air humidities yield a different quantity of water and its relative dry weight is found to be different. These variations of relative dry weight, of course, will be different for different samples and they will depend on the amount of water in the sample, the binding energy of which lies in the stated range of moisture content, i.e., they depend on the value of $\partial W/\partial \Delta F_2$ for a given sample. For various clays, soils, woods, and other colloidal capillary-porous solids the relative dry weight in the example given may vary by 2-4%, which is considerably greater than that permitted in the error measurements.

The discussions presented above are particularly important when investigating cement stones and concrete containing both strongly and weakly bound water. Actually, for many of the tests on concrete stones (for example, gas penetrability), it is very important to remove all the capillary and adsorbed water as far as possible, but without affecting the structural chemically bound water. In the case of normal drying at 105℃, part of the chemically weakly bound water is evaporated from cement stone [7]. Because of this, many researchers resort to drying with ethyl alcohol and ether [10], to drying over magnesium perchlorate

[11] at room temperature and, finally, to reduction of the net pressure of the air also at room temperature or with a small increase of temperature, taking into account that under such "mild" conditions of drying the structural water will not be evaporated. Nevertheless, the data considered above show that it is almost immaterial whether cement stone is dried by simple increase of temperature with the ambient atmospheric moisture or whether the air humidity is reduced without changing the temperature – the equilibrium moisture content of the sample will be determined mainly by the value of ΔF_1 of the water vapor in the air and will depend to a slight degree on the temperature at which the value of ΔF_1 is attained.

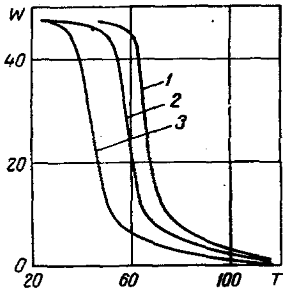

Fig. 2. Dependence of equilibrium moisture content W(%) of calcium hydrosulfoaluminate on the drying temperature T (°C) for an 80% relative humidity of the ambient air (at 20°C) (1); 50% (2); and 20% (3).

On the other hand, drying by normal heating in contrast from the other methods mentioned above possesses the advantage that it permits in the first place fixing reliably the buildup of equilibrium by the constancy of the sample weight and, secondly, knowing the value of ΔF_2 at which the sample is dried. For this, it is necessary to know only the temperature of the drying air and its relative humidity. As regards the level of ΔF_2 at which cement stone can be dried without risk of removing the chemically bound water, it is necessary to determine it from the $\Delta F_2 = \Delta F_2(W)$ curves for those compounds which are present in the cement stone.

This is shown in Fig. 2, where the equilibrium moisture content of calcium hydrosulfoaluminates (one of the components of cement stone) is calculated on the basis of data from [7] as a function of the drying temperature for different relative humidities of the ambient air at 20°C. Thus, with a relative humidity of the laboratory air of 20%, evaporation of the water of crystallization from the sample begins even at 40°C; if, however, the air humidity is equal to 80%, then the sample can be heated to 60°C without destruction of its structure.

Finally, the results given enable a strict thermodynamic division to be made of the water in dispersed solids into weakly and strongly bound water. At present, in order to determine the dry weight of the substance, the accepted method is drying at 105°C which, with the normal humidity of air in the laboratory, corresponds to an equilibrium free energy of ~0.8 kJ/g. This value can be taken conveniently as an arbitrary limit. Water with lower binding energy and, consequently, removeable under normal conditions at a temperature of 105°C, is assumed to be weakly bound and water with a higher binding energy is assumed to be strongly bound. Despite the arbitrariness and apparent randomness of such a limit, its introduction is sensible, as it carries a strictly thermodynamic basis into the already-existing practice of provisional division of water into "structural" and "weakly bound," which can be removed by drying at a temperature of up to 150°C.

NOTATION

ΔF_1	is the free energy of water vapor in air;
ΔF_2	is the free energy of bound water in dispersed solid;
T_1	is the temperature of drying air, °C;
T_2	is the temperature of dispersed solid, °C;
T_3	is the temperature of air in laboratory, °C;
p_1	is the water vapor pressure (absolute air humidity);
p_S	is the saturated water vapor pressure at temperature T_1;
φ	is the relative humidity of air, %;
R	is the gas constant;
M	is the molecular weight of water;
W	is the moisture content of dispersed solid;
ΔL_2	is the internal binding energy (thermal effect) of water in dispersed solid.

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