Journal of Thermal Analysis, Vol. 31 (1986) 61–72

THE APPARATUS FUNCTION OF QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS, INCLUDING HEAT CONVECTION AND RADIATION

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(Received January 21, 1985; in revised form June 29, 1985)

The apparatus function, i.e. the response of the equipment to a heat pulse, is derived for DTA instruments where, besides heat conduction, convection and radiation are considered. The solution of the heat-balance equation is described by a superposition of two exponential functions, which leads to the dependences of the calibration factor and the time constants on the heat capacity, the heating rate and the temperature. For the experimental determination, the relations are transformed into expressions which can easily be obtained from the calibration measurements.

DTA is increasingly used for quantitative evaluations and kinetic applications. The required calibration factor and the apparatus function often depend on the heat capacity of the sample, the scanning rate and the temperature. If the device is employed under different measuring conditions and only few calibration values are available, it is favourable to know these dependences as expressions in closed form. The variability of the instrument parameters is caused by non-linear components of the heat transfer. It is the purpose of this paper to describe the influences of the heat capacity of the sample, the scanning rate and the temperature on the apparatus data analytically.

Starting from the theory of Vold [1], the relation between the heat flow and the differential temperature has been examined in detail [2] and discussed for special experimental conditions and problems [3]. In particular, it is known that the apparatus function can be described as a sum of two exponential functions [4]. However, the influence of the scanning rate on the time constant in the apparatus function has not been specified; experimentally, a decrease with increasing heating rate has been found [5].

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In the present paper, the dependences of the calibration factor and the time constants on the heat capacity, the scanning rate and the reference temperature are deduced for the case of non-constant thermal contact resistance, constant scanning rates of the reference temperature and small differential temperatures between sample and reference.

Derivation of the apparatus function

At time $t = 0$, a heat amount ΔQ be converted in the sample. ΔQ causes a heat flow $\psi(t)$, which leads to a temperature alteration at the temperature sensor of the sample. The apparatus function is the response of the instrument caused by the perturbation ΔQ, i.e. the indicated measuring signal $\Delta T(t)$.

Model. The device (Fig. 1) is considered to consist of the sample with sample container and the reference with container, which are symmetrically coupled with a block. The temperature sensors are attached to the containers. The differential temperature $\Delta T = T_S - T_R$ between the sample and reference is measured as a function of time. The temperature of the reference can be controlled by means of the block according to a given programme. It is assumed that the system has arrived at a stationary state, i.e. during a measurement the heating or cooling rate $\beta = \mathrm{d}T_R/\mathrm{d}t$ is constant or zero. The following mathematical assertion is made for the case of heating and an exothermic process in the sample ($\Delta T > 0$). It is also valid for other stationary states.

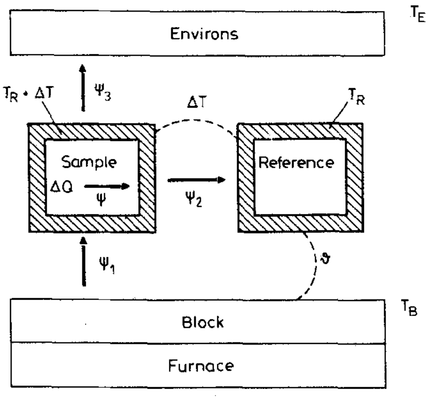

Fig. 1 Scheme of the equipment

The heat transfer between block and sample container is described by the heat flow ψ_1. Thermal conduction, convection and radiation are considered to contribute to this heat transport. The temperature difference $\vartheta = T_B - T_R$ between the block and the measuring cell, determining this heat transfer, is not exactly defined because, between the furnace and the containers, a temperature gradient exists along the block, maintaining the flow ψ_1. Therefore, in the following derivation the temperature difference ϑ is determined from the stationary state of the heating and is thereby eliminated.

Furthermore, there is a heat flow ψ_2 between sample and reference introduced, described by thermal conduction. Finally, a heat leakage is admitted, i.e. a heat dissipation ψ_3 that releases a heat loss from the sample and reference to the environment, e.g. by the temperature sensors. Since this represents only a correction, exclusively thermal conduction is considered. (It is easily possible to extend the derivation to the case when the flow ψ_3 includes convection and radiation, e.g. if the block does not enclose the sample and reference completely.)

