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REACTION KINETICS CALCULATED BY THE SINGLE-POINT METHOD. A SYNTHESIS OF THE BORCHARDT—DANIELS THEORY AND THE KISSINGER THEORY OF DIFFERENTIAL THERMAL ANALYSIS

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A joint consideration of the basic kinetic equation of DTA (Borchardt–Daniels method) and of the mathematical conditions for characteristic points of the DTA curve (Kissinger method) results in a system of three equations with three unknowns (kinetic constants). By solving this system, one can obtain formulae for the calculation of kinetic constants from any single point of the thermoanalytical curve. Rules are given for determining the characteristic and particular points in the DTA curve. The concept of the mean heating rate of the sample is introduced and a graphical method is described for its determination. The relationship between the fraction unreacted at the characteristic point (the shape of the peak) and the order of reaction is established. The dehydration reaction of copper sulphate pentahydrate was studied by the gradientless DTA method and good agreement was found between the kinetic constants determined with different computation methods.

The papers by Borchardt and Daniels [1] and by Kissinger [2] occupy a particular place in the theory of DTA. In [1] the model of the gradientless sensor of the DTA instrument was introduced for the first time into the theory of the method, and a practical implementation of this model was developed for liquid samples, thereby founding gradientless calorimetry. In [2] the characteristic points of the thermoanalytical curve were considered systematically for the first time and the possibility of their utilization for kinetic analysis was demonstrated. The above papers, however, could not provide a comprehensive view of the fundamental theoretical and practical problems of the method, and need further development and an increase in accuracy. In particular, the theory of Borchardt and Daniels makes use of very many approximations regarding heat exchange conditions in the sensor of the instrument and also regarding the nature of the reaction studied, and for this reason has limited applicability. The absence of the concept of characteristic points in this theory renders it incomplete to a certain extent. As to Kissinger's theory, it contains a number of erroneous statements, as will be demonstrated in the following. These, however, do not affect the main results and can easily be corrected,

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after which it turns out that the two approaches [1] and [2] are not unrelated, but can readily be united into a single kinetic theory of DTA. The combined theory discussed below is applicable to a sensor with a thermally insulated sample holder, approaching in its parameters the gradientless model described in [1] and in earlier papers [3, 4].

The absence of temperature gradients in the sample holder with the sample allows a description of the thermal balance of the cell by the equation

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}t}+C\frac{\mathrm{d}T}{\mathrm{d}t} = -K\Delta T = -K(\Delta T_B+\Delta T_p) \tag{1}$$

where $\frac{\mathrm{d}\Delta H}{\mathrm{d}t}$ is the heat absorption rate of the reaction; C is the overall heat capacity of the holder and the sample; $\frac{\mathrm{d}T}{\mathrm{d}t} = \varphi$ is the rate of temperature change of the sample; K is the heat transfer coefficient of the cell (a calibration constant of the instrument); ΔT is the differential temperature, equal for DTA without reference sample to the temperature change over the thermal barrier of the cell; ΔT_B is the constant component of this temperature change when the linear heating regime is reached; and ΔT_p is the additional temperature, i.e. the deviation of the temperature from the linear regime as a result of the reaction, equal to the height of the DTA peak. Before the reaction starts:

$$\Delta T = \Delta T_B = -\tau\Phi_0 \tag{2}$$

where τ is the time constant of the cell, $\tau = \frac{C}{K}$ = const.; and Φ_0 is the heating rate of the block. During the reaction, $\Delta T_B = \Delta T_{Bh} = -\tau\Phi_h$, where Φ_h is the hypothetical heating rate of the sample [5]; ΔT_{Bh} is the baseline of the reaction from which the additional temperature ΔT_p is counted. If τ = const., then $\Phi_h = \Phi_0$ and $\Delta T_{Bh} = -\tau\Phi_0$.

To change over from the rate of heat absorption to the rate of reaction, let as assume that

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = \Delta H_t\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{3}$$

where α is the fraction reacted (conversion); ΔH_t is the overall heat of reaction. It follows from Eqs (1), (2) and (3) that

$$\Phi = \Phi_0-\frac{\Delta T_p}{\tau}-\frac{\Delta H_t}{C}\cdot\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{4}$$

Let us integrate Eq. (1) from the start of the reaction to the moment t:

$$\Delta H = -K\int_0^t \Delta T_p\,\mathrm{d}t+C\varphi_0 t-C\int_0^t \varphi\,\mathrm{d}t \tag{5}$$

or

$$-\Delta H = KA + C\Delta T_p \tag{5a}$$

where A is the peak area in the DTA curve, and ΔT_p is the peak height.

