EQUILIBRIUM MOISTURE CONTENT OF FOODSTUFFS

G. K. Filonenko and A. I. Chuprin

Inzhenerno-Fizicheskii Zhurnal, Vol. 13, No. 1, pp. 98–104

UDC 641.0:530.093

Experimental data obtained for the equilibrium moisture content of 11 materials by the dynamic method provide a basis for an analysis of the hygroscopic properties of foodstuffs. Equations of the sorption and desorption isotherms are given.

Foodstuffs are capillary-porous colloidal materials and their interaction with moisture in the hygroscopic region depends on the molecular interaction of the material with the surrounding moist air. The mechanism of this action and the way in which moisture is bound with the material are different for different materials. In practice the removal of moisture requires the expenditure of heat to overcome the energy of binding of the moisture with the material and to evaporate the moisture. H Hence, the classification of the ways of binding of moisture with materials in the hygroscopic region is based on the evaluation of the binding energy [1]. The moisture-binding energy for a particular specific moisture content is calculated from the sorption and desorption isotherms.

An isolated system consisting of a material and damp air tends to the most probable and unique state—thermodynamic equilibrium—which is characterized by the equality of the factors affecting the rate of the process in the whole system: the temperature and water vapor pressure. In equilibrium the temperature of the material becomes equal to that of the surrounding air and the partial pressure of water vapor above the material is equal to the partial pressure of water vapor in the surrounding air. With such a system we can, of course, have cases where the material absorbs moisture from the air and becomes moist (sorption process) [2] or, conversely, gives up moisture to the air and becomes drier (desorption process). The direction of the process depends on the initial moisture content of the material. It is obvious that the equilibrium moisture content of the material characterizes its hygroscopic moisture capacity.

Numerous investigations have shown that the equilibrium moisture content of a particular material depends on the relative humidity of the air φ, the temperature, the direction of the process (absorption or desorption of moisture), and other factors [3,4].

It is impossible at present to obtain an analytical relationship between the bound moisture and the relative humidity of the air in the whole range of φ. Hence, the collection of experimental data on equilibrium moisture content is of great importance in the theory and practice of drying of foodstuffs [5,6].

In fact, the removal of hygroscopic moisture from a material requires the expenditure of heat to overcome the moisture binding energy and to evaporate this moisture. For a material with a given moisture content the binding energy is

$$E = -RT \ln \varphi.$$

The specific mass capacity of a material in the hygroscopic region is determined from the isotherms.

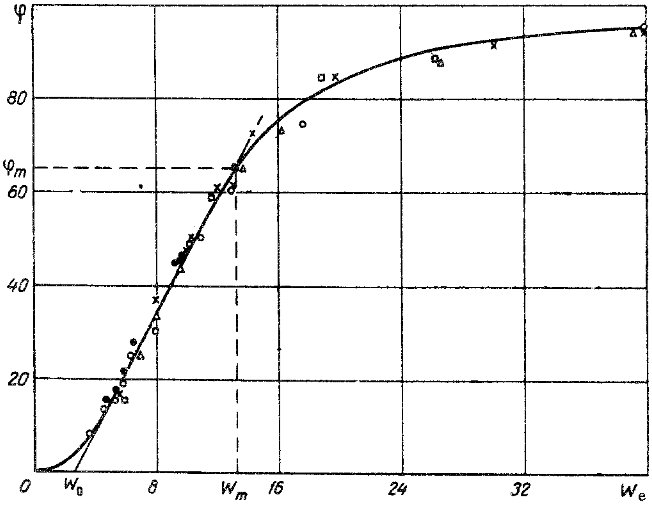

Fig. 1. Isotherm of potato crackers at T = 313° K (drawn from mean points).

An investigation of the families of isotherms obtained at different temperatures can provide the value of the thermogradient coefficient. From the amount of adsorption-bound moisture (the moisture of the monomolecular layer) determined from the isotherms, the specific surface of the solvent for water can be calculated with a known degree of accuracy. Finally, the sorption and desorption isotherms are used to determine the optimum storage conditions for the product.

Hence, a complete understanding of drying and moistening processes, the practical accomplishment of these processes, and the choice of the optimum drying conditions and the parameters of the drying agent require a complete investigation of the sorption and desorption isotherms.

The most common way of determining the equilibrium moisture content up till now has been the tensimetric method with solutions of salts and acids. It should be noted, however, that the long duration of the experiment renders the tensimetric method unsuitable for the majority of foodstuffs, since a moist product is destroyed by mold long before equilibrium is attained.

