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Abstract

Full Text

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ANALYSIS OF THE FORMS OF BONDING AND THE STATE OF MOISTURE ABSORBED BY A DISPERSE BODY BY MEANS OF KINETIC DRYING CURVES

(Presented by Academician P. A. Rebinder, 8 X 1959)

Drying is a complex process, not only in heat engineering but also in physicochemistry; its regularities depend first of all on differences in the forms of bonding and in the state, within the body, of the absorbed moisture. The influence of the forms of moisture bonding on the drying process is most clearly represented by drying-kinetics curves ([1–4])—the drying thermogram, which is the curve of the change in temperature of a thin (1-2 mm) sample of the moist substance being dried, and the drying curve—the curve of loss in weight of the same body.

Figure 1 presents kinetic drying curves typical of different groups of bodies. The drying thermograms were recorded with self-recording apparatus ([5]) in terms of the temperature difference $\Delta\theta$ between the substance being dried and the constant temperature of the surrounding air, while the drying curves were recorded in terms of W, the weight of the moisture contained in the body.

Fig. 1. Drying-kinetics curves. Drying thermograms (I, III, V) and drying curves (II, IV, VI) of thin samples, moistened with water, of coarsely porous ($1a$), colloidal capillary-porous ($1b$), and polycapillary-porous ($1v$) substances. W –moisture content, $\Delta\theta$ –temperature, τ –time.

Before the experiment the samples were moistened with water to full moisture

capacity; in this case, above the surface of the substance being dried in the cuvette there was always a small layer of free liquid. Therefore drying of the samples always began with evaporation of the excess free water; in connection with this, all thermograms have an upper horizontal segment, bounded by the position of singular point 1, corresponding to evaporation of free liquid.

By projecting the singular points of the thermograms onto the corresponding drying curves, one can determine the moisture content of the substance being dried at one or another singular point (see Table 1). For comparison, Table 1 includes values of the moisture content of the same substances obtained by us by other methods, as well as values taken from the literature ([6,7]).

The drying thermogram of quartz sand (1*a* in Fig. 1), in its form and in the positions of the singular points on it, is typical for the drying of coarsely porous bodies, during whose drying capillary moisture evaporates from pores with a radius greater than 10^{-5} cm. We have shown ([2]) that the moisture content of a coarsely disperse substance at the first singular point of the thermogram corresponds to the maximum

moisture capacity (soaking moisture), at the second point—the beginning of evaporation of joint water, located in the form of isolated water cuffs at the contact points of individual sand grains, and at the third point—the evaporation of joint moisture at the moment of drying when the curvature of the menisci of the water cuffs becomes less than 10^{-5} cm.

Table 1

Differential moisture content as a percentage of the weight of dry substance at 20–25°, as determined by various methods (in percent)

Moisture-binding body	Amount of hygroscopic moisture: by adsorption isotherm	Amount of hygroscopic moisture: by point 3 of thermogram	Maximum amount of adsorbed moisture: by adsorption isotherm	Maximum amount of adsorbed moisture: by heat of wetting	Maximum amount of adsorbed moisture: by indicator method	Maximum amount of adsorbed moisture: by hygroscopic method	Maximum amount of adsorbed moisture: by point 4 of thermogram	Moisture of monomolecular adsorption: by adsorption isotherm	Moisture of monomolecular adsorption: by point 5 of thermogram
Adsorbents									
Silica gel	32.6	31.8	13.9	—	—	—	14.1	7.2	8.3
MSM									

Moisture-binding body	Amount of hygroscopic moisture: by adsorption isotherm	Amount of hygroscopic moisture: by point 3 of thermogram	Maximum amount of adsorbed moisture: by adsorption isotherm	Maximum amount of adsorbed moisture: by heat of wetting	Maximum amount of adsorbed moisture: by indicator method	Maximum amount of adsorbed moisture: by hygroscopic method	Maximum amount of adsorbed moisture: by point 4 of thermogram	Moisture of monomolecular adsorption: by adsorption isotherm	Moisture of monomolecular adsorption: by point 5 of thermogram
Silica gel KSM	33.5	32.5	17.6	—	—	—	18.3	8.1	8.9
Silica gel VZhK2	83.6	87.0	7.0	—	—	—	6.6	2.6	3.0
Silica gel E	170.0	172.0	10.0	—	—	—	9.8	3.4	3.0
Activated carbon	37.8	39.6	3.6	—	—	—	4.5	—	—
Clays									
Zhabinka bentonite	41.1	42.5	—	22.7	—	19.7	21.9	—	14.9
Pyzhev bentonite	28.8	31.1	—	20.1	20.7	19.2	21.4	—	14.0
Pobiyanka bentonite	30.1	31.5	—	21.0	—	18.0	21.6	—	14.5
Gorbsky bentonite	—	23.1	—	11.5	—	10.0	11.4	—	7.2
Chasov-Yar clay	16.0	14.8	—	5.4–7.0	7.1	6.5	6.8	—	3.5
Poltava clay	17.1	18.0	—	6.0	6.8	7.0	6.0	—	3.8
Soils									