It is assumed that the differential temperature ΔT is much less than all other temperature differences and temperatures, so that quadratic terms in ΔT can be neglected and the heat flows are superposed without mutual interference. This means that the heat flows can be described by the corresponding temperature differences and the stationary state is hardly disturbed by ΔQ.

The time-dependence of the heat transient in the sample and to the sample container is described by $\psi = \psi_0 \exp(-t/\tau^*)$ with the time constant τ^* for the heat relaxation in the sample and its holder. The energy conservation requires

$$\int_0^\infty \psi(t)\,\mathrm{d}t = \Delta Q \tag{1}$$

which results in

$$\psi = \frac{\Delta Q}{\tau^*} \exp\left(-\frac{t}{\tau^*}\right) \tag{2}$$

The heat flow ψ_1 from the block to the sample container amounts to

$$\psi_1 = A_1(\vartheta - \Delta T) + A_c(\vartheta - \Delta T)^2 + A_r[(T_R + \vartheta)^4 - (T_R + \Delta T)^4] \tag{3}$$

The first term represents the heat conduction and the heat transfer at the interfaces. For a single thermal resistance between the block and the container, we have

$$\frac{A_1}{S} = \frac{1}{\dfrac{l}{\lambda} + \dfrac{1}{\alpha_B} + \dfrac{1}{\alpha_C}}$$

with S = surface (of the container)
l = length (distance between block and container)
λ = thermal conductivity (of the material in the space between block and container)
α_B, α_C = heat-transfer coefficient at the block and at the container, respectively.

Through the second term in (3), the heat convection between the block and the sample container is included. According to the usual approximation for the total heat-transfer coefficient [6], besides the constant portion of the transfer coefficient contained in A_1, a constituent is included that shows a linear increase with the temperature difference. In air

$$\frac{A_c}{S} = 0.07 \text{ W m}^{-2} \text{ K}^{-2}$$

where S is the surface (of the container). The third term in (3) describes the contribution of the radiation to the heat transfer. In the case of parallel walls of area S

$$\frac{A_r}{S} = \varepsilon\sigma$$

where Stefan–Boltzmann constant $\sigma = 5.67 \cdot 10^{-8}$ W m^{-2} K^{-4} and ε is the emitting power of the block and the container. As for the expansion of the bracket term, expressions with ϑ^3 are neglected.

The heat balance. The temperature change at the sample container is represented by the sum of the heat flows

$$C\frac{\mathrm{d}(T_R+\Delta T)}{\mathrm{d}t} = \psi+\psi_1-\psi_2-\psi_3 \tag{4}$$

The heat capacity C of the sample with its container is assumed to be constant during a measurement and to be equal to the heat capacity of the reference and its holder. The heat conductivity between the sample and the reference is described by $\psi_2 = A_2\Delta T$, and the heat dissipation by $\psi_3 = A_3(T_R+\Delta T-T_E)$, where T_E is the environmental temperature.

The stationary state. First, (4) is considered for the case $\Delta T = 0$ (no reaction in the sample). Evidence that, in the case of radiation, ϑ decreases for high temperatures with T_R^{-3} (the reason for this is that the heat transport by radiation goes with $[(T_R+\vartheta)^4-T_R^4] = 4\vartheta T_R^3+\ldots$). The solution of Eq. (4) leads to

$$\vartheta = (2\Lambda_4)^{-1}\{\sqrt{4\Lambda_4[C\beta+\Lambda_3(T_R-T_E)]+\Lambda_5^2}-\Lambda_5\} \tag{5}$$

with

$$\Lambda_4 = \Lambda_c+6\Lambda_r T_R^2 \text{ and } \Lambda_5 = \Lambda_1+4\Lambda_r T_R^3 \tag{6}$$

The temperature difference ϑ between the block and the cell rises with the heating rate β, the heat capacity C and the heat losses. To see the influence of T_R, we consider the case when only radiation takes place. With $\Lambda_1 = \Lambda_2 = \Lambda_3 = \Lambda_c = 0$, (5) changes into

$$\vartheta = \frac{1}{12\Lambda_r T_R^2}\{\sqrt{24\Lambda_r T_R^2 C\beta+16\Lambda_r^2 T_R^6}-4\Lambda_r T_R^3\}$$

which can be simplified to

$$\vartheta = -\frac{T_R}{3}+\sqrt{\frac{C\beta+\frac{T_R^2}{9}}{6\Lambda_r T_R^2}}$$

The expansion of the root for high T_R leads to

$$\vartheta = -\frac{T_R}{3}+\frac{T_R}{3}\left(1+\frac{1}{2}\frac{3C\beta}{2\Lambda_r T_R^4}\right)$$

i.e.

$$\vartheta = \frac{C\beta}{4\Lambda_r T_R^3}$$

So that ϑ is proportional to T_R^{-3}.

