Journal of Thermal Analysis, Vol. 7 (1975) 369—372

CORRELATION BETWEEN SAMPLE GEOMETRY AND KINETICS

G. V. Malinin

V. G. Khlopin Radium Institute, Leningrad

(Received August 16, 1973)

The influence of the specimen shape on the form of the kinetic equation for thermal reactions was demonstrated by means of the spectral function theory.

Specimens used for thermal analysis are bodies of finite size. As the sample is heated, a temperature gradient is set up from the edge to the centre. This causes some investigators to have doubts about the possibility of studying kinetics by thermoanalytical methods. For example, Garn notes: "An important question in evaluating kinetic data is whether or not the data are independent of the geometry of the specimen" [1].

This problem is by no means simple, but the present paper is an attempt at its solution.

Let us observe and record any property of a process that takes place in a specimen, e.g., the derivative of the change of sample weight with respect to time (DTG). Let $\phi(t)$ be the derivative of the weight change with respect to time for any point of the sample with temperature $T_{\text{wall.}}$ The derivative of the weight change with respect to time for some other point of the sample with temperature $T = T_w - \Delta T$ is denoted by $f(t)$. For a quasi-steady state (2) we can write

$$f(t) = \phi \left(t - \frac{\Delta T}{b}\right) \tag{1}$$

where b is the heating rate, and t is the time. (It is clear that Eq. (1) is a better approximation to reality, the greater the amount of heat devoted to heating the specimen and the less the amount required for reaction.)

Let $\phi_{(\omega)}$ be the spectrum of the function ϕ(t)

$$\Phi(\omega) = \int_{-\infty}^{\infty} \phi(t) \exp(-i\omega t) dt. \tag{2}$$

Then the spectrum of the function $f(t)$ can be obtained

$$\int_{-\infty}^{\infty} f(t) \exp(-i\omega t) dt = \phi(\omega) \exp\left(-i\omega \frac{\Delta T}{b}\right). \tag{3}$$

The spectrum of the process $Q(t)$ recorded by DTG is equal to the sum (in the limit the integral) of the spectra from all points of the sample.

Let us choose a crucible with the form of an infinite cylinder. The equation of heat flow for this case exhibits good agreement with the experimental data if the height of the crucible is greater than twice the diameter (4).

The spectrum of the total process for a powdery substance located in the cylinder is of the form

$$Q(\omega) = 2\pi \int\limits_0^R \phi(\omega) \exp\left(-i\omega \frac{R^2 - r}{4a} \right) rdr = 4a\pi \frac{\phi(\omega)}{i\omega} \left[1 - \exp\left(-i\omega \frac{R^2}{4a} \right) \right] \tag{4}$$

where R is the external radius of the cylinder, r is the radius at the point under consideration, and Q is the thermal diffusivity.

Now, if we know the spectral function, the derivation of the expression for $Q(t)$ is quite simple. Using the theory of spectra [3], we obtain

$$Q(t) = 4a\pi \int\limits_{t-\frac{R^2}{4a}}^{t} \phi(\tau)d\tau \tag{5}$$

with the notations already adopted.

If we repeat similar arguments for a crucible of spherical form, we can write the following expression

$$Q(\omega) = 4\pi \int\limits_0^R \phi(\omega) \exp\left(-i\omega \frac{R^2 - r^2}{6a} \right) r^2dr = 12\pi a \frac{\phi(\omega)}{i\omega} \cdot$$

$$\cdot \left\{ R - \sqrt{\frac{\pi}{2}} \sqrt{\frac{6a}{\omega}} \exp\left(- i\omega \frac{R^2}{6a} \right) \left[C\left(\sqrt{\frac{\omega}{6a}} R \right) + iS\left(\sqrt{\frac{\omega}{6a}} R \right) \right] \right\} \tag{6}$$

where R is the radius of the sphere, and r is again the radius at the point under consideration. $C(\beta)$ is the Frensel cosine-integral, and $S(\beta)$ the Fresnel sine-integral.

