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A THEORETICAL CONTRIBUTION TO THE ANALYSIS OF DTA-PEAKS OF RAPID REACTIONS

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ABSTRACT

The paper introduces the idea of the signal potential Φ having the dimension of an electromotive force. This signal potential is given by a differential equation of the second order refered to the DTA-signal ΔU. Not ΔU, but Φ is directly proportional to the momentary reaction rate. In the equation there are only two factors τ and ζ which are specific instrument parameters and easily determinable.

A method is shown to transform a DTA-peak curve into the signal potential Φ as a function of time and temperature. $\Phi(t,T)$ is a true picture of the reaction rate course.

INTRODUCTION

Since the investigations by Borchardt & Daniels (ref. 1) in the early days of quantitative DTA the peak curve is supposed to be a source of information about reaction kinetics. It is very important to remember that the momentary DTA signal is generally not directly equivalent to the momentary heat flux or to the rate of the reaction in the sample. This fact is often not taken into account, because the successful consideration of the peaks caused by very slow reactions as reliable plots of the course of the rate of these reactions has frequently misled scientists to use this proceeding for other cases, as well.

Unfortunately Borchardt & Daniels themselves produced the uncertainty in the peak interpretation by introducing simplifications into the formulas which they had originally developed exactly within the scope of reasonable assumptions. The difficulties arose, when they did not specify the conditions clearly enough which are justifying the simplifications. The examples reported in reference 1 show the half-life of the chosen reactions to be of a higher magnitude than the time constant τ of the instrument. τ is given by dividing the heat capacity by the heat transfer coefficient. Only if $t_{1/2} \gg \tau$ the mentioned simplified formula reveals the value of the rate constant k_r with satisfying accuracy. The original unsimplified formula, however, is not easy to apply because of its complexity.

In order to avoid difficult arrangements it is prefered now to divide the approach to the problem into two steps. The first step is the transformation of the DTA-peak into the curve of the momentary heat flux as a function of time or of temperature respectively, and the second one is the analysis of the transformed curve for the kinetic characteristics such as the reaction order, the rate constant, and the activation energy. The present paper deals only with the first step because the science of chemical kinetics is disposing of methods which allow to analyse a reaction rate curve.

For the purpose of a greater mental distinction of the reaction rate and the DTA-signal the idea of a signal potential Φ is introduced as a tool which generalizes the proceeding to include such phenomena too, which are not describable by means of regular chemical kinetics. Because $\Phi = qE$, and $q = dQ/dt$, and E is the caloric sensitivity, Φ is a true picture of the rate of heat generation caused by any process in the sample. Φ is equidimensional to the signal ΔU.

FUNDAMENTALS

Because of the relationship between a DTA device and a heat conduction calorimeter which has already been shown up by S. Spiel (ref. 3), Hemminger & Hoehne (ref. 2) reported a differential equation of the second order refered to the difference of temperatures in order to describe the heat flux q_r from or into a reacting sample more precisely:

$$q_r = (\Delta T + a d\Delta T/dt + b d^2\Delta T/dt^2)/R_\omega \qquad (1)$$

wherein a and b are complicated and difficultly determinable constants having the dimensions of time and the square of time, respectively.

The present investigation gives a very similar result when introducing the first order differential equation dealing with the so-called thermometer problem into the heat flux equation by Borchardt & Daniels. The fundamentals of these authors' theory are shown by the figures 1 to 3. They described the reaction caused heat flux q_r by $q_r = \Delta T_r/R_\omega + C d\Delta T/dt$, but ΔT_r means only the difference of temperatures of the substances and not that of the thermocouples. In the case of unsteadiness there is also a difference between the measuring location and the substance to be expected which is governed by $T_S - T_M = \Delta T_{SM} = \tau_1 dT_M/dt$. Substituting T_S and T_R in ΔT by an arrangement like this, the equation for q_r becomes

$$q_r = \Delta T_{rm}/R_\omega + (\tau_1/R_\omega + C)d\Delta T/dt + \tau_1 C d^2\Delta T/dt^2 \qquad (2)$$