A more general kinetic equation of DTA, than Eq. (5a) can be obtained by introducing Eq. (4) into Eq. (5) and expressing the term $\int_0^t \Delta T_p \, dt$ in the form

$$-\int_0^t \Delta T_p \, dt = \frac{\varphi_0 t^2}{2} - \int_0^t \int_0^t \varphi_p \, dt \, dt \tag{5b}$$

After the necessary transformations, one obtains

$$-\Delta H_t \int_0^t \alpha \, dt = C \int_0^t \Delta T_p \, dt + K \int_0^t \int_0^t \Delta T_p \, dt \, dt \tag{6}$$

Successive differentiation of Eq. (6) yields

$$-\Delta H_t \alpha = K \int_0^t \Delta T_p \, dt + C\Delta T_p = KA + C\Delta T_p \tag{7}$$

$$-\Delta H_t \frac{d\alpha}{dt} = K\Delta T_p + C\frac{d\Delta T_p}{dt} \tag{8}$$

$$-\Delta H_t \frac{d^2\alpha}{dt^2} = K\frac{d\Delta T_p}{dt} + C\frac{d^2\Delta T_p}{dt^2} \tag{9}$$

By integration of Eq. (7) between infinite limits, one obtains

$$-\Delta H_t = KA_t \tag{10}$$

Equations (7) and (10) allow one to find α from the data of the DTA curve:

$$\alpha = \frac{KA + C\Delta T_p}{KA_t} = \frac{A + \tau\Delta T_p}{A_t} \tag{11}$$

and the fraction unreacted:

$$(1-\alpha) = \frac{K(A_t - A) - C\Delta T_p}{KA_t} = \frac{A_t - A - \tau\Delta T_p}{A_t} \tag{12}$$

Assuming that, similarly to the assumptions in [1] and [2], the rate of reaction is described by an equation of the form

$$\frac{d\alpha}{dt} = K_0 \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{13}$$

one finds that

$$K_0 \exp\left(-\frac{E}{RT}\right) = \frac{\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{(1-\alpha)^n} = \frac{\Big(K\Delta T_p + C\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}(KA_t)^{n-1}}{[K(A_t-A)-C\Delta T_p]^n} = B(n) \qquad (14)$$

Equation (14) can be expressed in a form better suited for further calculations:

$$K_0 \exp\left(-\frac{E}{RT}\right)(1-\alpha)^{n-1} = \frac{\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{1-\alpha} = \frac{\Delta T_p + \tau\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}}{A_t - A - \tau\Delta T_p} = B \qquad (15)$$

where the experimental value B is equal to the rate constant of the reaction multiplied by the factor $(1-\alpha)^{n-1}$. By taking the logarithm of Eq. (14), one obtains

$$\ln B(n) = \ln K_0 - \frac{E}{RT} \qquad (14a)$$

According to [1], the order of the reaction is found by selecting a value for n at which the plot $\ln B(n)$ *versus* $\frac{1}{T}$ is represented by a straight line. From the slope of this line to the abscissa, one can then determine the activation energy E, and from the intercept on the ordinate one obtains the frequency factor of the reaction, K_0.

Equation (14) contains three unknowns: E, K_0 and n. Besides the described trial-and-error method, one may attempt to solve a system of three equations with three unknowns of the type of Eq. (14a) for three different temperatures, i.e. three points in the DTA curve. If the reaction takes place within a narrow temperature interval, or changes its parameters during its course, both these methods may prove insufficiently accurate. The optimum method for such cases would be one in which the kinetic constants could be calculated for a single temperature, i.e. from the data for any single point of the DTA curve. For this purpose one must find two more equations, containing the constants sought for and experimentally measurable values which, together with Eq. (14a) or Eq. (15), would form a system of three equations with three unknowns. As will be demonstrated below, the missing equations can be obtained from the mathematical conditions for the characteristic points of the differential curve (Kissinger's method). Let us start our discussion with the point of maximum rate of reaction, i.e. the m point.

Before utilizing the conditions for the m point, we must determine the position of this point in the DTA curve.

In Kissinger's theory it is asserted that the m point is located at the top of the DTA peak. However, consideration of this question when the main kinetic equations of DTA, Eqs (8) and (9), are taken into account will demonstrate that this statement is erroneous. The authors of [6] also arrived at this conclusions, on the basis of analogous analysis.

Let us perform the construction shown in Fig. 1. The differential curve will be represented (with an accuracy satisfactory for the analysis) by the function $\Delta T_p = \sin\gamma$; the origin of the system of coordinates will be located at the inflexion point on the initial branch of the peak (i point). Then, $\frac{d\Delta T_p}{dt} = \cos\gamma$ and $\frac{d^2\Delta T_p}{dt^2} = -\sin\gamma$;