In the drying laboratory of Odessa Technological Institute of the Food and Refrigeration Industry a great deal of experimental work has been done on the equilibrium characteristics of foodstuffs. A special apparatus for determining the equilibrium moisture content by a rapid method is used (a flow of air is used and the time required is 8–12 hr).

Figures 1 and 2 show the desorption isotherms of eight foodstuffs: crackers—a product obtained by drying potato puree concentrate with starch and flavoring additives, dogberries, apricot kernels, peppercorns, peas, carrots, persimmon, and garden beet—products which are dried by convection.

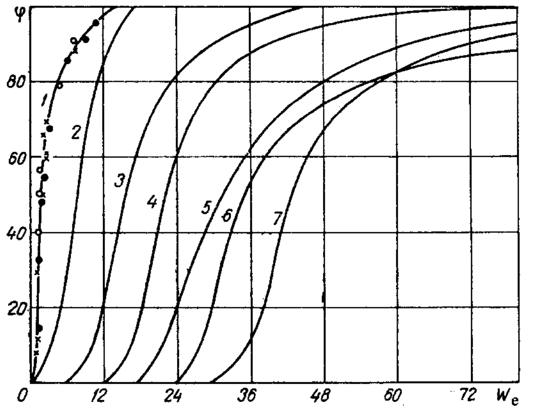

Fig. 2. Desorption isotherms: 1) dogberries, T = 293° K; 2) apricot kernels, T = = 293° K; 3) peppercorns, T = 303° K; 4) peas, T = 298° K; 5) carrots, T = = 293° K; 6) persimmon, T = 303° K; 7) garden beet, T = 293° K.

As the graphs in Figs. 1 and 2 show, the isotherms are asymmetric S-shaped curves which differ from one another not only in slope, but also in shape. The points marked in Fig. 1 are for different series of experiments, which illustrates the good reproducibility of the results of the rapid method.

The different shape of the different parts of the isotherms illustrate the different ways in which moisture is bound with the material. All the isotherms are drawn to pass through the origin. It is very difficult to investigate the relationship on this part of the isotherm and, hence, researchers produce the isotherms to the origin rather arbitrarily, assuming that when $\varphi = 0$, $w_e = 0$, irrespective of the temperature. This arbitrariness stems from the fact that it is very difficult to distinguish between removable water and chemically bound water. This region characterizes the adsorption-bound moisture of the monomolecular layer—the most tightly bound moisture. The amount of this moisture can be used to calculate the surface of the sorbent for water. According to Filonenko's suggestion, the adsorption-bound moisture of the monomolecular layer is given by the moisture content ω_0—the point of intersection of the produced linear part of the isotherm in Fig. 1 with the axis of equilibrium moisture content. Each isotherm has a linear portion. It is most distinct in the case of apricot kernels and terminates at $\varphi = 75\%$; it is less distinct in the case of apples where it terminates at $\varphi = 30\%$. The linear part of the isotherm characterizes the binding of moisture by sorption and the formation of polymolecular layers, but the capillaries are still not filling up with moisture. The end of the linear portion is characterized by the values φ_m and w_m. Beginning at these values the isotherm turns sharply to the right even with a very slight increase in φ. The relationship between the equilibrium moisture content and the relative humidity of the air on this part of the isotherm is of a less definite nature. It is difficult to determine experimentally the maximum hygroscopic moisture content of materials which swell to a limited extent and it can be obtained only by extrapolation of the curve. The isotherms actually turn to the right and do not intersect the line $\varphi = 100\%$. This can be attributed to the fact that at $\varphi = 100\%$ the water vapor pressure over the material must be equal to the vapor pressure over pure water. Bound water, however, is not pure water, but a solution with properties which differ from those of pure water. Hence, the water vapor pressure over the moist material will always be lower than over pure water. In view of the indefinite nature of the relationship, most research workers terminate the isotherms at $\varphi = 85$–90%.

The upper curvilinear part of the isotherm characterizes the moisture bound by capillary and osmotic forces, and by wetting water, the relationships governing the retention of such water are extremely indefinite. This end effect is characterized by a great scatter of the points at $\varphi > 85\%$.

The equilibrium moisture content depends to a lesser extent on the temperature. This relationship has received little study, especially in the case of foodstuffs. The equilibrium moisture content of most foodstuffs decreases with increase in temperature. Figure 3 shows families of isotherms for four products: potato crackers, apricots, apples, and plums. As the graphs show, the variation of the equilibrium moisture content with temperature is different even within one isotherm. This difference is most pronounced in the region up to $\varphi = 80\%$. For φ greater than 95% the curves practically merge.