Now ΔT_{rm} means the difference of measured temperatures of the thermocouples, but not that of the substances. Using the formal relations $CR_\omega = \tau_2$ and $\sigma\Delta T = \Delta U$ and $\sigma R_\omega = E$ (E is the caloric sensitivity) the equation can be presented in a more practicable form. $\sigma$is the so-called steepness of the thermocouple arrangement: σ = dΔU/dt.

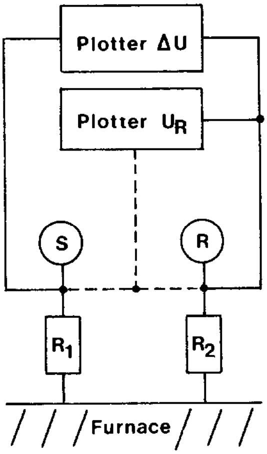

Fig. 1.
Very simplified model of a DTA device. The heat flux F to R is in the steady state case $q_r = (T_F-T_R)/R_2=(C_A+C_C+C_R)dT_F/dt$ wherein R_2 is the heat transport resistance (reasonably should be $R_1=R_2=R_\omega$), C is the heat capacity, the indices R,C, and A characterize the reference, the crucible, and the participating environment. In the case without reaction a similar equation describes the flux from F to S. Probably there is a difference in C_S and C_R.
That gives $-\Delta T_C = (C_S - C_R)R_\omega dT_F/dt$ or

$$-\Delta U_C = (C_S - C_R)E\beta \qquad (3)$$

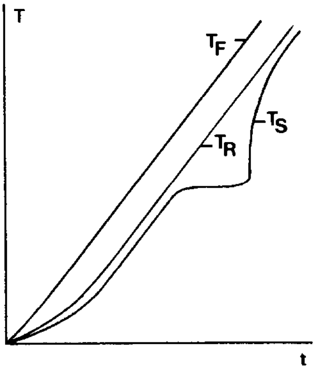

Fig.2.
Diagram showing the temperatures T_F, T_R and T_S. T_F and T_R are linear functions of time, the onset phase excepted. T_S is also linear in so far as a reaction or a phase transition does not occur. The example of an endothermic phase transition is shown.

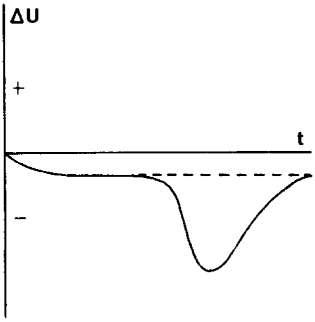

Fig. 3. Showing the ΔU-Plot.
The distance of the base line being parallel to time (in this case) is ΔU_C. The distance of the peak signal from the base line is ΔU_r.

THE SIGNAL POTENTIAL Φ

When the equation (2) is multiplied by σR_ω at either side, the left-hand side gives $q_r \sigma R_\omega$. For a shorter version this product $q\sigma R_\omega$ is substituted by Φ. Φ is called signal potential because it is equidimensional to an electric force. Besides Φ represents the electromotive force which would formally be generated by the difference of temperatures driving a steady heat flux of q, being equal to the unsteady q_r, through the heat transport resistance R_ω.

