RELATION BETWEEN THE DESICCATION RATE AND THE BODY TEMPERATURE IN THERMOGRAPHIC STUDIES

V. M. Kazanskii

UDC 66.047.31

An equation has been derived and experimentally verified for calculating the evaporation rate from a known thermogram, or vice versa, taken under conditions of thermographic testing.

Thermographic test methods, including the desiccation thermogram [1] and the differential thermal analysis [2], are mass transfer methods, i. e., methods based on the laws of heat and mass transfer between a specimen and the ambient medium under some given conditions. As a rule, mass transfer (evaporation) is the predominant process here and the temperature curves represent its trend [3]. For numerical computations related to thermographic analysis, therefore, it is most convenient to use the desiccation-rate curve (the derivatogram), although its direct and sufficiently accurate recording during a test is very difficult [4]. Recording the specimen temperature (the thermogram) during a test is much simpler and more accurate. It thus becomes necessary to establish a relation between the thermogram and the derivatogram which would allow one to compute derivatograms from known thermograms and vice versa.

We will first consider the simplest case: desiccation by the thermogram method. As is well known, the liquid evaporates here from the specimen at a constant ambient temperature, and the thermogram represents the temperature difference ΔT between the specimen (T_1) and the ambient atmosphere (T_0) as a function of time. The heat supplied to a specimen by way of heat transfer is spent on evaporating the liquid and raising the temperature of the specimen:

$$\alpha S\Delta T = L\frac{dm}{d\tau} + (c_0m_0 + cm)\frac{dT_1}{d\tau}. \tag{1}$$

This equation of heat balance does, in principle, relate the thermogram to the derivatogram. Until now, however, this equation has not been used for derivatogram computations, under the impression that the heat transfer coefficient α, being a function of the moisture content in the specimen as well as of the desiccation rate, would be rather difficult to either measure or calculate. Meanwhile, as will be shown here, during a thermogram recording the heat transfer coefficient α remains almost independent of both the moisture content and the desiccation rate. The other coefficients in Eq. (1) depend also negligibly little on the moisture content. To the first approximation, therefore, one may treat Eq. (1) as one with constant coefficients. On such a basis, as will be shown here, a derivatogram can be computed from a thermogram accurately within 3-7%, which is comparable to the usual accuracy of direct derivatogram measurements.

The fact that α depends neither on the evaporation rate nor on the moisture content, as has been established by the author in his experimental study [5], agrees with the conclusions of other authors [6]. Indeed, it has been shown in [7, 8] that the increase in α during the evaporation of a liquid from capillary-porous bodies is related not to an additional transfer of heat due to vapor diffusion (this is a small amount) but to a depending of the evaporation zone to the drop in moisture content and also to the errors in the measurement of the true surface temperature. As a consequence, to the thermal resistance of the boundary layer, which determines the magnitude of α, there is added the thermal resistance of a dry layer between the specimen surface and the evaporation zone, resulting in an apparently higher measured value of α. When those factors are insignificant, on the other hand, α appears only slightly dependent on the desiccation rate. It has been shown in [9], for example, that during evaporation from the free surface of the liquid α

Institute of Engineering-Construction, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 24, No. 2, pp. 302-308, February, 1973. Original article submitted July 6, 1972.

remains almost constant while the evaporation rate varies through a factor of 7-8.

During thermographic tests one usually maintains special conditions. They are always performed in the "soft" mode so as to keep the temperature gradients inside the specimen small and thus to improve the accuracy of temperature measurements at the surface. Furthermore, the thickness of a test specimen does not exceed 1-2 mm and, for this reason, the added depth of the evaporation zone is always much smaller than the thickness of the boundary layer, which during natural convection may be of the order of a few centimeters. Such test modes are required in the application of the thermographic methods, but they also ensure that α will, within test accuracy, depend negligibly little on the external mass transfer. In this way, the constancy of α (within 2-5%) during our thermogram—desiccation tests is now theoretically justified.

In order to use Eq. (1) for computations, one must know the three coefficients in it: L depends only on the kind of the evaporating substance and can easily be found in tables; the heat capacity $cm + c_0m_0$ is made up essentially of the heat capacity of the vessel with the temperature probe c_0m_0, constant for a given experiment but different from one experiment to another. The heat transfer in the specimen αS depends on the test conditions: temperature, pressure, and air velocity near the surface. Thus, in order to use Eq. (1) for computations, it becomes necessary to measure αS in each test mode and to measure the heat capacity c_0m_0 once for a given experiment.

