ONE CASE OF THE PROBLEM OF WEIGHT CURVES

AND DRYING DERIVATOGRAMS WITH DESORPTION

OF A MULTIFRACTIONAL WATER ABSORBATE

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UDC 66.047.9

The case of interpretation of weight curves and drying derivatograms of moist materials with a multifractional composition of the absorbate is considered. A method of evaluating the heats of dehydration of the fractions is proposed.

In a study of the dehydration of adsorbents the thermographic method is a powerful tool in investigating adsorption. As a rule the method is used for a qualitative analysis of the relation between the adsorbate and the adsorbent and the process of desorption [1-3]; at the same time the obvious relation between the shapes of the weight and drying rate curves and heat of adsorption (desorption) [3] enable us to hope for the possibility of measuring its value without technical reequipping of the method.

The complete information contained in the weight and drying rate curves can be obtained after a sufficiently rigorous solution of the problem of dehydration of a specimen of a particular shape at a temperature varying linearly in time. The latter condition at first sight seriously complicates the problem by the appearance of secondary effects (thermal diffusion, nonequilibrium diffusion [4]). However, it is possible to impose an additional condition of a quasi-steady state of the recording process in the experiment, which permits neglecting effects related with the thermal conductivity of the specimen. Furthermore, in most cases the heat of dehydration exceeds considerably the activation energy of diffusion, which, as will be shown below, markedly reduces the effect of diffusion on the dehydration process.

This article is devoted to the solution of the problem of the weight curves and drying derivatograms during dehydration of a spherical specimen for a sufficiently slowly varying temperature.

The distribution of the concentration C in time in a spherical isotropic specimen is given by the diffusion equation

$$\frac{1}{D} \cdot \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial \rho^2} + \frac{2}{\rho} \cdot \frac{\partial C}{\partial \rho} \tag{1}$$

and by the experimental conditions

$$T = T_0 + \alpha t \quad \text{and} \quad D = D_0 \exp\left(-\frac{W}{T}\right), \tag{2}$$

which imply a sufficiently slow change of temperature, permitting us to neglect the effects of thermal conductivity, thermal diffusion, and relaxation mechanisms of transfer, and, as a consequence, to postulate the immobility of the interface R = const.

The mass flow and concentration are continuous functions of their arguments in the region $\rho < R$, i.e., only within the specimen, up to its surface. Evaporation of moisture from the surface of the specimen is a typical adsorbate-gas phase transition; the heat of vaporization-dehydration q in the general case is not equal to W, and therefore the boundary conditions on the surface necessarily contain a singularity of the functions $\partial C/\partial \rho$ and $\partial^2 C/\partial \rho^2$, which can be introduced easily on the assumption of continuity of the
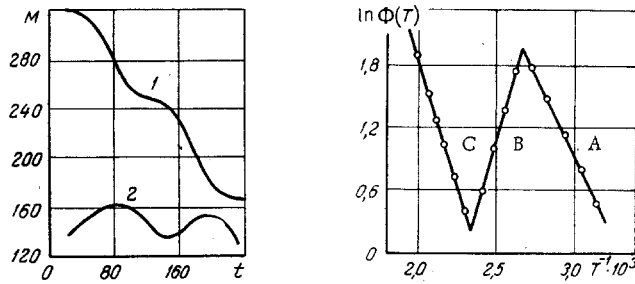
Fig. 1. Weight curves and drying derivatograms of wheat grain: 1) curve of the weight change of the specimen M, mg; 2) curve of the rate of weight change of the specimen during dehydration dm/dt; t, °C.

Fig. 2. Graph of the function $\Phi(T)$ according to the experimental results of drying wheat grain: A) dehydration of first fraction; B) transitional region, end of dehydration of first fraction and start of second; C) dehydration of second fraction.

mass flow, i.e., in terms of the first Fick law:

$$\frac{1}{S} \cdot \frac{dm}{dt} = -D\frac{\partial C}{\partial \rho}\bigg|_{\rho=R-0} = -D_R\frac{\partial C}{\partial \rho}\bigg|_{\rho=R+0}.$$

Here D_R is the fictitious diffusion coefficient reflecting the exchange between the absorbate–vapor phases on passage of the mass flow through the surface. The mass transfer process proper through the boundary layer is conveniently assigned by Newton's equation

$$\frac{1}{S} \cdot \frac{dm}{dt} = -\rho(KC_R - C_\infty)$$

with a mass-transfer coefficient in the case of molecular mass transfer $\beta \sim T^{-3/2}$ [5], $K \sim D_R$ [6], laboratory moisture content C_∞, moisture content on the surface of the specimen $C_R = C|_{\rho=R+0} = C|_{\rho=R-0} + 0(\rho)$ ($0(\rho)$ is a small quantity), and KC_R is the moisture content above the surface of the specimen [6].