Moisture-binding body	Amount of hygroscopic moisture: by adsorption isotherm	Amount of hygroscopic moisture: by point 3 of thermogram	Maximum amount of adsorbed moisture: by adsorption isotherm	Maximum amount of adsorbed moisture: by heat of wetting	Maximum amount of adsorbed moisture: by indicator method	Maximum amount of adsorbed moisture: by hygroscopic method	Maximum amount of adsorbed moisture: by point 4 of thermogram	Moisture of monomolecular adsorption: by adsorption isotherm	Moisture of monomolecular adsorption: by point 5 of thermogram
Soddy-gley	13.5	13.0	7.5	—	8.4–10.0	9.1	8.0	—	5.0
Chernozem-meadow	8.9	10.7	5.0	—	7.3–7.5	5.4	5.8	—	3.8
Deep chernozem	6.8	8.7	3.4	—	5.8–6.1	4.5	5.2	—	2.8
Soddy weakly podzolic	6.0	7.0	2.6	—	3.7–4.7	3.5	3.3	—	1.8
Polymers									
Potato starch, native	72.3	61.6	—	31–35	35.0	—	33.8	—	18.0
Gelatin	92.4	83.0[1]	—	—	—	—	34.2	—	29.7
Agar	—	87.1[2]	—	—	—	—	39.1	—	27.2
Sulfite cellulose	30.2	35.1	—	17.5	—	—	16.0	—	13.1

[1] Thermogram at 43.6°. [2] Thermogram at 42°.

Thermogram **1b** is typical for the drying of thin colloidal capillary- and quasi-capillary-porous bodies with a developed fine-pore structure. In our experiments, such bodies included clays of various minerals, soils of different types, starch, flour, egg powder, gelatin, agar, leather, cellulose, etc. The drying thermograms of colloidal bodies ([3], [4]) consist of a horizontal segment bounded by points 1–3, corresponding to the time of evaporation of osmotic moisture, and a lower S-shaped part of the curve, corresponding to the removal of hygroscopic

moisture from the body. By the singular points 4 and 5, the lower section of the thermogram is divided into three parts, corresponding to the time of successive removal during drying from the body of three types of moisture: moisture of capillary condensation from micropores with a radius of less than 10^{-5} cm (points 3, 4), moisture of polymolecular adsorption (points 4, 5), and, finally, the moisture most strongly bound to the substance—the moisture of monomolecular adsorption.

Thermogram *1* is typical for isothermal drying of a polycapillary-porous substance with a mixed macro- and microporous structure. In our experiments, the model for such bodies was thin layers of powders of silica gels and activated carbon of various structural types ([8]), wetted with water or methyl alcohol. At singular point 3, corresponding to the maximum hygroscopic moisture content of the substance, the thermogram is divided into two parts—the upper and the lower. In this case, the upper part, in the form of the curve and in the position of the singular points, is identical with the drying thermogram of a coarsely porous substance; it pertains to the time of successive evaporation, during drying, of capillary moisture differing in its state in the coarse pores of the intergranular space of the powders. The lower part of the thermogram has an S-shaped form, the same in shape as the drying thermograms of finely porous colloidal substances. In terms of the moisture content of the substance, each section of the lower part of the thermogram corresponds to the time of successive evaporation of hygroscopic moisture ([2]), differing in the forms and types of its bonding with the substance (see Table 1).

Thus, of the three drying thermograms typical for different groups of porous bodies, the thermogram of a polycapillary-porous substance (*1* in Fig. 1) is the more general one, since the drying thermograms of coarsely porous and colloidal substances are included in it as component parts of one and the same curve. Therefore, thermograms of isothermal drying of thin specimens of capillary-porous substances of different colloid-physical nature should be regarded as one of the particular cases of the same general drying thermogram of a polycapillary-porous substance, from which separate segments of the curve drop out owing to the absence, in the substance being dried, of moisture of one or another type of bonding. The general form of the thermogram of isothermal drying of a thin specimen of one or another substance and the number of singular points on it depend only on the differential water-absorbing capacity of the given substance with respect to moisture of different forms and types of bonding.