Since the curves sometimes cross at the top, this means that the equilibrium moisture content is greater, and not less, at higher temperature. This can be attributed to the fact that at temperatures above 330° K and high air humidity the material begins to be affected by the heat, which alters its structure and hygroscopic properties.

The degree to which the equilibrium moisture content depends on the temperature is different for different materials and varies over a wide range. In Fig. 2, curve 1 for dogberries corresponds to three temperatures (293°, 313°, and 333° K). As the graph shows, temperature has practically no effect in this case.

The sorptive properties of materials depend on their structure, which depends in turn on the processing [8]. Hence, the same raw material can be used to give products with different prescribed sorptive properties, as is done in the building materials industry, etc. It is obvious that the identity of the isotherms indicates similarity of the structures of the materials.

The equilibrium moisture content depends least of all on whether it is reached by sorption or desorption. The effect of the direction of the process is manifested in sorption hysteresis and the sorption and desorption isotherms do not quite coincide. The most likely of the numerous explanations of the hysteresis is that which attributes it to the irregular nature of

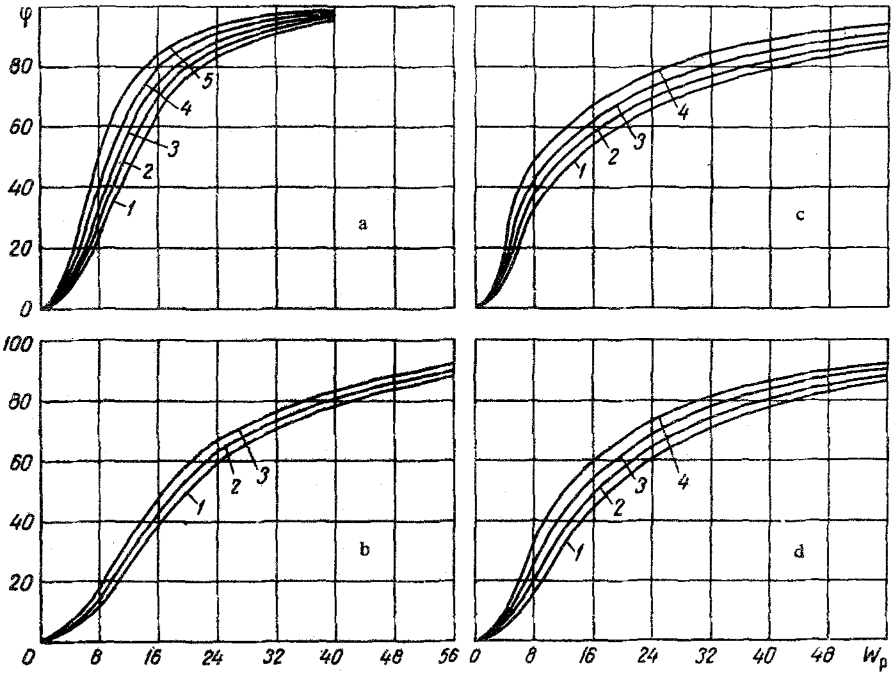

Fig. 3. Desorption isotherms: a) Potato crackers (1—293; 2—303; 3—313; 4—323; 5—333° K); b) apricots (1—293; 2—313; 3—333° K; c and d) apples and plums (1—293; 2—313; 3—333; 4—353° K).

Values of Coefficients k, a, B, and w_m for Isotherms of Some Foodstuffs

Material	Temperature, °K	w_{eI} in range $0–\varphi_m$		w_{eII} in range $\varphi_m–\varphi_{max}$		φ_m	w_m	Isotherms
Dogberries	293	40	50	1.9	60	45	1.75	Drawn through mean points
Apricot kernels	293	30	10	6	48	45	10.4	Desorption
Peppercorns	303	20	6.95	8.4	58	55	10.8	Desorption
Peas	298	25	7	7.4	51	55	11.4	Desorption
Carrots	293	5	8.2	17	80	35	9.5	Desorption
Persimmon	303	20	7.2	17	70	35	7.7	Desorption
Garden beet	293	40	6.9	9	47	50	13.0	Desorption
Potato crackers	293	15	4.78	12.92	51	65	16.1	Desorption
Apricots	293	17.5	3.55	22	75	40	16.2	Desorption
Apples	293	32	8.5	17.6	75	30	7.2	Desorption
Plums	293	13	3.77	20	75	30	12.8	Desorption

the process. Hence, some researchers draw the isotherms through the mean point.