The singularity thereby introduced on the surface is typical for adsorption in general and is related with the introduction of an interface, which in the given case is real only mathematically [6, 7].

Temperature (Time) Dependence of Moisture Content. Equation (1) reduces to the dimensionless form

$$\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial y}{\partial r} \tag{3}$$

by substitutions

$$\frac{R^2}{D} \cdot \frac{\partial}{\partial t} = \frac{\partial}{\partial \tau}, \quad \tau = \frac{D_0 W}{\alpha R^2}\int_{T_0/W}^{T/W} \exp\left(-\frac{1}{z}\right)dz, \quad r = \frac{\rho}{R}, \quad y = \frac{C}{C_0},$$

where $C_0 = C|_{t=0}$ = const, with boundary conditions

$$\frac{\partial y}{\partial r}\bigg|_{r=1-0} = \frac{\beta R}{D}\left(yK - \frac{C_\infty}{C_0}\right), \tag{4}$$

$$y|_{r=1+0} = y(1) = y|_{r=1-0} + 0(r).$$

For any τ the moisture content $M(\tau)$ of the specimen has the form

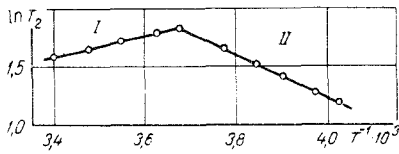$$M = \int_0^1 yr^2 dr. \tag{5}$$

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Fig. 3. Temperature dependence of the spin-spin (transverse) relaxation time T_2 of protons of water molecules in wheat grains. 1) Branch of the dependence of the life time of the water molecule in the 1st fraction; II) branch of the temperature dependence of the characteristic value of T_2 of protons of water molecules in the 1st fraction.

Differentiation of this equality with respect to τ and change of $dy/d\tau$ by means of (3) with subsequent partial integration gives with consideration of (4)

$$\frac{\partial M}{\partial \tau} = -3\,\frac{\beta R}{D}\left(Ky - \frac{C_\infty}{C_0}\right). \tag{6}$$

On the other hand, from (5) on the assumption that the solution of (3) is

$$y = y(\text{Fo}) \qquad \left(\text{Fo} = \frac{\tau}{r^2}\right),$$

the coupling equation easily obtained from here

$$\frac{\partial y}{\partial \tau} = -\frac{2r}{\tau}\cdot\frac{\partial y}{\partial r}$$

permits writting the second equation:

$$\frac{\partial M}{\partial \tau} = \frac{3}{2\tau}\,(y - M). \tag{7}$$

System of Eqs. (6) and (7) is a new formulation of the problem. Heretofore a multifractional composition of the adsorbate was not stipulated in the problem, in connection with which it is necessary to introduce conditions adapting the formalism being developed to the general case.

The multifractional adsorbate within the framework of the problem formulated is determined by the set q_i and W_i for all fractions. For example, q_i and W_i for chemosorption fractions exceed considerably the values of these quantities for fractions with physical adsorption (dispersion interactions, hydrogen bond [6]), the latter fractions in turn differ by the number of bonds and equilibrium distances between molecules. A uniquely determined set of characteristic diffusion coefficients D_i of the fractions corresponds to the set of activation energies W_i [8]; in this case such determination of the diffusion in the adsorbent mass does not change the form of Eq. (1), only the dependence on temperature T changes [8]. In other words, the formalism for the region $\rho < R$ remains unchanged, if we disregard the determination of τ.

In accordance with (6) dehydration occurs only when $K_y - (C_\infty/C_0) > 0$. A change of sign of the difference involves a change of direction of the mass flow, in which case the character of y and K is such that a monotonic change of temperature does not change the sign of the difference. At the same time the mass flow has two asymptotic zeroes for the same fraction. For given C_∞ and equilibrium value of C_R corresponding to it dehydration does not occur without an increase of temperature, after which, if the new value T = const or increases indefinitely, the mass flow, according to (6), again passes asymptotically to zero owing to the establishment of a new equilibrium or complete evaporation of the fraction.