The apparatus function. The apparatus function is the solution of (4) for the case $\Delta T \neq 0$ and $\Delta Q \neq 0$, in which, according to the above assumptions, (5) remains valid, which means that the stationary state is little disturbed. Furthermore, the assumption is made that, during the heat transient of the perturbation caused by ΔQ, the coefficient of ΔT can be regarded as a constant, i.e. $T_R = T_0+\beta t$ (t = time) is replaceable by constant average value in this time interval, which is possible if $\beta(\tau+\tau^*) \ll T_R$ (τ, see below). (4) changes into

$$C\frac{\mathrm{d}(\Delta T)}{\mathrm{d}t} = -[\Lambda_6+\Lambda_7\vartheta]\Delta T+\frac{\Delta Q}{\tau^*}\exp\left(-\frac{t}{\tau^*}\right) \tag{7}$$

with $\Lambda_6 = \Lambda_1+\Lambda_2+\Lambda_3+4\Lambda_r T_R^3$, $\Lambda_7 = 2\Lambda_c$ and is solved by

$$\Delta T = \frac{\Delta Q}{C}\frac{\tau}{\tau-\tau^*}\left[\exp\left(-\frac{t}{\tau}\right)-\exp\left(-\frac{t}{\tau^*}\right)\right] \tag{8}$$

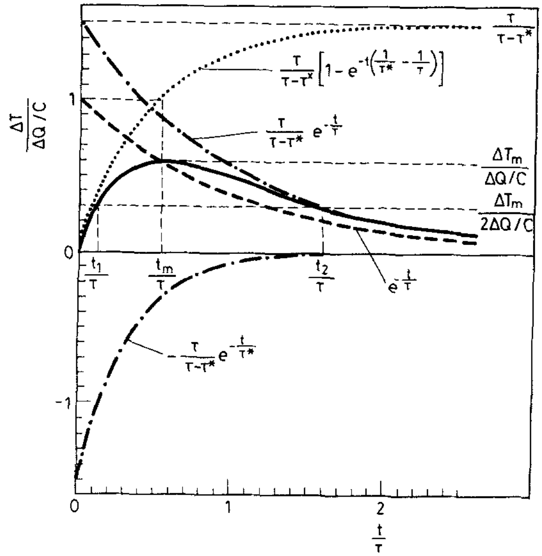

Fig. 2 The apparatus function for $\varkappa = \tau/\tau^* = 3$ (solid line)

(Fig. 2), where

$$\tau = \frac{C}{\Lambda_6 + \Lambda_7 \vartheta} \tag{9}$$

is the time constant for the heat transient of the heat quantity ΔQ with the adjoining parts of the apparatus. The apparatus function is symmetrical with respect to the time constants, i.e. it maintains its shape and is only altered by the factor τ^*/τ in case of the permutation of τ and τ^*. (8) can also be written in the form

$$\Delta T = \frac{\Delta Q}{C}\frac{\tau}{\tau-\tau^*}\left\{1-\exp\left[-t\left(\frac{1}{\tau^*}-\frac{1}{\tau}\right)\right]\right\}\exp\left(-\frac{t}{\tau}\right)$$

in which, for $\tau \to \infty$, the first term describes the temperature increase in the sample if the cell gives off no heat. This component is superposed on the exponential decrease due to the thermal interaction with the adjoining material. Moreover, the expression $(\Delta Q/C)\exp(-t/\tau)$ is a limit curve, i.e. the apparatus function in the case $\tau^* \to 0$.