Fig. 2. Diagram of the kinetics of successive evaporation of moisture during drying of thin capillary-porous materials of different nature. *I*—thermogram, *II* —drying curve. Types of moisture bonding: *a*—osmotic moisture of a colloidal body or moisture in the capillary state in pores; —contact moisture of pores; —capillary moisture of micropores; —moisture of polymolecular adsorption; — moisture of monomolecular adsorption. *a*, $-r > 10^{-5}$ cm; $-r < 10^{-5}$ cm

On the basis of the considerations set forth, in Fig. 2 we present a scheme of the drying kinetics of thin materials, visually representing the general law

Fig. 2. Diagram of the kinetics of successive evaporation of moisture during drying of thin capillary-porous materials of different nature. *I*—thermogram, *II* —drying curve. Types of moisture bonding: *a*—osmotic moisture of a colloidal body or moisture in the capillary state in pores; —contact moisture of pores; —capillary moisture of micropores; —moisture of polymolecular adsorption; — moisture of monomolecular adsorption. *a*, $-r > 10^{-5}$ cm; $-r < 10^{-5}$ cm

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of the kinetics of successive removal from a material of moisture of different forms and types of bonding with the substance. The scheme provides for the possibility of removing from a body moisture of two principal forms of bonding: physicochemical and physico-mechanical, subdivided by the singular points of the thermogram into six types. Physico-mechanically bound moisture includes three types of capillary moisture, two of which represent capillary water differing in special states (capillary and contact) in the coarse pores of the body, while the third is capillary moisture of micropores. Moisture of the physicochemical form of bonding may consist of osmotic water and two types of adsorbed moisture —moisture of polymolecular and monomolecular layers (loosely and strongly bound moisture).

Since drying is a thermal-power process in which the sequence of moisture evaporation is determined by the degree of intensity of its bond with the substance, the proposed scheme may also be regarded as a scheme for classifying the moisture removed during drying according to the different forms and kinds of its bonding with the substance. In this connection, of course, it should be borne in mind that the energetic bond of moisture with the substance is a true one only in cases where adsorbed moisture is bound. The bond of moisture of all other kinds is only equivalent to a bond energy equal to the energy of isothermal removal of it during drying ([9]).

A classification of moisture based on the regularities of drying kinetics not only does not contradict the rational scheme for classifying moisture according to the forms and kinds of its bond with a substance proposed by P. A. Rebinder ([9]), but, on the contrary, refines it in the direction of further detailing the individual kinds of bonding.

The scheme in Fig. 2 has been taken by us as the basis for a new thermographic method of quantitative analysis of the moisture absorbed by a body according to the forms and kinds of its bonding with the substance. The experimental aspect of applying the new method consists in the simultaneous recording, by means

of self-recording apparatus, of the drying thermogram and the drying curve of a thin specimen of the substance under investigation. From the form of the thermogram obtained, it is immediately possible to determine to which of the groups, in terms of differential water-absorbing capacity, the given substance belongs. For quantitative analysis it is necessary, from the drying curve, to determine the moisture content of the material corresponding to each singular point of the thermogram, and, in accordance with the general scheme of Fig. 2, to determine the amounts of moisture of the different forms and kinds of bonding with the given substance.

As can be seen from Table 1, the results of analyzing the differential water-absorbing properties of various substances with the aid of kinetic drying curves lie within the range of values determined by other laboratory methods. The error in determining moisture of one or another kind of bonding by the thermographic method depends on the accuracy with which the drying-kinetics curves are recorded. In our experiments the thermograms were recorded with an accuracy down to hundredths of a degree, and the drying curves with an accuracy down to tenths of a percent of the moisture content of the substance. Therefore the error of determination was no more than 1–2%.

The new kinetic method for analyzing the forms and kinds of bonding of moisture with a substance is advantageously distinguished by the fact that, from the results of a single experiment, it makes it possible to determine the water-retaining capacity with respect to all possible forms and kinds of moisture bonding, with a comparatively small expenditure of time (several hours).

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Note: Figure translations are in progress. See original paper for figures.