The simplest way to determine αS is during the initial test period, when excess free liquid evaporates above the specimen surface. The evaporation rate $(dm/d\tau)_0$ and the temperature difference ΔT_0 are then constant. From (1) we find now

$$\alpha S = \frac{L}{\Delta T_0}\left(\frac{dm}{d\tau}\right)_0. \tag{2}$$

Since the evaporation rate is constant, it can be measured quite accurately by plain weighing (without plotting the mass curve) and thus determining the loss of mass Δm_0 within a sufficiently long period of time $\Delta\tau_0$. This yields

$$\alpha S = \frac{L\Delta m_0}{\Delta T_0 \Delta\tau_0}. \tag{3}$$

Inserting into (1), we obtain

$$\frac{dm}{d\tau} = \frac{\Delta m_0}{\Delta\tau_0 \Delta T_0}\Delta T + \frac{c_0m_0 + cm}{L}\frac{dT}{d\tau}. \tag{4}$$

Determining the heat capacity of the vessel c_0m_0 requires only one evaporation test with the pure liquid such as water, for example. The evaporation rate is first constant, then drops sharply, and finally remains equal to zero. For the last stage we have

$$\alpha S\Delta T + c_0m_0\frac{d(\Delta T)}{dt} = 0. \tag{5}$$

The solution to this differential equation is

$$\Delta T = A\exp\left\{-\frac{\alpha S\tau}{c_0m_0}\right\}. \tag{6}$$

From here

$$\ln\Delta T = \ln A - \frac{\alpha S\tau}{c_0m_0}. \tag{7}$$

The slope of the last thermogram segment in semilogarithmic coordinates $\ln\Delta T$, τ yields $\alpha S/c_0m_0$. The magnitude of αS for a given test mode is found from the first stage of the test, as shown earlier. Thus, c_0m_0 is determined from a single evaporation test with pure water. The heat capacity of the specimen cm must be calculated separately, however, but this may be done very roughly, inasmuch as cm is usually not greater than 10-20% of c_0m_0. In order to check this entire procedure, evaporation tests with pure water were performed under various conditions: at 320°K and at 380°K. As a result, the last segments of the thermograms in $\ln\Delta T$, τ coordinates were found to be straight lines (within test accuracy). The heat capacity c_0m_0 calculated from these curves was the same within 2%, although αS differed by as much as a factor of 2.

The validity of Eq. (4) for calculating the evaporation rate has been established by a test set up as shown in [10, 11]. The evaporating liquids were water, methyl alcohol, and benzene. Two specimens of

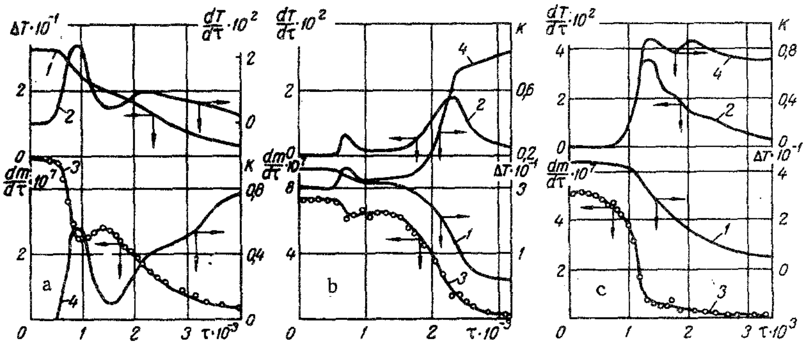

Fig. 1. Kinetic curves obtained by recording the desiccation thermograms for: (a) fine-porosity silica gel moistened with water, (b) coarse-porosity silica gel moistened with water, (c) cement moistened with methyl alcohol. ΔT (°K) (1), $dT/d\tau(\cdot 10^2$(°K/sec)) (2), $dm/d\tau(\cdot 10^8$(kg/sec)) (3), K (dimensionless) (4). Test time $\tau(\cdot 10^{-3}$ sec).

silica gel with different porosities and a concrete specimen served as the disperse phase. Formula (4) was verified under various conditions. It is well known that α increases with increasing air pressure, with rising temperature of the specimen, and with higher velocity of the ventilating air [12, 13]. For this reason, the measurements were performed at low air temperatures and pressures ($T = 320$°K, $p = 2.5 \cdot 10^3$ Pa) as well as at high temperatures and pressures ($T = 380$°K, $p = 10^5$ Pa). The velocity of ventilating air in the temperature—pressure chamber of the test apparatus was also higher in the second mode.

The desiccation thermogram $\Delta T(\tau)$ was recorded together with the mass curve $m(\tau)$. The latter was plotted to a very large scale [11]: the chart sensitivity reached 0.3 mg/mm toward the end of the test, when the total change in mass amounted to about 4 g, and this ensured a quite reliable computation of the derivatogram.