Now, using the abbreviations mentioned in the precedent paragraph and those which will be explained later, the equation to calculate Φ can be written in its final form including only two instrument parameters τ and ζ

$$\Phi = \Delta U_r + \tau d\Delta U/dt + (\tau^2/\zeta)d^2\Delta U/dt^2 \qquad (4)$$

The signal potential Φ is the sum of the momentary DTA signal ΔU_r over the base line and the first derivation of ΔU at this point of time multiplied by the time constant τ and the second derivation multiplied by the square of the time constant τ divided by a dimensionless magnitude ζ. The calculation of Φ point by point from the peak curve $\Delta U_r = f(t)$ gives finally the signal potential Φ as a function of time t and of temperature T because the sample temperature is calculable from the time-linear increasing temperature of the furnace or of the reference respectively. Remembering τ to be the sum of $\tau_1 + \tau_2$ it may be written:

$$\tau_2/\tau_1 = \gamma \qquad (5)$$

$$\tau = (1 + \gamma)\tau_1 = \tau_2(1 + \gamma)/\gamma \qquad (6)$$

$$\tau_1\tau_2 = \tau^2/\zeta \qquad (7)$$

$$\zeta = 2 + \gamma + 1/\gamma \qquad (8)$$

Because $1/\gamma \ll 1$: $\quad \gamma \approx \zeta - 2 \qquad (9)$

Because of the fact Φ being proportional to q_r, Φ must be zero if $q_r = 0$. This does not imply that the signal ΔU_r is to be zero in any case if q_r is zero. After a short heat impulse q_r drops immediately to zero but the signal ΔU_r does not do so. Probably the signal even increases for a moment and decreases thereafter following the function $\Delta U_r = \exp[-(t-t_m)/\tau_2]$. In the case of an impulse this gives the opportunity to calculate τ_2 from the slope of the plot of ΔU_r against Δt where Δt is running from the ΔU_r-maximum to infinity.

The magnitude of ζ may be estimated by use of the condition that the equation (4) has to give $\Phi = 0$ when the impulse is terminated. In a first run τ is set equal τ_2, and ζ is found by trial. Then τ can be estimated by equations (9), (5) and (6). The values are to be improved by recurrence. It must be taken into account that τ and ζ are functions of temperature.

Another paper which is dealing with the exact determination of γ and then of ζ will be published together with the results of the investigation of the temperature dependency of τ,γ,ζ and E.

$\Phi(t,T)$ has interesting properties. In the case of a straight base line being parallel to the time axis, integrating $\Phi(t)$ within the limits from $t = 0$ (peak onset) to $t = t_\omega$ (peak end practically) gives the same result as integrating the peak ΔU_r itself within the identical limits in spite of a great difference existing propably in shape between the two. The dimensions of the integration results are identical, too.

The connection of the signal potential Φ to the reaction rate γ is given by the simple equation

$$r = \frac{dx}{dt} = - \Phi/\Delta H_r E = \Phi . \int_{t=0}^{t_\omega} \Phi dt \qquad (10)$$

As the change of enthalpy ΔH_r belonging to the total conversion of the sample and E, the caloric sensitivity, are constants, $\Phi(t,T)$ represents a real picture of the reaction rate.

PEAK ANALYSIS IN PRACTICE

For the purpose of transforming the peak curve into the curve of the signal potential Φ by hand, the differential quotients can be replaced by quotients of differences. Setting $\Delta U_r = y = f(t)$ the value of $d\Delta U/dt$ at the point of t_2 is calculable with satisfactory accuracy by

$$f'(t_2) = [(y_3 - y_2) + (y_2 - y_1)]/2\Delta t \qquad (11)$$

The points t_1, t_2, and t_3 have to be equidistant. Now setting $f'(t) = y$ equation (11) is also applicable to calculate $d^2\Delta U/dt^2$ correspondingly. The method to estimate values of τ and of ζ has been shown in the precedent paragraph. The sum $f(t_2) + \tau f'(t_2) + (\tau^2/\zeta)f''(t_2)$ is the required $\Phi(t_2)$. This proceeding is applied point by point. The curve of $\Phi(t)$ is the final result.

The transformation can easily be performed by means of a computer or a similar device fitted with the DTA-instrument, but it is always necessary to have the option of checking up the single steps, i.e. the original peak curve has to be recorded in any case. The chart speed should correspond to the problem.