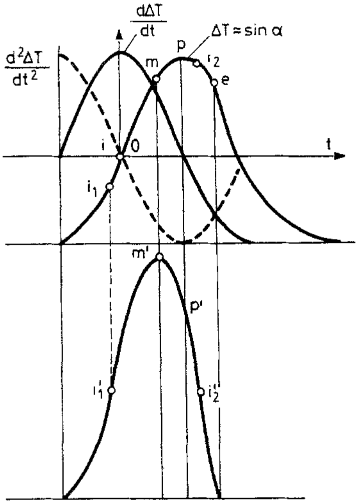

Fig. 1 Idealized DTA curve and distribution of the characteristic points in it: i — inflexion point; m — point of maximum rate of reaction; i_1 and i_2 — points of maximum positive and negative acceleration of the reaction. In the lower part: transformed DTA peak described by Kissinger's theory

the plots corresponding to these functions are also presented in Fig. 1. Let us write the conditions for the inflexion point:

$$(a)\left(\frac{d\Delta T_p}{dt}\right)_i = \max; \quad (b)\frac{d^2\Delta T_p}{dt^2} = 0 \tag{16}$$

and for the point of maximum rate of reaction:

$$(a)\left(\frac{d\alpha}{dt}\right)_m = \frac{K\Delta T_m + C\left(\frac{d\Delta T_p}{dt}\right)_m}{KA_t} = \max; \quad (b)\left(\frac{d^2\alpha}{dt^2}\right)_m = 0 \tag{17}$$

Hence,

$$A_t\left(\frac{d^2\alpha}{dt^2}\right)_m = \left(\frac{d\Delta T_p}{dt}\right)_m + \tau\left(\frac{d^2\Delta T_p}{dt^2}\right)_m = 0 \tag{18}$$

It is clear from Fig. 1 that Eq. (18) cannot be satisfied in the section of the curve below the i point or at the i point itself, since here $\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} > 0$ and $\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2} \geq 0$ (the sum of two positive numbers cannot be equal to zero); also, Eq. (18) cannot be satisfied at the p point, i.e. at the top of the peak, since at this point $\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} = 0$, while $\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2} < 0$; in contrast, in the section of the curve between the i point and the p point, the signs of $\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$ and $\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2}$ are opposite, and Eq. (18) can be satisfied if the values are suitable. The exact position of the m point can be found by utilizing Eq. (17a); for this purpose one has to construct the relationship between the right-hand side of Eq. (17) and the coordinates of the point in the curve; the point where the right-hand side of Eq. (17a) reaches the maximum value will be the m point. In an analogous manner one can find the points at which the reaction will have maximum positive and negative acceleration. For these points, the conditions

$$A_t\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}t_2}\right)i_1 = \left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right)i_1 + \tau\left(\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2}\right)i_1 = \max \tag{19}$$

$$A_t\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\right)i_2 = \left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right)i_2 + \tau\left(\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2}\right)i_2 = \max \tag{20}$$

must be satisfied. It may be seen in Fig. 1 that the i_1 point is located lower than the i point, while the i_2 point lies between the p point and the e point, i.e. the end-point of the reaction.

This end-point may be defined as the point at which exponential decline of the curve

$$\Delta T_p = \Delta T_i \exp\left(-\frac{t}{\tau}\right) \tag{21}$$

begins; in this equation, time is counted from the e point on, since from here on the equation obtained from Eq. (8) at $\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = 0$ is satisfied. The function (21) is actually the solution of this differential equation, and the DTA curve is its graphical representation. Thus, Eq. (8) with $\frac{\mathrm{d}\Delta H}{\mathrm{d}t} \neq 0$ is valid up to the e point, whereas after this point, Eq. (8) with $\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = 0$ is valid; different functions correspond to these two equations, and hence at the e point different functions will meet, and the DTA curve will have a break in continuity, i.e. two different values for the derivative

$\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$ will exist: one for approaching the e point from the right-hand side, and the other for approaching it from the left-hand side: the expression for the first can be obtained from Eq. (8) at $\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = 0$:

$$\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right)_e = -\frac{\Delta T_e}{\tau} \tag{22}$$

Consequently, only one inflexion point will appear in the DTA curve. The second point, which might appear visually to be an inflexion point, is in fact a particular point of the curve: the continuity break point indicating the end of the reaction. For this reason, the concept used in [2] for determining the shape index S of the peak is erroneous. (The shape index is the ratio of the slopes of the tangents to the curve at the inflexion points on the ascending and descending branches of the peak.) These tangents should not be drawn at the i and e points, but at the i_1 and i_2 points, for which the condition used in [2] to find the relationship between S and the order of reaction n, i.e. $\frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3} = 0$, is valid.

The above analysis demonstrates that Kissinger's error lies in determining the positions of the characteristic points in the differential curve incorrectly. It is a consequence, in fact, of his using, the form

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K\Delta T_p \tag{23}$$

for the DTA equation, and not Eq. (8). However, Eq. (8) can be transformed into the form of Eq. (23), and the DTA peak transformed correspondingly. After this, Kissinger's theory will become fully applicable to the transformed peak. For this purpose, let us write Eq. (8) in the following form:

$$-\frac{\Delta H}{K}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Delta T_p + \tau\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} = \Delta T'_p$$

To find $\Delta T'_p$, one must add the term $\tau\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$ to the height of the peak; the value of τ can be taken from Eq. (22) or from the integral form of this equation, $\tau = \frac{A}{\Delta T_p}$; the term $\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$ is found by graphical derivation of the curve. The points i_1 and i_2 for which the conditions (19) and (20) are satisfied can be used as base points, as well as the m point (Eq. 17), the p point, where $\Delta T'_p = \Delta T_p$, and the e point, where $\Delta T'_p = 0$.

