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THEORY AND PRACTICE OF TRANSFORMING A DSC-PEAK OF A RAPID PROCESS INTO THE REACTION RATE CURVE

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ABSTRACT

The intrinsic inertia of a DSC unit causes a more or less pronounced deviation of the recorded signal curve $\Delta U(t)$ from the time behaviour of the pertinent variable heat flow $q(t)$. In a former treatise (ref.4), the term 'signal potential Φ' was introduced to characterize the product of q and the caloric sensitivity E. An equation was elaborated linking Φ with ΔU and thus permitting the transformation of the signal curve into $\Phi(t)$ as the true reflection of $q(t)$. The present paper is aimed at explaining the determination of the equipment-specific parameters of this equation. The parameters are described as functions of temperature.

INTRODUCTION

Owing to the relationship existing between the equipment used for the quantitative DTA, on the one hand, and the heat conduction calorimeters, on the other hand, which can be used not only for the measurement of thermal quantities Q but, on principle, also for that of heat flows q, a DTA-instrument ought to be suitable not only for the determination of the reaction enthalpies ΔH_r but also for kinetic measurements on reactive systems, where the heat flow out of or into the sample inspected is at any time strictly proportional to the reaction rate $r = dx/dt$ (ref.1). Ideally, ΔU is proportional to q. When the heat flow is strongly variable, the intrinsic inertia of the instrument interferes, however, with the simple interrelationship between the DTA-signal and the heat flow (e.g ref.3). That is why the signal curve $\Delta U(t)$ must deviate the more strongly from the reaction rate curve $r(t)$ searched for, the more quickly the reaction takes its course.

In order to be able to directly compare with each other the configurations of the curves $\Delta U(t)$ and $r(t)$, the ordinates of $r(t)$ must be multiplied by the factor $-E\Delta H_r$. The product is called signal potential Φ and features the same dimension as ΔU:

$$\Phi = -rE\Delta H_r \qquad (1)$$

The transformation of the signal curve which, during the course of the thermoanalytical investigation is recorded as a peak curve, into the curve of the signal potential, avoids the kinetic misinterpretation of the measurement, as only

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the Φ-curve is the true reflection of the reaction rate curve. The equation which links ΔU with Φ and which has been proposed in a former paper (ref.4), is particularly suitable for the carrying-out of this transformation. Apart from these 2 magnitudes, the equation comprises no more than 2 additional equipment-specific parameters. In the aforementioned paper, a method permitting the estimation of the parameters had been proposed also for those instruments which comprise a heating element for the generation of a defined rectangular heat impulse. Now, a mathematically more precise method will be shown consenting a more generalized application.

In the case of very slow reactions there is, however, such a high degree of coincidence between the Φ-curve and the peak curve that the transformation can be dispensed with. To decide this, the paper proposes a criterion permitting the estimation of the deviation between the two curves.

THEORY

Principles

For the heat conduction calorimeter, CALVET & PRAT established for the signal a differential equation of the second order which linked the said signal with the heat flow. According to HEMMINGER & HOEHNE (ref.3), this equation was to be applicable also for the DTA. This was proven by the fact that, proceeding from the formulation found by BORCHARDT & DANIELS, the differential equation was derived in a new way and specifically for the DTA (ref.5). By using the term 'signal potential Φ', it adopted a particularly simple form:

$$\Phi = \Delta U_r + (\tau_1 + \tau_2)d\Delta U/dt + \tau_1\tau_2 d^2\Delta U/dt^2 \qquad (2)$$

ΔU is the total value of the signal at the time taken into consideration. ΔU_r is the portion relating to the reaction and presenting itself as the distance from the base line ΔU_C: $\quad \Delta U_r = \Delta U - \Delta U_C \qquad (3)$

The parameters τ_1 and τ_2 are the so-called time constants of the instrument, which are to be determined.

The Determination of the Time Constants

In the theoretical case of the infinitesimal heat impulse transmitting a finite amount of heat Q, the signal potential Φ is infinitely large only at the time t_0. $\Phi = 0$ for $t > 0$. Then the solution of eq.2 is:

$$\Delta U_r = (e^{-t/\tau_2} - e^{-t/\tau_1})QE/(\tau_2 - \tau_1) \qquad (4)$$

The peak curve as set out in eq.4 has only one turning point, viz. at t_i (behind the apex at t_p). t_p and t_i are determined by a single and a double differentiation and zeroizing of the relative derivations. This results in:

$$t_p = \tau_1\tau_2 \ln(\tau_2/\tau_1)/(\tau_2 - \tau_1) \qquad (5)$$

and $t_i = 2t_p$ (6)

The realization of an infinitesimal heat impulse is impossible. The real impulse is always of a finite length of time, causing the initial section of the recorded peak ΔU_r to take a course which deviates from the ideal peak pursuant to eq.4. Only at the termination of the impulse, the real peak curve will adopt smoothly that configuration which almost completely corresponds to the ideal one. This is achieved shortly in front of the apex.