The more or less distinct deviation of the shape of $\Phi(t)$ from the shape of the peak curve $\Delta U_r(t)$ gives an idea of the kind and the rate of a process going on in the sample.

The experimental investigation was carried out by using a Netzsch-DSC 444 fitted with a heating element at the sample cell for calibration by electric means. A heat impulse was given by a constant current of 27 mA and of 5 seconds of duration. The resistance of the heating element at 254°C was $R_\Omega = 135.8\ \Omega$ $E = E_0/\eta(T) = 17.4\ \mu V/mW$. Then Φ should theoretically be $\Phi = q_r E = i^2 R_\Omega E = 1{,}726\ \mu V$. The DTA-record is a peak of regular shape. Fig. 4 shows this peak and the

Φ-curve calculated from this peak by the methods of this paper.

The impulse is a short one compared with the time constant τ which is found to be 19 sec. The estimated value of ζ is 23. The calculated Φ(t) fits in with the theoretic impulse rectangle satisfyingly.

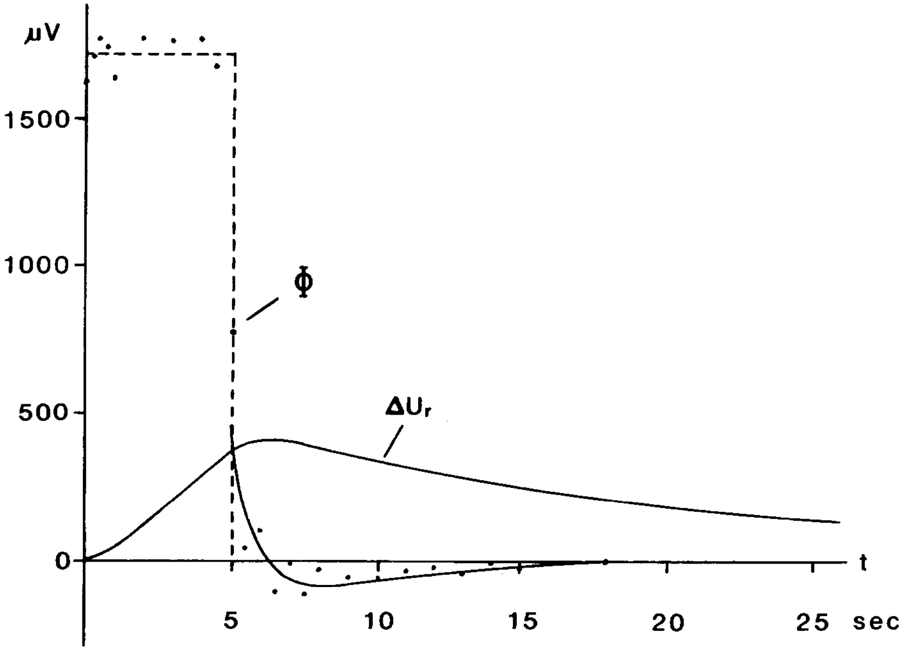

Fig. 4 showing the principal section of a peak caused by a rectangular heat impulse, the impulse itself (its height in units of qE) and the values of Φ calculated from the peak point by point. Heating rate β = 5 degrees C per minute.

The signal curve ΔU_r exhibits intense bendings at the onset range and at the apex. Especially in these ranges the measurements of the signal height ΔU_r and of the corresponding time t must be very exact ones. Here the measurement points should have a distance as narrow as possible. This demand is often not to be satisfied because the measuring error weighs with the smallness of the magnitudes considered. Therefore the trial is recommended to approach the line of values by means of a polynomial.