By connecting these base points by a continuous line, a peak is obtained (shown in the lower part of Fig. 1) whose area is equal to the area of the original peak, but the characteristic points m', i'_1 and i'_2, i.e. the points corresponding to the maximum rate of reaction and to the maximum positive and negative acceleration of the reaction coincide with the peak height and with the inflexion points in the ascending and descending branches of the curve, as assumed in Kissinger's theory.

To obtain one of the equations of the system consisting of three equations, let us take the derivative of Eq. (13) and make use of the condition (17b):

$$\frac{d^2\alpha}{dt^2} = \frac{d\alpha}{dt}\left[\frac{E\varphi}{RT^2} - K_0 \exp\left(-\frac{E}{RT}\right) n(1-\alpha)^{n-1}\right] \tag{24}$$

$$\frac{E\varphi_m}{RT_m^2} = K_0 \exp\left(-\frac{E}{RT_m}\right) n(1-\alpha_m)^{n-1} \tag{24a}$$

where α_m is the fraction reacted at the m point at the temperature of maximum rate of reaction T_m, and Φ is the momentaneous (true) heating rate of the sample at the m point. Joint solution of Eqs (15) and (24a) results in an equation with two unknowns, E and n:

$$\frac{E\varphi_m}{RT_m^2} = nB_m \tag{25}$$

The third equation of the system is obtained by integrating Eq. (13). For $n \neq 1$:

$$\frac{1}{n-1}\left[\frac{1}{(1-\alpha)^{n-1}} - 1\right] = \frac{RT^2}{E\Phi} K_0 \exp\left(-\frac{E}{RT}\right)\left(1 - \frac{2RT}{E}\right) \tag{26}$$

where, for integration of the rate constant, the method of integrating by parts [7] is applied. The value Φ in Eq. (26) is the mean heating rate of the sample in the temperature interval studied (how to find it is described in the experimental part of this paper). Neglecting the term $\frac{2RT}{E}$, which is small in comparison to 1, one obtains from Eq. (26) for the m point:

$$\frac{E\bar{\Phi}_m}{RT_m^2} = \frac{K_0\left(-\frac{E}{RT_m}\right)(n-1)(1-\alpha_m)^{n-1}}{1-(1-\alpha_m)^{n-1}} = \frac{B_m(n-1)}{1-(1-\alpha_m)^{n-1}} \tag{26a}$$

Equations (15), (24a) and (26a) form the desired system of three equations with three unknowns. Solving this system for the case $\Phi_m = \bar{\Phi}_m$ yields

$$n(1-\alpha_m)^{n-1} = 1 \tag{27}$$

For reactions of the first order, integration of Eq. (13) yields

$$-\ln(1-\alpha) = \frac{RT^2}{E\bar{\Phi}} K_0 \exp\left(-\frac{E}{RT}\right) \tag{28}$$

where, as earlier, the small term $\frac{2RT}{E}$ is neglected. Joint solution of Eqs (28), (25) and (15) at $n = 1$ yields at the m point

$$-\ln(1-\alpha_m) = 1$$

and hence

$$\alpha_m = 1-e^{-1} = 0.63 \tag{27a}$$

Joint solution of Eqs (27) and (24a) yields at the m point for all values of n

$$\frac{E\varphi_m}{RT_m^2} = K_0 \exp\left(-\frac{E}{RT_m}\right) \tag{29}$$

Equation (27) may be solved for α_m, but not for n. For this reason, n is found by selection or by the plot representing the relationship

$$\alpha_m = \left(1-\frac{1}{n}\right)^{\frac{1}{n-1}}$$

The analysis performed above demonstrates that the m point has the following important properties: (a) the fraction reacted at the m point is a function of one independent variable only, namely the order of reaction n. For reactions of the first order this fraction is equal to the defined value 0.63, i.e. α_m does not depend on the experimental conditions, nor on the reaction parameters; (b) at the m point the rate constant of a reaction of any order is equal to $\frac{E\Phi_m}{RT_m^2}$; this expression may hence be utilized to find the value of the activation energy, by varying the heating rate. By writing Eq. (29) for two different heating rates, taking the logarithms of the equations obtained and solving them jointly, one obtains

$$\frac{T_{m1}T_{m2}\ln\dfrac{\varphi_1}{\varphi_2}\dfrac{T_{m2}^2}{T_{m1}^2}}{T_{m2}-T_{m1}} = -\frac{E}{R} \tag{30}$$