In contrast with the ideal case, the peak curve relating to the real impulse shows 2 turning points at the times t_{i1} and t_{i2}. $t_{i1} < t_p < t_{i2}$. Since, subsequent to the end of the impulse, $\Phi = 0$, in the real case the difference $\Delta t_{ip} = t_{i2} - t_p$ will adopt that value which, because of eq.6, is valid in the ideal case for t_p pursuant to eq.5.

The time constant τ_2 is obtained by laying off ΔU_r against the time t acc. to:

$$\ln\Delta U_r \simeq -(1/\tau_2)t + \ln v \qquad \text{for } t > t_{i2} \qquad (7)$$

The ratio $\gamma = \tau_2/\tau_1$ of the two time constants is obtained by a graphical or numerical evaluation of the equation

$$(\ln\gamma)/(\gamma - 1) = \Delta t_{ip}/\tau_2 \qquad (8)$$

In the case of DTA-instruments which like the model NETZSCH DSC 444 comprise a heating element fixed to the sample cell, the heat impulse experiment aimed at determining τ_1 and τ_2 at the selected temperature T, is carried out with a rectangular pulse transmitting a defined amount of heat. With other instruments, an indefinite amount of heat is, e.g. transmitted by briefly touching the sample cell with a heated metal bar or by means of a focussed light flash. Due to eq.4, the amount of heat Q only influences v in eq.7. The time constants τ_1 and τ_2 thus determined by means of a thermal pulse experiment are complicated functions of the temperature T. It has been found that a simplified presentation is arrived at by putting

$$\tau_1 + \tau_2 = \tau \qquad (9)$$

$$\tau_1\tau_2 = \tau^2/(2 + \gamma + 1/\gamma) = \tau^2/\zeta \qquad (10)$$

A critical analysis of all calibration problems connected with the DSC showed that all dependences on temperature can be expressed in terms of simple functions of a single temperature function, viz. $\eta(T)$ (ref.5). The determination of $\eta(T)$ is a byproduct of the calibration operations aimed at the assessment of the caloric sensitivity E within the working range of the instrument. E itself is a function of T; see e.g. ref.2. When E_0 is the sensitivity at a conveniently selected temperature T_0, then we have:

$$\eta(T) = E_0/E \qquad (11)$$

Regarding the dependence of τ and γ on T, it has been found (ref.5):

$$\tau = 2\tau_0/\{1 + \eta(T)\} \qquad (12)$$

$$\gamma = 2\gamma_0(T_0 + 273)^{2/3}/[\{1 + \eta(T)\}(T + 273)^{2/3}] \qquad \text{for } \gamma > 2 \qquad (13)$$

Here, τ_0 and γ_0 have been referred to the same temperature T_0 as E_0. The values E_0, τ_0, γ_0 and the function $\eta(T)$ characterize the DTA-instrument used. In conjunction with eq.9 and eq.10, eq.2 achieves a configuration especially suitable for practice:

$$\Phi = \Delta U_r + \tau d\Delta U/dt + (\tau^2/\zeta)d^2\Delta U/dt^2 \qquad (14)$$

CONCLUSION

The theory laid down in abbreviated form, furnishes a criterion which allows to decide wether the transformation of the ΔU_r- into the Φ-curve is necessary or not. There is no doubt as to the coincidence between the two curves, whenever the ratio $\Phi(t)/\Delta U_r(t)$ for all t in the reaction interval is found to be very close to 1. In a case like this, the transformation could be dispensed with, whereas otherwise it would have to be carried out. In practice it is sufficient to evaluate the deviation of Φ from ΔU_r at the forward turning point:

$$\Phi(t_{i1})/\Delta U_r(t_{i1}) - 1 = \tau/t_{i1} \qquad (15)$$

As soon as this deviation exceeds half of the equipment-specific average error, then the transformation is an absolute must in order to avoid additional errors. The transformation can be performed 'by hand' or by means of a computer (ref.4).

Only in the case of an ideal base line, the area under the Φ-curve is equal to the area under the original peak. Because of eq.1 the Φ-area is always proportional ΔH_r. Therefore the integration of eq.14 between the peak onset (t = 0) and its termination ($t = t_\infty$) yields an equation which is helpful for the exact computation of the reaction enthalpy out of the peak area in case of a non-ideal base line.

For the purpose of the exact kinetic interpretation of the Φ-curve, it is important to know the sample temperature T_S at any time t within the reaction interval. If the steepness $\sigma = dU(T)/dT$ of the thermocouple arrangement is known and when measuring the reference temperature T_R, then T_S can be computed by:

$$T_S(t) = T_R(t) + \{\Delta U(t) + [\tau/(\gamma + 1)]d\Delta U(t)/dt\}/\sigma \qquad (16)$$

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