. The formation of a new fraction upon dehydration of the adsorbent is related with unique saturation of the preceding fraction. For example, if chemosorption is possible physical absorption begins only after the intake of the amount of moisture necessary for completion of the first fraction; construction of the first physical fraction of the adsorbate ends with complete population of the adsorption centers, etc. The dehydration process, opposite to this, in the presence of a linearly varying temperature and with the selection of a sufficiently slow recording rate is such that dehydration of the next fraction, with greater q, begins only when $K_y - (C_\infty/C_0) > 0$ for this part of the adsorbate. It is necessary to note that for temperature below the critical, at which the difference vanishes, the mass flow, despite the negative sign of the difference, remains equal to zero for the next fractions by virtue of saturation stipulated above. Thus, the problem in formulating system of Eqs. (6) and (7) remains completely unchanged both for the monofractional and for the multifractional composition of the adsorbate, including the diffusion process, for which the values of D in system (6)-(7) are taken as corresponding to the fraction with $y \neq 0$ and $K_y - (C_\infty/C_0) > 0$ at the given instant, i.e., dehydration of the multifractional adsorbate is described by system (6)-(7) piecewise in order of increasing fractional heats of dehydration.

System of Eqs. (6)-(7) on the assumption $Ky \gg C_\infty/C_0$ reduces to one equation

$$\frac{\tau}{M}\cdot\frac{dM}{d\tau} = -\frac{3}{2}\cdot\frac{ax}{ax+1} \tag{8}$$

with $a = 2/3\cdot R\beta/D_0$, $x = \tau\exp(-W_1/T)$, $W_1 = q - W$, which is easily integrated on the assumption $\beta = $ const. For the molecular process of mass transfer with $\beta \sim T^{-3/2}$ the latter simplication leads to an error in

measuring q of not more than 140 kJ/kg per each 100°C of the recording for possible values of q not less than 900 kJ/kg (rupture of one hydrogen bond).

Two cases are real: with q > W and q = W. The solution of Eq. (8) corresponds to the first, and to the second ($W_1 = 0$) corresponds

$$\frac{1}{M} \cdot \frac{dM}{d\tau} = -\frac{3}{2} \cdot \frac{a}{a\tau + 1} .$$

The last equation is integrated exactly; its solution has the form

$$M = (a\tau + 1)^{-3/2}. \tag{9}$$

After simple operations we obtain from (9) a function $\Phi(T)$ approximating the thermographic drying material of the form

$$\Phi(T) = M^{-5/3} \frac{dM}{dT} = \frac{\beta}{\alpha R} \exp\left(-\frac{W}{T}\right) . \tag{10}$$

The construction of the left-hand side of (10) from the curves M(T) and dM/dT does not present particular difficulty, the construction of its graphs in coordinates $\ln(-M^{-5/3}(dM/dT))$ and $1/T$ (see Fig. 2) allows calculating W; in so doing it is necessary to add a correction of 140 kJ/kg per each 100°C of the recording to the value found.

The first case q > W with Eq. (8) reduces to integration of the approximate formula (8)

$$\frac{1}{M} \cdot \frac{dM}{dx} = -\frac{3}{2} \cdot \frac{a}{ax + 1} , \tag{11}$$

which is obtained from (8) by substituting $x = \tau \exp(-W_1/T)$ with $d/d \simeq x/\tau \, d/dx$ for $W_1/T \cdot aR^2/DT \ll 1$. The solution of (11) coincides formally with (9):

$$M = (ax + 1)^{-3/2}.$$

The rules of treating the experimental drying material in this case remain unchanged, but as a result of calculation the value of the heat of dehydration q is found, and the activation energy of diffusion has practically no effect on the shape of the curves M(T) and dM/dT.

As a consequence of the stepwise dehydration of the fractions it is possible to find the relative distribution of the mass of the water adsorbate by fractions. Actually, the start of dehydration of the fraction corresponds to one of the zeroes of the mass flow found by (6) and its end to the other. Vanishing of the flow leads to the appearance of plateau sections on the derivatograms of the mass. Thus the value of the segment between two plateaus on the axis of the masses is proportional to the concentration of the fraction.