In [2] this equation is found in the derived form

$$\frac{\ln\dfrac{\varphi}{T_m^2}}{\mathrm{d}\left(\dfrac{1}{T_m}\right)} = -\frac{E}{R} \tag{31}$$

In [2], Eq. (23) does not appear in its explicit form. It is utilized implicitly in two cases: when the author assigns the point of maximum rate of reaction to the top of the peak, and when he assumes that at the inflexion point $\frac{d^3\alpha}{dt^3} = 0$. Equation (23) allows one to obtain formulae for the fraction reacted and for the fraction unreacted at the point of the curve:

$$\text{(a)}\ \alpha = \frac{A^1}{A_t} \quad \text{(b)}\ 1-\alpha = \frac{A_t - A'}{A_t} \tag{32}$$

where A' is the area of the transformed peak in Fig. 1. It also allows one to obtain an equation of the type of Eq. (15):

$$K_0 \exp\left(-\frac{E}{RT}\right)(1-\alpha)^{n-1} = \frac{\Delta T}{A_p - A'} = B' \tag{33}$$

Since Kissinger, in [2], did not develop Eqs (32) and (33), he was compelled to make use of varying heating rates in order to find E and to introduce the shape index S of the peak to find n. Thereby, the possibility of determining the kinetic constants at any point of the thermoanalytical curve was lost, i.e. the task of performing kinetic analysis by means of this curve was not fully achieved (similarly as in [1], where the concept of the characteristic points of the DTA curve is absent).

The third equation for the system is found by utilizing the mathematical conditions for the inflexion point of the DTA curve:

$$\text{(a)}\ \left(\frac{d\Delta T_p}{dt}\right)_i = \max \quad \text{(b)}\ \left(\frac{d^2\Delta T_p}{dt^2}\right)_i = 0 \tag{34}$$

From Eq. (9) one has

$$\frac{d^2\Delta T_p}{dt^2} = \frac{A_t}{\tau}\frac{d^2\alpha}{dt^2} - \frac{1}{\tau}\frac{d\Delta T_p}{dt} \tag{35}$$

Introducing Eqs (8), (15) and (24) into Eq. (35) and applying the condition expressed in Eq. (34b), one finally obtains

$$\frac{E\varphi_i}{RT_i^2} = nB_i + \frac{1}{\tau}\left[\frac{\tau\left(\frac{d\Delta T_p}{dt}\right)_i}{\Delta T_p + \tau\left(\frac{d\Delta T_p}{dt}\right)_i}\right] = nB_i + \frac{a_i}{\tau} \tag{36}$$

where B_i is the value of B at the i point, and a_i is the experimental value at this point of the expression in brackets. By solving Eqs (36) and (26) jointly, one obtains

$$(1-\alpha_i)^{n-1} = \frac{B_i + a_i\tau^{-1}}{nB_i + a_i\tau^{-1}} \tag{37}$$

and for a reaction of the first order, from Eqs (36) and (28):

$$1-\alpha_i = \exp\left(-\frac{B_i}{B_i + a_i\tau^{-1}}\right) \tag{38}$$

Equations (37) and (38) allow one to find the fraction unreacted at the i point as a function of the kinetic parameters of the reaction and of the experimental conditions.

The third equation of the system is then found by utilizing the mathematical conditions for the top of the peak (p point):

$$\begin{gathered}\text{(a)}\ \left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right)_p = 0 \quad \text{(b)}\ \left(\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2}\right)_p = \max \\ \text{(c)}\ \left(\frac{\mathrm{d}^3\Delta T_p}{\mathrm{d}t^3}\right)_p = 0 \quad \text{(d)}\ \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_p = \frac{\Delta T_p}{A_t}\end{gathered} \tag{39}$$

Let us now form the second derivative of Eq. (8) and solve it relative to $\frac{\mathrm{d}^3\Delta T_p}{\mathrm{d}t^3}$:

$$\frac{\mathrm{d}^3\Delta T}{\mathrm{d}t^3} = \frac{A_t}{\tau}\frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3} - \frac{1}{\tau}\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2} \tag{40}$$

The second derivative of Eq. (13) yields

$$\begin{aligned}\frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3} &= \frac{\mathrm{d}\alpha}{\mathrm{d}t}\left[\left(\frac{E\varphi}{RT^2}\right)^2\left(1-\frac{2RT}{E}\right) - \frac{3n\frac{\mathrm{d}\alpha}{\mathrm{d}t}E\varphi}{(1-\alpha)RT^2} + \left(2-\frac{1}{n}\right)\left(\frac{n\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{1-\alpha}\right)^2\right] = \\ &= \frac{\mathrm{d}\alpha}{\mathrm{d}t}\left[\left(\frac{E\varphi}{RT^2}\right)^2 - \frac{E\varphi}{RT^2}3nB + \left(2-\frac{1}{n}\right)n^2B^2\right]\end{aligned} \tag{41}$$