Typical results of these measurements and calculations are shown in Fig. 1. Curves 1 represent the desiccation thermograms, curves 2 represent the rate of temperature change, and curves 3 represent the evaporation rate. The solid curves 3 were obtained by test, while the points were calculated according to Eq. (4). Curve 4 represents the ratio of heat spent on raising the specimen temperature to total heat supplied (this will be discussed later). According to the graphs, the calculated values agree closely with the measured derivatogram (within a 3-7% error). The calculated values deviate from the measured ones on the high side as well as on the low side, which indicates that the error is a random one and probably due to inaccurate measurements of temperature and evaporation rate. The calculated derivatogram concurs with the measured one throughout the entire test range, at both high and low evaporation rates. For instance, the calculated derivatograms for silica gels rise slowly after the first drop (Fig. 1a, b), just as the measured curves.

Thus, the results indicate that Eq. (4) with constant coefficients does relate the derivatogram to the thermogram within an error not greater than 3-7% and, therefore, is entirely suitable for computations.

On the basis of Eq. (1) one can also solve the reverse problem, namely compute the desiccation thermogram from a known derivatogram. Indeed, Eq. (1) for ΔT is a linear differential equation with constant coefficients. Its solution is [14]

$$\Delta T = \Delta T_0 \exp\left\{-\frac{\alpha S\tau}{c_1 m_1}\right\}\left[\int \frac{L}{c_1 m_1}\frac{dm}{d\tau}\exp\left\{\frac{\alpha S\tau}{c_1 m_1}\right\}d\tau + A_1\right]. \qquad (8)$$

Although it is much easier during a test to record the thermogram than the derivatogram and although it usually is not necessary to compute the thermogram from a known derivatogram, Eqs. (8) and (1) are of interest as means for a complete analysis of the characteristic ranges of thermograms and derivatograms. Such an analysis is important especially with regard to the straight segments of desiccation thermograms, which are singled out for a study of the forms of bond between liquids and disperse materials [1]. Let us consider this problem more thoroughly.

The thermogram will be represented in terms of a power series

$$\Delta T = \sum_{i=0}^{i=n} a_i \tau^i. \tag{9}$$

Then, according to (1), the evaporation rate becomes

$$\frac{dm}{d\tau} = \sum_{i=0}^{n} \frac{a_i}{L} [\alpha S \tau^i + i c_1 m_1 \tau^{(i-1)}]. \tag{10}$$

It is easy to ascertain by a simple substitution that to a linear segment on the thermogram

$$\Delta T = a_0 + a_1 \tau \tag{11}$$

there corresponds a linear segment on the derivatogram

$$\frac{dm}{d\tau} = \left(\frac{\alpha S a_0}{L} + \frac{c_1 m_1 a_1}{L} \right) + \frac{\alpha S a_1}{L} \tau. \tag{12}$$

To a parabolic segment on the thermogram there also corresponds a parabolic segment on the derivatogram, with the respective second derivatives, which determine the direction of curvature, having the same signs on both diagrams:

$$\frac{d^2(\Delta T)}{d\tau^2} = 2a_2; \quad \frac{d^2}{d\tau^2} \left(\frac{dm}{d\tau} \right) = \frac{2\alpha S}{L} a_2. \tag{13}$$

In other words, a convex segment on the derivatogram always corresponds to a convex segment on the thermogram. If the latter is represented by a polynomial of a higher than second degree, however, then the convex and the concave segments on the derivatogram may not correspond to those on the thermogram.

Solving the reverse problem on the basis of Eq. (8) is more difficult. If the derivatogram is represented in terms of a power series

$$\frac{dm}{d\tau} = \sum_{i=0}^{n} b_i \tau^i, \tag{14}$$

then inserting (14) into (8) yields

$$\Delta T = \sum_{i=0}^{n} g_i \tau^i + A_1 \exp\left\{ -\frac{\alpha S \tau}{c_1 m_{1.}} \right\}, \tag{15}$$

where g_i are constant coefficients. The first term in (15) is a polynomial of the same degree as in (14). The second term in (15) represents a "drag" in the thermogram following a sharp change in the evaporation rate. The magnitude of this term depends on the heat capacity of the vessel with the specimen $c_1 m_1$ and can generally be appreciable.

For illustration, curves 4 in Fig. 1 represent the coefficient

$$K = \frac{c_1 m_1}{\alpha S \Delta T} \frac{dT}{d\tau}. \tag{16}$$

This coefficient indicates what fraction of the heat supplied to a specimen is spent on raising the temperature of the latter. These graphs indicate also that the term which accounts for the heat capacity of a specimen is very significant, especially at low evaporation rates (toward the end of the test), and may not be disregarded.

It has been shown in [4] that the shape of a desiccation thermogram for typical disperse materials is the same as the shape of the respective derivatogram. The preceding analysis of Eqs. (1) and (8) confirms this concidence in time between the respective linear segments on both diagrams. There is no exact proportionality between them, however, so that segments of higher-degree curvatures must be different on both diagrams.

