A THERMODYNAMIC ANALYSIS OF THE DRYING THERMOGRAM METHOD

V. M. Kazanskii

UDC 536.423

A thermodynamic analysis of dispersed particle drying is used to formulate the conditions which must be satisfied in order to correctly record and interpret drying thermograms.

Information concerning pore structures and the bonding of liquids to dispersed particles has been obtained by the analysis of drying thermograms, i.e., curves showing the temperature changes occurring within a body during the drying process [1]. Information acquired in this manner can be considered trustworthy only if the conditions under which the thermogram was recorded were both strictly controlled and consistent with the requirements laid down by drying process theory. The experimental techniques involved in the recording of drying thermograms have been described in detail in [7, 9]. The experience of more than a decade has shown however, that erroneous results can be obtained from thermogram analysis unless certain conditions have been rigorously satisfied during the recording process. A discussion of these conditions is especially important now when the drying thermogram method is being widely used in many laboratories, often, unfortunately, with insufficient care for details.

It is well understood [1] that the drying thermogram method draws on the kinetic principles of liquid vaporization from thin dispersed particle films, the parameters of the surrounding air being held constant. The rate of bound liquid vaporization from a sample is then determined by the difference in mass-transfer potentials, and liquid and vapor mobilities, in the sample and in the surrounding air. This implies that reproducible thermograms can be obtained only if recording is carried out with predetermined and carefully controlled values of the drying air parameters and liquid and vapor mobilities. Both aspects of this problem will be considered in the present paper.

An important consideration here is the fact that thermal exchange between the sample and the surrounding air is controlled by mass transfer, the thermogram itself being only a reflection of mass transfer processes [2]. From this it follows that the form of the thermogram must be determined by the form of the hygrogram, i.e., by the time variation of the liquid vapor pressure above the sample. The fact that the properties of dispersed particles are usually determined from the thermogram rather than the hygrogram traces back to the ease with which accurate thermograms can be recorded. As has already been pointed out in [3], however, mass transfer can with profit be considered separately from thermal exchange in a first-approximation discussion of the optimal conditions for application of the drying thermogram method.

The first prerequisite for thermogram recording is that those parameters of the surrounding air which fix the drying rate be held constant. There are four such parameters, namely, the temperature, pressure, and circulation velocity of the air, and the chemical potential, i.e., the mass transfer potential, of the liquid vapors in the air [4]. The values of the first three of these parameters can be set arbitrarily, and need only be held constant during the recording. On the other hand, the absolute value of the fourth parameter μ is significant, and on two counts. In the first place, the sample loses more and more of its bound water as the recording proceeds, this loss continuing until the value of μ for the sample liquid becomes equal to the value of μ for the liquid vapors in the surrounding air. If, therefore, a series of experiments is carried out on various samples of the same material, with the μ value of the vapors in the drying air held constant at a different value in each experiment, liquid vaporization will cease at a different

---

Kiev Institute of Construction Engineering. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 25, No. 3, pp. 419-423, September, 1973. Original article submitted November 3, 1972.

point in each experiment and the final mass content of liquid vary from one sample to the other. It is obvious that thermograms obtained under such conditions will not be consistent. In the second place, the value of μ fixes the degree of deliquification, thereby determining the "dry" sample weight against which the mass content of the sample is then calculated. It is, therefore, useful to select a certain standard value μ_0 under which all experiments are to be carried out.

In working with water it is reasonable to set μ_0 equal to 0.8 kJ/g, this making, as pointed out in [6], the dividing point between weak and strong water bonding in dispersed bodies. According to [10]

$$\mu = \frac{RT_1}{M} \ln \frac{p_\mathrm{v}(T_1)}{p_\mathrm{liq}}. \tag{1}$$

Thus it is necessary to vary the pressure p_l of water vapor in the thermostat in order to maintain the thermodynamic potential constant at μ_0 in experiments extending over a wide interval of temperatures. This can best be done by lowering the total pressure in the thermostating system [7]. Here it is useful to bubble the air through water at room-temperature T_2, before allowing it to enter the system, thus assuring constancy of water vapor pressure p_H (T_2) at the input, i.e., at atmospheric pressure. The air pressure in the system will then be given by the expression

$$p = p_\mathrm{at} \frac{p_\mathrm{liq}}{p_\mathrm{v}(T_2)}, \tag{2}$$

which, together with (1), gives

$$p = p_\mathrm{at} \frac{p_\mathrm{v}(T_1)}{p_\mathrm{v}(T_2)} \exp\left\{-\frac{\mu M}{RT_1}\right\}. \tag{3}$$

The form of (3) is such as to indicate that the pressure required here is closely dependent on the temperature, especially when the temperature and pressure are both low. It can be seen that maintenance of constant pressure in the thermostat is just as important as the thermostating itself.