At the p point, according to condition (39b) and Eq. (40):

$$\left(\frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3}\right)_p = \frac{1}{A_t}\left(\frac{\mathrm{d}^2\Delta T_p}{\mathrm{d}t^2}\right)_p \tag{42}$$

Utilizing Eqs (35) and (39a), one obtains from Eqs (42), (24) and (15)

$$\left(\frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3}\right)_p = \left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\right)_p\frac{1}{\tau} = \frac{1}{\tau}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_p\left(\frac{E\varphi}{RT_p^2} - nB_p\right) \tag{42a}$$

Solving the equation obtained jointly with Eqs (41) and (39d) yields a quadratic equation in the term $E\varphi/RT_p$

$$\left(\frac{E\varphi}{RT_p}\right)^2 - \frac{E\varphi}{RT_p}\left(3nB_p + \frac{1}{\tau}\right) + \left(2-\frac{1}{n}\right)n^2B_p^2 + \frac{nB_p}{\tau} = 0 \tag{42b}$$

Table 1 Calculation formulae for the single-point method

	$n\neq 1$				$n=1$			
$\frac{E}{R}=$	$\frac{T^2B(n-1)}{\bar{\varphi}[1-(1-\alpha)^{n-1}]}$			(1a)	$\frac{T^2B}{\bar{\varphi}\ln\frac{1}{1-\alpha}}$			(1b)
$K_0=$	$B\exp\frac{E}{RT}(1-\alpha)^{1-n}$			(2a)	$B\exp\left(\frac{E}{RT}\right)$			(2b)
	Point of maximum rate of reaction (m point)							
$\alpha_m=$	$\varphi_m=\bar{\varphi}_m$ $1-\left(\frac{1}{n}\right)^{\frac{1}{n-1}}$	(3a)	$\varphi_m>\bar{\varphi}_m$ $1-\left(\frac{1}{n}-\frac{\Delta_m(n-1)}{n}\right)^{\frac{1}{n-1}}$	(3b)	$\varphi_m=\bar{\varphi}_m$ 0.63	(3c)	$\varphi_m>\bar{\varphi}_m$ $1-e^{-(1+\Delta_m)}$	(3d)
$\frac{E}{R}=$	$\frac{T_m^2nB_m}{\varphi_m}$	(4a)	$\bar{\Phi}_m=\Phi_m$ $\frac{T_m^2B_m}{\varphi_m(1-\alpha)_m^{n-1}}$	(4b)	$\frac{T_m^2B_m}{\varphi_m}$			(4c)
	Inflexion point (i point)							
	$\varphi_i=\bar{\varphi}_i$							
$\alpha_i=$	$1-\left(\frac{B_i+a_i\tau^{-1}}{nB_i+a_i\tau^{-1}}\right)^{\frac{1}{n-1}}$			(5a)	$1-\exp\left(-\frac{B_i}{B_i+a_i\tau^{-1}}\right)$			(5b)
	$\varphi_i<\bar{\varphi}_i$							
$\alpha_i=$	$1-\left(\frac{B_i+a_i\tau^{-1}+\Delta_iB_i(n-1)}{nB_i+a_i\tau^{-1}}\right)^{\frac{1}{n-1}}$			(6a)	$1-\exp\left(-\frac{B_i(1-\Delta_i)}{B_i+a_i\tau^{-1}}\right)$			(6b)

		Top of the peak (p point)		
		$\varphi_p = \bar{\varphi}_p$		
$\alpha_p =$	$1-\left(1-\frac{2(n-1)}{3n+(\tau B_p)^{-1}-\sqrt{c}}\right)^{\frac{1}{n-1}}$	(7a)	$1-\exp\left(\frac{2}{3+(\tau B_p)^{-1}-\sqrt{c^1}}\right)$	(7b)
		$\varphi_p > \bar{\varphi}_p$		
$\alpha_p =$	$1-\left(1-\frac{2(n-1)(1+\Delta_p)}{3n+(\tau B_p)^{-1}-\sqrt{c}}\right)^{\frac{1}{n-1}}$	(8a)	$1-\exp\left(-\frac{2(1+\Delta_p)}{3+(\tau B_p)^{-1}-\sqrt{c^1}}\right)$	(8b)
$\frac{E}{R} =$	$\frac{T_p^2 B_p[3n+(\tau B_p)^{-1}-\sqrt{c}]}{2\varphi_p}$	(9a)	$\frac{T_p^2 B_p[3+(\tau B_p)^{-1}-\sqrt{c^1}]}{2\bar{\varphi}_p}$	(9b)