Figure 1 shows the isotherm for potato crackers drawn from points obtained by sorption and desorption. It is obvious that it is difficult to separate points obtained by the dynamic method of determining equilibrium moisture content.

We have already pointed out that the isotherms represent a complex relationship between the equilibrium moisture content of a material and the degree of saturation and temperature of the air. The way in which moisture interacts with a material is different at different stages. Hence, it is difficult to represent the isotherm by one equation. According to Filonenko's suggestion the isotherm can be divided into two parts (Fig. 1): 1) from w_0 to w_m; 2) from w_m upward.

The part from 0 to w_0 is of limited practical importance and is excluded from the analysis. The value w_0 characterizes the adsorption-bound water of the monomolecular layer. The linear part from w_0 to w_m, which represents the sorption-bound water, is given by the equation

$$w_{p_I} = \frac{a+\varphi}{k}. \tag{1}$$

The coefficient k characterizes the temperature dependence of the equilibrium moisture content on this part. For different materials this dependence is different:

$$\text{for crackers} \quad k = 4.75 + 0.00075\,t^2, \tag{1a}$$

$$\text{for apricots} \quad k = 3.44 + 0.00025\,t^2, \tag{1b}$$

$$\text{for apples} \quad k = 8.2 + 0.00075\,t^2, \tag{1c}$$

$$\text{for plums} \quad k = 3.64 + 0.00035\,t^2. \tag{1d}$$

The curvilinear portion from w_m upward, which represents capillary-bound and osmotic water, is described very accurately by Filonenko's equation:

$$w_{p_{II}} = \frac{B(\varphi - \varphi_m)}{b - (\varphi - \varphi_m)} + w_m. \tag{2}$$

On this part of the isotherm the temperature dependence of the equilibrium moisture content is characterized by the coefficient B. It is obvious that the value of w_m also depends on the temperature:

for crackers

$$B = 13.4 - 0.00122\,t^2, \tag{2a}$$

$$w_m = 18.8 - 0.135\,t; \tag{2b}$$

for apricots

$$B = 2.3 - 0.05\,t^2, \tag{2c}$$

$$w_m = 17.7 - 0.736\,t; \tag{2d}$$

for apples

$$B = 18 - 0.000125\,t^2, \tag{2e}$$

$$w_m = 8 - 0.04\,t; \tag{2f}$$

for plums

$$B = 20.4 - 0.001\,t^2, \tag{2g}$$

$$w_m = 14.4 - 0.075\,t. \tag{2h}$$

The table gives the values of the coefficients k, *a*, b, B, and also the values of w_m for the isotherms of some foodstuffs.

The collection of experimental data of sorption isotherms at different temperatures will help to establish quantitative and qualitative relationships between the coefficients k and B on one hand, and the temperature and physicochemical properties of foodstuffs, on the other.

NOTATION

w_e is the equilibrium moisture content of material on dry weight basis, %; φ is the relative humidity of air, % or fractional; w_0 is the moisture content characterizing adsorption-bound water of the monomolecular layer; w_m and φ_m denote the point on the isotherm representing the upper limit of linear relationship between w_e and φ; *a* and b are constants for isotherms; k and B are temperature-dependent coefficients in equations of isotherms; E is the moisture binding energy; R is the universal gas constant; t is temperature.

REFERENCES

1. P. A. Rebinder, collection: All-Union Scientific and Technical Conference on Acceleration of Drying and Improvement of the Quality of Dried Materials in the Main Branches of Industry and Agriculture [in Russian], Profizdat, 1958.

2. J. W. MacBain, The Sorption of Gases and Vapors by Solids [Russian translation], Goskhimizdat, Moscow, 1934.

3. A. V. Luikov, Transport Phenomena in Capillary-Porous Bodies [in Russian], Gostekhizdat, Moscow, 1954.

4. A. V. Luikov, Theory of Drying [in Russian], Gosenergoizdat, Moscow, 1950.

5. G. K. Filonenko and P. D. Lebedev, Dryers [in Russian], Gosenergoizdat, Moscow, 1952.

6. L. I. Nikitina, Tables of Equilibrium Specific Moisture Content and Moisture Binding Energy [in Russian], Gosenergoizdat, Moscow, 1963.

7. G. K. Filonenko and A. I. Chuprin, USSR patent No. 185481, Ofitsial'nyi byulleten Komiteta po delam izobretenii i otkrytii pri SM SSSR, no. 17, 1966.

8. A. S. Ginzburg, Drying of Foodstuffs [in Russian], Pishchepromizdat, Moscow, 1960.

14 January 1967

Technological Institute of the
Food and Refrigeration
Industry, Odessa