All that has just been said continues to apply with equal force in work with dispersed bodies which have been wet with liquids other than water [8]. Other equations will, naturally, then have to be used in calculations. Water vapor is distinctive in that it is always present in the atmosphere. For this reason, the potential of water vapor in the air must be maintained at the standard value μ_0, even when working with other liquids. If this condition is not satisfied, vaporization of the working liquid will be accompanied by water vapor sorption, thereby distorting the final results.

In actuality, what is required here is that the temperature and pressure be held constant over only a limited region around the sample, not throughout the entire volume of the thermostat. Vaporization of the liquid from the dispersed body leads to the establishment of a temperature and mass-content field (boundary layer) around the sample, The usual practice being to carry out work of this kind under natural convection, or with gentle aeration of the sample, it follows that this boundary layer can be several centimeters deep. While it is true that the temperature and mass-content will vary from point to point in the thermostat during an experiment, such variation will have no effect on the form of the thermogram, this being determined by the kinetics of liquid vaporization. From the practical point of view, it is best to surround the test sample with a preformed metallic wire screen, separated from the sample by 2-5 cm. This can give much better results than an attempted thermostating of the stagnant air in the thermostat.

Since the boundary layer surrounding the sample is comparatively thick, the thermogram can be recorded with the aid of a sensor placed, not in the sample, but in the boundary layer itself. Special studies showed that thermograms recorded with sensors located in the sample, and at various distances above it, all had the same general form, differing only in scale if the experiment was carried out slowly. This similarity in thermogram form disappeared when the drying rate was increased, possibly because of slow heating of the cell and the resultant delay in recording the sample temperature. On the other hand, rapid drying is not recommended for thermographic analysis, for reasons which will be outlined below.

There are a number of advantages to recording the thermogram in the boundary layer, especially when working with nonfriable substances. This is possible, however, only if the mass-transfer boundary layer is similar to the thermal boundary layer. This condition will always be satisfied in the air above the sample. If the wire screen distorts the mass-transfer boundary layer, the thermogram must be recorded closer to the sample, moving the sensor up to the screen itself.

A second group of factors to be considered here includes the sample dimensions and the rate of liquid vaporization. Since the vaporization rate fixes the form of the thermogram, and is, itself, determined by the mass-content of the upper surface of the sample, it should be possible to calculate the mean, integral mass-content from a weight curve recorded in the course of the experiment. For this reason, the drying rate and sample depth must be so chosen that the difference between these two mass-contents will be less than the experimental error δu:

$$u_{\text{up}} - u_1 \approx \frac{1}{2}(u_{\text{up}} - u_1) \leqslant \delta u. \tag{4}$$

From the mass balance conditions which must apply at the upper sample surface, it follows that

$$\frac{dm}{d\tau} = \frac{\lambda_m S}{h}(u_{\text{п}} - u_1). \tag{5}$$

From this, the expression for the rate of vaporization from unit surface area follows as:

$$\frac{1}{S} \cdot \frac{dm}{d\tau} \leqslant \frac{2\lambda_m \delta u}{h}. \tag{6}$$

In the derivation of (6) it was assumed that the time required for phase transition is so short that it can be neglected in comparison with the time required for mass transport within the sample. It can be assumed that this condition will be satisfied in every actual recording of a thermogram, the time required for phase transition of molecules with velocities of the order of 10^2 m/sec through a boundary layer 10^{-5} m deep being about 10^{-7} sec [5, 10].

Equation (6) can be said to mark out conditions for a steady state drying process; only if these conditions are satisfied will the kinetic drying thermogram give results characterizing the properties of the sample itself.

A condition for steady state thermal exchange of the form:

$$T_{\text{up}} - T_1 \leqslant \delta T, \tag{7}$$

must apply here, along with (6); simple rearrangement carries this into

$$\frac{1}{S} \cdot \frac{dm}{d\tau} \leqslant \frac{\lambda_q \delta T}{Lh}. \tag{8}$$

Equation (8) cannot be considered as exact, no account of heat leak through the bottom of the cell or of the heat required for maintaining the sample temperature having been taken in its derivation. The simple form of equations (6)-(8) is, however, adequate for the analysis in view here.

The method of drying thermograms was first proposed for work with thin dispersed body films [1]. The conditions of (6)-(8) give a thermodynamic specification of the depth of film under which steady state thermal and mass exchange can be established with such bodies.