The calculation results were checked by measurements by the nuclear magnetic resonance (NMR) methods [9] and by recording the weight curves and drying derivatograms of specimens of wheat grain with an initial moisture content of 50% of dry weight. The first method in its spin–echo modification permits, without dehydration, measuring the activation energy of molecular diffusion of each of the fractions by constructing the temperature dependences of the NMR relaxation times [10] and the second method the heats of dehydration. In addition, from the results of measurements by the spin–echo NMR method it is possible to estimate the concentration of fractions [10], which permits a complete check of the problem of dehydration.

The results of the drying experiment are presented in Fig. 1. The values of the water concentrations in the fractions that were found from the M(T) curve proved to be equal to 2/1 (the numerator is the first fraction dehydrated at low temperatures). The fractional composition of the adsorbate and the water concentration in the fractions according to the NMR results agree well with these data.

The energy forms of the experimental material are presented in Figs. 2 and 3. The dehydration branches of the graph of the function $\Phi(T)$ (Fig. 2A, C) are approximated by straight lines in coordinates $\ln(-M^{-5/3}(dM/dT))$ and $1/T$; the values of the heats of dehydrations according to these branches are: $(1220 + 140)$ kJ/mole (6.25 kcal/mole) and $(1740 + 120)$ kJ/mole (8.5 kcal/mole). The activation energies of diffusion corresponding to this, according to the data in Fig. 3, were kJ/mole (4.25 kcal/mole) and 800 kJ/mole (3.45 kcal/mole).

The values of the heats of dehydration found correspond to the rupture of two hydrogen bonds by molecules of both fractions upon desorption, which is consistent with Becker's data [11] on adsorption of

water in grain. The lattice of the adsorbate of the fraction with the smaller heat of dehydration, although it has, as in the second fraction, two bonds per molecule, is distorted considerably and apparently is a secondary formation. The results of the NMR measurements should evidently be interpreted as diffusion with rupture of only one hydrogen bond, i.e., in this case the molecules have two hydrogen bonds each differing in the degree of distortion in the fractions. The corresponding heats of dehydration in this connection are equal to the doubled values of the activation energy: 1830 kJ/mole (7.9 kcal/mole) and 1980 kJ/mole (8.5 kcal/mole), which does not contradict the experiment on drying.

The experiment on drying thus pertains to the second case of the problem of dehydration with Eq. (8) considered above, for which diffusion is insignificant. This distinctive feature is possibly a rather particular, if not general, case of adsorption. During diffusion the molecule at the time of change of position remains within the phase, i.e., as an adsorbent, and the other molecules of the adsorbate continue to act so that its potential energy does not vanish at the time of movement.

The formalism of the problem of drying is constructed on the macroscopic process of dehydration. Precisely for this reason the scope of problems that can be solved with the use of the results of the problem are not limited just to adsorption. As objects we can use also crystal hydrates in the study of polymorphic transformations (crystal hydrate—anhydrous form) during dehydration. Of interest in this aspect would be the set up of experiments on anisotropy of desorption of fibrous adsorbents (asbestos, wood) having an important practical value. In conjunction with this, when setting up a particular experimental problem it is necessary to take into account the limitation of the applicability of the formalism of the problem of dehydration (desorption), which presuppose a discrete distribution of the bond energies. In other words, in cases of investigating adsorption the saturation of the adsorbent should be limited to values close to the population of the monolayer, otherwise the continuous distribution of bond energies caused by molecular exchange in the polymolecular adsorbate precludes the possibility of using the approximating formula.

NOTATIONS

C is the moisture concentration in the specimen, kg/m^3;

C_∞ is the moisture content of laboratory air, kg/m^3;

t is the time, sec;

ρ is the radius-vector modulus, m;

T is the Kelvin temperature;

D is the coefficient of diffusion of moisture in specimen, m^2/sec;

α is the recording rate, deg/sec;

R is the radius of specimen, m;

q is the heat of vaporization (dehydration);

W is the activation energy of moisture diffusion in specimen (both in units of the Boltzmann constant);

S is the total surface of specimen, m^2;

m is the mass (moisture content), kg;

β is the coefficient of mass transfer through boundary layer;

C_0 is the concentration at initial instant $t = 0$, $C_0 = C|_{t=0} = const$;

T_2 is the NMR spin-spin (transverse) relaxation time of protons of water molecule.

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