With the aid of Eq. (4) one can also compute the mass curve for a specimen from its thermogram. Indeed, integrating (4) yields

$$m(\tau) = \frac{\Delta m_0}{\Delta \tau_0 \Delta T_0} \int \Delta T d\tau - \frac{c_1 m_1}{L} \Delta T. \tag{17}$$

In order to compute the mass curve according to formula (17), it is necessary only to measure the loss of mass Δm_0 within a sufficiently long period of time $\Delta \tau_0$ at the beginning of the test (during the evaporation of free liquid). This can be done by means of plain (not recording) scales. Thus, the application of formula (17 makes feasible, in principle, a thermographic analysis on the basis of the desiccation thermogram without direct recording of the mass curve.

We will now consider testing by differential thermal analysis. In this case the test specimen 1 and the inert (not changing throughout the test) specimen 2 are both placed in a medium whose temperature T_0 rises linearly with time. The thermogram here represents the temperature difference between test specimen (T_1) and inert specimen (T_2). In the light of the earlier discussion, one can write for both specimens:

$$\alpha_1 S_1 (T_1 - T_0) = L_1 \frac{dm_1}{d\tau} + c_1 m_1 \frac{dT_1}{d\tau}, \tag{18}$$

$$\alpha_2 S_2 (T_2 - T_0) = L_2 \frac{dm_2}{d\tau} + c_2 m_2 \frac{dT_2}{d\tau}. \tag{19}$$

The inert specimen is usually selected so that the surface and the heat capacity of both specimens be the same, with also equal heat transfer coefficients. Then, subtracting (19) from (18) and considering that the mass of the inert specimen remains constant, we have

$$\alpha_1 S_1 \Delta T = L_1 \frac{dm_1}{d\tau} + c_1 m_1 \frac{d(\Delta T)}{d\tau}. \tag{20}$$

This equation is identical in form to Eq. (1), but ΔT has a different meaning here. Consequently, Eq. (1), or the identical Eq. (20), is within a narrow temperature range valid not only for the thermogram mode but also for the differential thermal analysis of desiccation. When desiccation for a differential thermal analysis covers a wide temperature range, then Eq. (1) remains valid but its coefficients can no longer be considered constant and, therefore, computations become more unwieldy. Nevertheless, in this case too Eq. (1) is quite useful as a basis for distinguishing on kinetic diagrams between the evaporation of volatile components from a specimen and other phase transformations (e. g., recrystallization).

Thus, we have established a quantitative relation between the thermogram and the derivatogram of a desiccation process, making it possible to completely compute any one of these curves when the other is known.

NOTATION

α	is the coefficient of external heat transfer;
S	is the surface area of the specimen;
T	is the temperature;
L	is the latent heat of evaporation;
τ	is the time;
m	is the mass;
c	is the specific heat;
A	is the integration constant;
a_i, b_i, g_i	are the constant coefficients in the T and $dm/d\tau$ series expansions.

LITERATURE CITED

1. M. F. Kazanskii, Dokl. Akad. Nauk SSSR, 130, No. 5, (1960).
2. L. G. Berg, Introduction to Thermography [in Russian], Izd. Akad. Nauk SSSR, Moscow (1961).
3. V. M. Kazanskii, in: Proc. Fourth All-Union Confer. on Heat and Mass Transfer [in Russian], Minsk (1972).
4. V. M. Kazanskii and L. N. Belyi, Inzh. Fiz. Zh., 7, No. 12, 66 (1964).
5. V. M. Kazanskii, in: Structural Thermophysics [in Russian], Izd. Énergiya, Moscow (1966).
6. P. N. Romanenko, V. N. Kharchenko, and Yu. P. Semenov, Inzh. Fiz. Zh., 9, No. 6, 816 (1965).
7. A. V. Lykov, Inzh. Fiz. Zh., 5, No. 11, 12 (1962).
8. A. V. Lykov and G. V. Vasil'ev, Inzh. Fiz. Zh., 14, No. 3, 395 (1968).
9. V. I. Balakhonova, Inzh. Fiz. Zh., 12, No. 1, 3 (1967).
10. M. F. Kazanskii, R. V. Lutsyk, and V. M. Kazanskii, in: Heat and Mass Transfer in Disperse Systems [in Russian], Izd. Nauka i Tekhnika, Minsk (1965).
11. M. F. Kazanskii, R. V. Lutsyk, and V. M. Kazanskii, Inzh. Fiz. Zh., 11, No. 5, 587 (1966).
12. É. R. Éckert and R. M. Dreick, Introduction to the Theory of Heat and Mass Transfer [Russian translation], Izd. GÉI, Moscow (1961).

13. P. A. Novikov and V. A. Solov'ev, in: General Problems in Heat and Mass Transfer [in Russian], Izd. Nauka i Tekhnika, Minsk (1966).
14. M. Ya. Vygodskii, Handbook of Higher Mathematics [in Russian], Izd. Nauka, Moscow (1966).