These equations indicate that the steady state drying rate should be inversely proportional to h. The drying rate can vary over wide limits, depending on the rate of air circulation in the thermostat and the presence of fittings that might impede mass transfer from the sample surface. The essential thing here is that the thermodynamic potential of the drying air be maintained constant at μ_0.

Despite the high precision of temperature and mass determinations in the modern laboratory, and the correspondingly low values of δT and δu, the conditions laid down in (6) and (8) cannot be considered as excessively rigorous. In analysis of the form of liquid bonding in the dispersed solid, δT is a measure of the accuracy of locating the critical points on the thermogram, which, unfortunately, is always lower than the accuracy of a recording of the temperature itself.

Equations (6) and (8) indicate that the permissible sample depth at fixed drying rate should vary with the coefficients of thermal and mass transfer. Not only is there very little λ_m data, but the values available prove to vary markedly with the mass-content. Tests as to whether the conditions of (6) and (8) are satisfied are, for this reason, usually made experimentally, comparison being made of the results of experiments on a single sample at various values of h and $dm/d\tau$. Experience has shown that initial drying rates as high as $2 \cdot 10^{-4}$ kg/(sec $\cdot$ m^2) are permissible in studies on the vaporization of water from highly dispersed friable materials in the form of films 1-2 mm thick.

In studies on certain weak liquid bonding effects, it is sometimes useful to so work that the condition of (6) is satisfied, but that of (8) crudely violated. An example here could be an experiment with a thick-walled fluoroplastic cell (in place of the thin-walled metallic cell) from which exchange of thermal energy could occur only with a great deal of difficulty [9]. Here the thermogram could not possibly reflect rapid alterations in the drying rate. A succession of slight changes in the drying rate of liquid bonding energy would of necessity lead to entirely spurious traces on the thermogram.

This is an instance in which marked departures from the steady state permit the detection of very weak equilibrium liquid bonding effects on the kinetic drying curves, effects so weak, in fact, that they can be followed only with difficulty if one is limited to equilibrium methods. It should, however, be noted that departures from the conditions of (6) and (8) are permissible only if the thermogram is to be subjected to a special detailed analysis. The usual study of the form of liquid bonding in the dispersed solid requires that both conditions be satisfied.

This discussion of the conditions which must be satisfied in recording drying thermograms is not exhaustive; here we have considered only those requirements whose violation cannot be detected from the thermogram itself but which essentially affect the results of thermographic analysis.

NOTATION

μ	is the chemical potential;
M	is the molecular weight;
u_{up}, u_l, u_i	are the mass contents of sample (of the upper layer, lower layer, and integral);
T_{up}, T_l, T_i	are the temperatures of sample (of the upper layer, lower layer, and integral);
T_1	is the temperature in the thermostat;
T_2	is the temperature in the laboratory;
h	is the thickness of sample;
S	is the area of sample;
λ_q, λ_m,	are the thermal conductivity and mass conductivity of sample, respectively;
L	is the specific heat of evaporation of liquid;
p_{liq}	is the pressure of liquid vapours in the thermostat;
p_v	is the pressure of saturated vapors;
p	is the total pressure in the thermostat;
p_{at}	is the atmospheric pressure.

LITERATURE CITED

1. M. F. Kazanskii, Dokl. Akad. Nauk SSSR, 130, No. 5, 1059 (1960).
2. V. M. Kazanskii, IFZh, 24, No. 2 (1973).
3. V. M. Kazanskii, in: Thermal and Mass Transfer, Vol. 6 [in Russian], Minsk (1972), p. 144.
4. L. M. Nikitina, IFZh, 6, No. 4, 67 (1963).
5. D. P. Timofeev, Kinetics of Adsorption [in Russian], Izd. AN SSSR, Moscow (1962).
6. V. M. Kazanskii, IFZh, 20, No. 5, 787 (1971).
7. M. F. Kazanskii, R. V. Lutsyk, and V. M. Kazanskii, in Thermal and Mass Exchange in Dispersed Systems [in Russian], Nauka i Tekhnika, Minsk (1965), p. 136.
8. V. M. Kazanskii, R. V. Lutsyk, and A. F. Mel'nikova, IFZh, 22, No. 2, 259 (1972).
9. V. M. Kazanskii, P. P. Lutsyk, and M. F. Kazanskii, IFZh, 16, No. 5, 798 (1969).
10. J. H. deBoer, Dynamic Character of Adsorption [Russian translation], IL, Moscow (1968).