In the case of the example demonstrated above, the peak onset range was describable by an expression $\Delta U_r = a(t^2 - t^3/4)$, showing satisfying conformity with the peak curve up to $t \leqq 1$ s. By dimensional analysis the more precise approach is expected to be $\Delta U_r = a(t^2 - t^3/b\tau_1)$ where $b \cong 4$. Then the factor a has the dimensions of an electromotive force divided by the square of time.

$$\Delta U_r = a(t^2 - t^3/4\,\tau_1) \qquad (12)$$

$$d\Delta U/dt = a(2t - 3t^2/4\tau_1) \qquad (13)$$

$$d^2\Delta U/dt^2 = a(2 - 6t/4\tau_1) \qquad (14)$$

At the peak onset (t = 0) both ΔU_r and $d\Delta U/dt$ are zero, but in the case of a rectangular heat impulse Φ is not zero at t = 0. $\Phi = i^2R_\Omega E$. If t = 0, then $d^2\Delta U/dt^2 = 2a$. At the onset is $\Phi = (\tau^2/\zeta)d^2\Delta U/dt^2$, therefore:

$$\tau^2/\zeta = \Phi(0)/(2a) \qquad (15)$$

The approach given by equ. 12 is valid in the range of time $0 < t < t_k$. At $t = t_k$ the value of $d^2\Delta U/dt^2$ becomes zero. The value of "a" is calculable at any time smaller than t_k by inserting the time t and the measured $\Delta U_r(t)$ into equ. 12:

$$a = \Delta U(t)/(t^2 - t^3/4\tau_1) \qquad (16)$$

For the first run it is set $\tau_1 = 1$. By doing this, an approximative value of a is got (a_x). Setting at first $\tau = \tau_2$, equ. 15 shows the way for calculating an approximative value of ζ_x. $\gamma \cong \zeta - 2$ gives an approach γ_x to the value of $\gamma = \tau_2/\tau_1$. Then $\tau_1 = \tau_2/\gamma$ and $\tau = \tau_2(\gamma + 1)/\gamma$. The repeated application of equations (15) and (16) using the values of γ and τ just calculated gives improved results of ζ and γ.

Example: $\tau_2 = 18.0$ s was found from the slope of the descending peak curve. At $t = 1$ s the example of figure 4 yields $\Delta U(1) = 39.8$ µV. In the first run of calculation τ_1 is assumed to be 1, then equ. 16 gives $a_x = 53.1$ µV/s^2.
If $\Phi(0) = 1\ 726$ µV, then $(\tau^2/\zeta)_x = 16.3$ s^2 or $\zeta_x = 2a_x\tau_2{}^2/\Phi = 19.9$.
$\gamma \cong \zeta_x - 2$ gives 17.9s, thus $\tau_1 = \tau_2/\gamma = 18.0/17.9 = 1.01$ s and $\tau = 18.0 \cdot 18.9/17.9 = 19.0$ s. Using these values of τ_1 and of τ the calculations by means of the equations 15 and 16 are repeated. That gives finally $\tau^2/\zeta = 15.2$ s^2. Then is $\zeta = 23$, $\gamma = 21$, $\tau_1 \cong 0.8$ s, and $\tau = 18.8$ s.

CONCLUSION

By introduction of the idea of a signal potential Φ a relatively simple connection between the curves of the signal ΔU (Peak) and of the reaction rate $dx/dt = -\Phi/\Delta H_r E$ has been found (see equ. 4). The formula contains the parameters τ and τ^2/ζ. Methods are shown for estimation of these parameters and for the practical application of the formula to transform the peak curve into the rate curve. It is even possible to restore a short rectangular heat impulse from the peak curve which was caused by that impulse. In case of a regular chemical reaction the equation 22 of the paper of Borchardt & Daniels (ref. 1) is after placement of ΔT by Φ unrestricted to be applied to calculate the rate constant k.

The greater the reaction rate the more differs the rate curve as a function of time from the peak curve in thermal analysis by means of the scanning technique.

The possibility of exact modelling of a real process by transforming a peak curve into the $\Phi(t)$-curve enhances the confidence in kinetic investigations by means of quantitative DTA.

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