Using integral tables [5], after calculation we can find the equation of $Q(t)$ for the spherical specimen

$$Q(t) = 12\pi\, aR \int\limits_{t-\frac{R^2}{6a}}^{t} \phi(\tau) \sqrt{1 + \frac{\tau - 1}{R^2} 6a\, d\tau} . \tag{7}$$

Comparison of Eqs (5) and (7) show that the curves $Q(t)$ differ from each other. This formulation implies an obvious generalization: the shape of the specimen has an influence upon the form of the kinetic equation for the reaction.

Mathematical analysis of Eqs (5) and (7) leads to an expression for the time $t_{\max}$ when the rate of the process reaches a maximum. For the cylindrical specimen $Q(t)$ reaches an extremum at $t_{\max}$ satisfying the following equation

$$\phi(t_{\max}) = \phi\left(t_{\max} - \frac{R^2}{4a}\right). \tag{8}$$

The analogous equation for the sphere is

$$\phi(t_{\max}) = \int_0^1 \phi\left(t_{\max} - \frac{R^2}{6a} + \frac{R^2}{6a}\xi^2\right) \mathrm{d}\xi\,. \tag{9}$$

It should be noted that a for a powdery substance is usually equal to $1 - 10 \cdot 10^{-3}$ cm^2/sec and R^2/a is equal to $1 - 10 \cdot 10^2$ sec if $R = 1$ cm.

From Eqs (8) and (9) we can find the correlation between the temperature T_m of the peak on the DTG curve and the heating rate. Only for the case when the temperature gradient in the crucible is slight, i.e. the inequality (10) is valid

$$\frac{E_a}{RT_m^2} \cdot \frac{bA}{a} < 1 \tag{10}$$

where E_a is the activation energy, A is the geometrical coefficient (for cylindrical and spherical crucibles A is equal to the square of the external radius), and R is the gas constant, does the expression characterizing the correlation between T_m and b have a simple form.

Thus, for reactions which are described by the equation

$$\alpha = 1 - (1 - kt)^n \tag{11}$$

where α is the conversion, and k is the rate constant, T_m and b are related by the following equation (2)

$$\ln\frac{b^i}{b^j} = \frac{E_a}{R} \cdot \frac{T_m^i - T_m^j}{T_m^i \cdot T_m^j}\,. \tag{12}$$

For reactions described by the Avrami–Erofeev equation

$$\alpha = 1 - \exp\left(-k^n t^n\right) \tag{13}$$

the relationship between T_m and b has the form

$$\ln\frac{b^i}{b^j} + \frac{n-1}{n}\,\frac{T_m^i - T_{in}}{T_m^j - T_{in}} = \frac{E_a}{R}\,\frac{T_m^i - T_m^j}{T_m^i \cdot T_m^j} \tag{14}$$

where T_{in} is the initial temperature of the reaction.

It is obvious that the nature of the correlation between T_m and b depends on the nature of the reaction under consideration. The simple expression (12) can be utilized only to obtain a rough estimate of E_a.

Literature

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RÉSUMÉ — Etude de l'influence de la forme des creusets porte-échantillon sur les courbes de décomposition thermique. Mise en évidence d'une relation simple entre la température au maximum de la courbe TGD et la vitesse d'échauffement.

ZUSAMMENFASSUNG — Es wurde der Einfluß der Probenform auf den Verlauf der Zersetzungskurve untersucht. Hierbei wurden Angaben über eine einfache Beziehung zwischen der Temperatur des Maximums der DTG-Kurve und der Aufheizgeschwindigkeit erhalten.

Резюме — Рассмотрено влияние формы навески на вид кинетических кривых реакций, идущих в веществе пробы при нагревании. Получено условие, при выполнении которого между температурой максимума пика кривой ДТГ и скоростью нагревания печи существует простая связь.