Explanation to table 1

$$B = \frac{\Delta T_p + \tau \frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}}{A_t - A - \tau \Delta T_p} \qquad \alpha = \frac{A + \tau \Delta T_p}{A_t}$$

$$\Delta_m = \frac{\varphi_m}{\bar{\varphi}_m} - 1 \qquad \Delta_i = 1 - \frac{\varphi_i}{\bar{\varphi}_i}$$

$$\Delta_p = \frac{\varphi_p}{\bar{\varphi}_p} - 1 \qquad a_i = \frac{\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right)_i}{\frac{\Delta T_i}{\tau} + \left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right)_i}$$

$$c = n^2 + 2n(\tau B_p)^{-1} + (\tau B_p)^{-2} + 4n$$

$$c' = 5 + 2(\tau B_p)^{-1} + (\tau B_p)^{-2}$$

and hence

$$\frac{E\varphi}{RT_p^2} = \frac{B_p}{2}\left[3n+(\tau B_p)^{-1} \pm \sqrt{n^2+2n(\tau B_p)^{-1}+(\tau B_p)^{-2}+4n}\right] \tag{43}$$

If $\varphi_p = \bar{\varphi}_p$, the system of the three equations (43), (26) and (15) can be solved and the relationship between the order of reaction and the fraction unreacted at the p point can be found:

$$(1-\alpha_p)^{n-1} = 1 - \frac{2(n-1)}{3n+(\tau B_p)^{-1} \pm \sqrt{n^2+2n(\tau B_p)^{-1}+(\tau B_p)^{-2}+4n}} \tag{44}$$

For reactions of the first order, let us solve Eq. (43) jointly with Eqs (28) and (15) at $n=1$:

$$1-\alpha = \exp\left(-\frac{2}{3+(\tau B_p)^{-1} \pm \sqrt{5+2(\tau B_p)^{-1}+(\tau B_p)^{-2}}}\right) \tag{45}$$

A comparison of the formulae for calculating the i, m and p points (Table 1) demonstrates that the formula for the m point is simplest, and the formula for the p point is the most complicated, i.e. the simpler (more accurate) the characteristic point found in the DTA curve, the more complicated (less accurate) the calculation for that point. The choice between the various possible calculation alternatives will depend on the individual particularities of the reaction studied (the type of the DTA curve).

Experimental

To confirm our theory, we used as model reaction the dehydration of copper(II) sulphate pentahydrate:

$CuSO_4.5H_2O \rightarrow CuSO_4.3H_2O + 2H_2O$
$CuSO_4.3H_2O \rightarrow CuSO_4.H_2O + 2H_2O$

taking place in the above two steps under the chosen conditions. The DTA curve is shown in Fig. 2. Heating was carried out at a rate of 12 deg/min in nitrogen atmosphere at a pressure of 25–30 Torr. Analytical grade reagent was used. The sample (6.0 mg) was placed in a crucible of aluminium foil which was then inserted tightly into the sample holder, a thin-walled copper bowl (4.4 × 8.0 mm), to the side of which the thermocouple (wire diameter 0.2 mm) was soldered with silver. The sample holder was fastened to the thermally insulated wire supports in the cavity of the heating block (diameter of cavity 10 mm). The sample was lightly compressed onto the bottom of the crucible; it formed a thin layer in good thermal contact with the crucible and hence with the sample holder. The holder construction and the packing mode of the sample ensure a high degree of isothermalness of the sensor and centralization of its parameters, so that (from the aspect of the heat transfer theory) the sensor may be considered a system without temperature gradient and hence the equations derived above are applicable. The heat capacity of the holder with the sample, calculated from literature data, is 0.1—0.01J/deg, and the heat transfer coefficient of the cell, determined by electric calibration, is $K_1 = 4.0 \pm 0.1$ mW/deg at 85° and $K_2 = 4.3 \pm 0.1$ mW/deg at 115°; hence, $\tau_1 = \frac{C}{K_1} = 25$ s and $\tau_2 = 23.25$ s. These values are in good agreement with the τ values found by calculation from the tail branch of the peak in the section sufficiently removed from the end-point of the reaction, by the formula

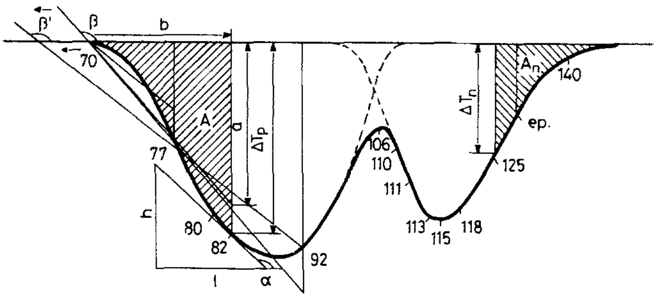

Fig. 2 DTA curve of the dehydration of copper sulphate pentahydrate A — peak area; ΔT_p — peak height; $\frac{d\Delta T_p}{dt} = \tan\alpha = \frac{h}{l}$ — slope of the tangent to the point in the DTA curve; $\frac{d\Delta T'_p}{dt} = \tan\beta = \frac{a}{b}$ — the same for the auxiliary peak

$$\tau = \frac{11.32\, A_n}{\Delta T_n} \tag{46}$$

where 11.32 s/cm is the reciprocal chart speed and the meanings of A_n and ΔT_n are to be seen in Fig. 2. Since $\tau \approx$ const, in the temperature interval studied, the baseline of the reaction should be a straight line parallel to the time axis. In fact, as seen from Fig. 2, after the reaction the curve returns to the same horizontal line from which it deviated at the start of the reaction.