Discussion of the apparatus function and the calibration of the DTA equipment

Characteristic values. The apparatus function can be characterized by

— the ratio of the time constants $\varkappa = \tau/\tau^*$

— the position t_m of the maximum:

$$t_m = \tau \frac{\ln \varkappa}{\varkappa - 1}$$

— the height ΔT_m of the maximum:

$$\Delta T_m = \frac{\Delta Q}{C} \exp\left(-\frac{t_m}{\tau}\right) = \frac{\Delta Q}{C} \varkappa^{-\frac{1}{\varkappa - 1}}$$

— the area

$$\int_0^\infty \Delta T \mathrm{d}t = \frac{\Delta Q}{C} \tau$$

— the rise at $t = 0$:

$$\left(\frac{\mathrm{d}(\Delta T)}{\mathrm{d}t}\right)_{t=0} = \frac{\Delta Q}{C} \frac{1}{\tau^*}$$

— the times t_1 and t_2 at which the differential temperature amounts to $\Delta T_m/2$.

Dependence of the time constants on the conditions of operation. The time constant τ^* depends only on the conductivity and the mass of the sample material and its spatial distribution in the sample container, if the containers of the sample and reference are maintained. The time constant τ, however, depends on the heating rate β, the temperature T_R of the measuring cell and the heat capacity C. From (9), (7), (5) and (6), it follows that

$$\tau = C\left(\Lambda_6 + \frac{\Lambda_c}{\Lambda_4} \{\sqrt{4\Lambda_4[C\beta + \Lambda_3(T_R - T_E)] + \Lambda_5^2} - \Lambda_5\}\right)^{-1} \tag{10}$$

Expression (10) can be simplified according to the special values of the relevant material constants. For the limiting cases, for instance:

— only thermal conduction to the block, reference and environment (which is valid for a compact metallic arrangement containing the sample and the reference):

$$\tau = \frac{C}{\Lambda_1 + \Lambda_2 + \Lambda_3}$$

— the quadratic term in ϑ predominates (a suitable approximation to free-hanging containers):

$$\tau = \frac{C}{\sqrt{4\Lambda_c C\beta}}$$

— only radiation:

$$\tau = \frac{C}{4\Lambda_r T_R^3}$$

If the actual heat transfers are unknown, $\tau(C, \beta, T_R)$ can be approximated by

$$\tau = \frac{C}{\sqrt{a+bC\beta+(e+gT_R^3)^2}} \tag{11}$$

where the constants $a \ldots g$ are determined from the calibration adjustment with different β and T_R.

Normalization. Division of (8) by the area (see characteristic values) leads to the normalized apparatus function:

$$A(t) = \frac{1}{\tau-\tau^*}\left[\exp\left(-\frac{t}{\tau}\right) - \exp\left(-\frac{t}{\tau^*}\right)\right] \tag{12}$$

The calibration factor. The apparatus function can be determined experimentally in the known way and thereby the instrument calibrated, if a known heat pulse of amount Q_p is released in the sample container and the corresponding DTA curve $V(t)$ is measured (e.g. as an electric signal of the differential temperature sensor). Due to the time-dependent heat transient in the sample and with the adjacent system, the measuring curve $V(t)$ is blurred relative to the heat quantity $Q_p\delta(t)$ realized at $t = 0$ ($\delta(t)$ being the Dirac function). This distortion proceeding during the experiment can be described as a convolution

$$kV(t) = Q_p\delta(t) * A(t) = Q_p A(t) \qquad (13$$

in which k is a factor characterizing the applied device (inverse calorimetric sensitivity). In order to calibrate the ordinate axis in units of the heat flow, the area below the measuring curve is put equal to Q_p:

$$\int_0^\infty kV(t)\,\mathrm{d}t = Q_p \tag{14}$$

If the factor k and the time constants are constant during the time interval in which $V(t)$ essentially deviates from the base line, k can be placed before the integral. The area below $V(t)$ can be determined from the characteristic values of the measuring curve $V(t)$, which are defined analogously to the specified values of the apparatus function:

$$\int_0^\infty V(t)\,dt = \gamma V_m(t_2 - t_1) \qquad (15$$

γ is a correction factor plotted vs. τ/τ^* in Fig. 3. The time constants can be specified from Fig. 4 with the help of t_1, t_2 and t_m. (The ambiguity in Fig. 4 is due to the symmetry of the apparatus function in τ and τ^*; it has to be estimated from the equipment whether $\tau/\tau^* > 1$ or < 1.) With (14) and (15), the factor k can be determined from the measuring curve $V(t)$.

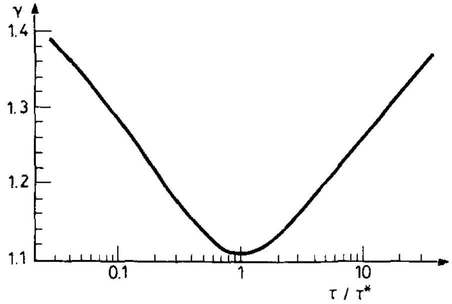

Fig. 3 Correction factor γ for the determination of the area below the measured curve $V(t)$ with the help of $V_m(t_2 - t_1)$

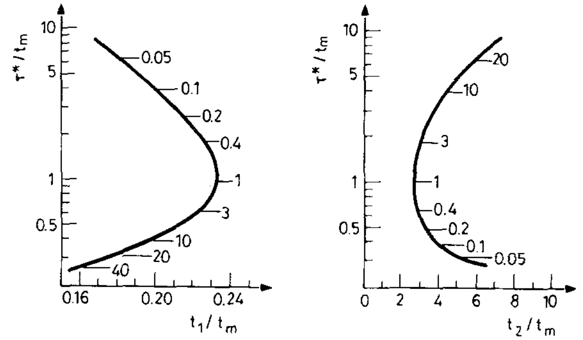

Fig. 4 Connection between the time constants τ^* and τ with the measured half-times t_1 and t_2 related to t_m, the measured time at which the maximum occurs. The curves are provided with the parameter $\varkappa = \tau/\tau^*$ in order to distinguish between the two branches

Under all conditions of operation, the measuring signal is in the same way proportional to the differential temperature ΔT:

$$V(t) = s\Delta T(t) \tag{16}$$

s is a constant scale factor; in electrical recording, it results from the electrical sensitivity of the temperature sensors and the amplification factor. If k and s are unified to the calibration factor K, (16), (14) and (8) lead to

$$K = ks = \frac{C}{\tau} \tag{17}$$

From (10)

$$K = \Lambda_6 - \frac{\Lambda_c\Lambda_5}{\Lambda_4} + \frac{\Lambda_c}{\Lambda_4}\sqrt{4\Lambda_4[C\beta + \Lambda_3(T_R - T_E)] + \Lambda_5^2} \tag{18}$$

The calibration factor is proportional to the values of the heat transport and depends on C, β, T_R and T_E in the second approximation. Analogously to (10), the calibration factor (18) can be simplified for the limiting cases of predominant heat-transfer mechanisms or, corresponding to (11), approximated by an expression of the form

$$K = ks = \sqrt{a + bC\beta + (e + gT_R^3)^2} \tag{19}$$

The constants $a \ldots g$ are determined from four calibration measurements. With the help of the characteristic values and Fig. 4, it is possible to test the validity of the model.

For an actually measured DTA curve $S(t)$ according to (13) holds:

$$kS(t) = \frac{\mathrm{d}Q(t)}{\mathrm{d}t} * A(t) = \int_0^t \frac{\mathrm{d}Q(t')}{\mathrm{d}t'} A(t - t')\,\mathrm{d}t' \tag{20}$$

where $\mathrm{d}Q/\mathrm{d}T$ represents the heat flow searched for, realized in the sample. If the convolution (20) taking place during the experiment is neglected, which is possible provided that $\mathrm{d}Q/\mathrm{d}t$ is scarcely varied in the time interval $\tau + \tau^*$, (20) can be replaced by the approximation

$$kS(t) \approx \frac{\mathrm{d}Q}{\mathrm{d}t}$$

i.e. the heat flow directly follows from $S(t)$ and $k = k(C, \beta, T_R)$. Because of (14), the area of a peak (also of the blurred measuring curve) is equal to the heat quantity realized in the sample.

Deconvolution. The distortion caused by the apparatus function has to be removed by deconvolution [7] if the half-life of the apparatus function is of the same order of magnitude as the time interval in which a reaction takes place:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = kS(t) \overset{*}{\underset{*}{\,}} A(t) \tag{21}$$

An example of the reconstruction methods is the recurrence in the course of which the original function

$$W(t) = \frac{dQ}{dt}$$

is obtained by steps. The approximation after m steps is found as

$$W_m(t) = W_{m-1}(t) + [kS(t) - A(t) * W_{m-1}(t)] \qquad (22)$$

For the special measurement condition C, β, T_R and for any point of time t, the values of k and A can be calculated with a computer by means of (12), (17), (10), (11) and thus the actual values of k and A can be employed in (22). The deconvolution can start with $W_{m-1}(t) = W_0(t) = kS(t)$. A better convergence of the method follows if, from $S(t)$, a function $W_0(t)$ is estimated which approaches the distribution function $W(t)$ better than $kS(t)$.

The results are valid for stationary states. If the heat capacity varies during an experiment due to a reaction in the sample, τ also varies and thereby A and K, too. If a stationary state occurs again after the reaction, the two states can be put together. For the transition from C_0, τ_0 and K_0 to the new values altered by ΔC, $\Delta\tau$ and ΔK, an approximate expression of the form

$$C = C_0 + \frac{\Delta C}{2}\left[1 + \frac{2}{\pi}\arctan\left(\frac{2t - t_b - t_e}{t_e - t_b}\right)\right] \qquad (23)$$

can be used, where t_b and t_e are the beginning and the end of the change.

References

1 M. J. Vold, Anal. Chem., 21 (1949) 683.

2 R. Calvet and H. Prat, Microcalorimétrie, Masson et Cie, Paris 1956;
A. D. Cunningham and F. Wilburn, Differential Thermal Analysis (ed. R. C. Mackenzie) Academic Press, London 1970;
D. Schultze, Differentialthermoanalyse, VEB Deutscher Verlag der Wissenschaften, Berlin 1969.
W. Hemminger and G. Höhne, Grundlagen der Kalorimetrie, Akademie Verlag, Berlin 1980.
J. Norwisz, J. Thermal Anal., 17 (1979) 555.
V. A. Vertogrdsky, J. Thermal Anal., 18 (1980) 455.

3 W. Lugscheider, Ber. Bunsenges. Physik. Chem., 71 (1967) 228.
F. W. Wilburn, J. R. Hesford and J. R. Flower, Anal. Chem., 40 (1968) 777.
G. Willmann and H. Endl, Z. Anal. Chem., 273 (1975) 11.
G. Dragon, J. Thermal Anal., 9 (1976) 405.
G. Van Der Plaats, Thermochim. Acta, 72 (1984) 77.

4 L. G. Homshaw, J. Thermal Anal., 19 (1980) 215.

5 E. Becker, diploma paper, Päd. Hochsch. Halle 1983.

6 R. Döhring, M. Koch and H. Zeltner, Wärmetechnische Isolierungen, VEB Fachbuchverlag, Leipzig 1981.
7 E. Stepanek, Praktische Analyse Linearer Systeme durch Faltungsoperationen, Akad. Verl.-gesellsch. Geest u. Portig, Leipzig 1976.
E. Cesari, P. C. Gravelle, J. Gutenbaum, J. Hatt, J. Navarro, J. L. Petit, R. Point, V. Torra, E. Utzig and W. Zielenkiewicz, J. Thermal Anal., 20 (1981) 47.

Zusammenfassung — Die Apparatefunktion, das ist die Reaktion der Anordnung auf einen Heizimpuls, wird für eine Differential-Thermo-Anlage abgeleitet, wobei neben Wärmemeitung auch -Konvektion und -Strahlung zugelassen sind. Die Lösung der Wärmebilanzgleichung wird durch die Überlagerung zweier Exponentialfunktionen beschrieben, wobei sich die Anhängigkeiten des Gerätefaktors und der Zeitkonstanten von der Wärmekapazität, der Heizrate und der Temperatur ergeben. Zur experimentellen Bestimmung werden die Ausdrücke zu leicht aus den Kalibrierungsmessungen zugänglichen Größen aufbereitet.

Резюме — Для приборов ДТа выведена аппаратурная функция — отклик установки на тепловой импульс, в которой, кроме теплопроводности, учитывались тепловая конвекция и тепловое излучение. Решение уравнения теплового баланса проведено наложением двух экспоненциальных функций, что привело к зависимости градуировочного коэффициента и постоянных времени от теплоемкости, скорости нагрева и температуры. При экспериментальном определении эти соотношения преобразовывались в выражения, легко получаемые из градуировочных измерений.