In agreement with the above equations of reaction, two peaks are observed in the DTA curve, in the intervals 70–103 and 103–130°, respectively, corresponding to the two dehydration steps. The heats of these reactions are 84.8 and 53.0 J/mol water, respectively. Both peaks have continuous, rounded-off tops and end-points substantially shifted towards the upper part of the tail branch of the peak. This indicates a slow end-stage of the process, proceeding in a significant temperature interval; in contrast, the initial stage of the reaction is rapid, particularly in the second dehydration step, where the slope of the descending branch is high and the temperature interval between the beginning and top of the peak is narrow. The dehydration process of the crystal hydrate may presumably be regarded as consisting of two stages: in the first, the destruction of the crystal lattice takes place (using up energy) and the water molecules migrate to the surface of the sample, and partially into the gas phase; in the second stage, desorption of water from the surface, i.e. drying, takes place, and the drying process appears extended owing to the energetic inhomogeneity of the surface and of the water molecules adsorbed on it.

The results of the kinetic computation and the required initial data are listed in Table 2 for a series of points in the curve, in the sequence of rising sample temperature. The data listed are: temperature of the sample, height of the peak, slope of the peak, area of the peak, momentaneous (true) heating rate of the sample, mean heating rate, fraction unreacted, activation energy for $n = 1$, activation energy for $n = 1.5$, frequency factor, and activation energy calculated by the multipoint method, i.e. from Eq. (13) in the linear form

$$\ln \frac{\frac{d\alpha}{dt}}{(1-\alpha)^n} = -E/RT + \ln K_0 \qquad (47)$$

using a programmed computer and the least squares approach. Before discussing the results in Table 2, let us consider in greater detail the method of determining the mean heating rate $\bar{\Phi}$ figuring in the formulae of the theory (Table 1).

Mean heating rate $\bar{\Phi}$ and method of its determination

In integration of the rate constant (cf. Eq. 26), it is accepted usage to consider the heating rate a constant value equal to the given heating rate of the block. However, the physical meaning of the value figuring in Eq. (26) is not the heating rate of the block, but the heating rate of the sample (of the space in which the reaction takes place), which for this reason cannot be considered constant. If it is removed outside the integral sign, it turns into a mean rate value, which is difficult to determine by analytical methods. However, there is no difficulty in finding $\bar{\Phi}$ by the graphical method described below.

The integral of the left side of Eq. (26) is a single-value function of α and consequently of the area and height of the peak (cf. Eq. 11). The equality (26) will not be destroyed if we exchange the peak A (height ΔT_p) for a peak A' with height $\Delta T'_p$

Table 2 Calculated kinetic data on the dehydration of $CuSO_4 . 5H_2O$

$\cdot T$°C	$-\Delta T$°C	$-\frac{d\Delta T_p}{dt}$	$-A$,°C·s	φ, °C/s	$\bar{\varphi}$, °C/s	$1-\alpha$	$10^3\frac{d\alpha}{dt}$	E, kJ/mol from Eq. (1a) $n=1.0$	$n=1.5$	K_0	E, kJ/mol from Eq. (47) $n=1.5$
					First dehydration step						
74	1.3	.066	20.4	.134	.193	.948	2.89	298.4	302.6	$6.0\cdot10^{42}$	
76	2.3	.094	43.6	.106	.188	.901	4.57	262.9	269.6	$77.6\cdot10^{36}$	272.9
77	3.4	.101	73.6	.098	.184	.844	5.83	226.9	236.6	$1.1\cdot10^{33}$	291.3
77.3	3.7	.110	90.6	.081	.182	.820	6.56	227.4	239.1	$2.4\cdot10^{33}$	309.7
80	5.7	.063	209.4	.136	.175	.653	7.2	154.2	171.4	$21.6\cdot10^{22}$	255.4
82	6.5	.039	308.5	.160	.172	.537	7.34	135.0	156.7	$1.7\cdot10^{21}$	225.7
84	7.0	.026	406.0	.174	.171	.428	7.50	128.7	158.0	$2.5\cdot10^{21}$	
86	7.3	.011	493.5	.188	.170	.336	7.44	128.7	166.8	$55.4\cdot10^{21}$	188.1
88	7.3	0	569.4	.200	.169	.26	7.24	132.9	183.1	$12.0\cdot10^{24}$	191.9
92	6.9	-.04	696.2	.240	.169	.147	5.81	135.8	211.1	$11.5\cdot10^{28}$	183.5
					Second dehydration step						
110	3.4	.109	96.2	.090	.090	.717	9.6	546	592		
111	4.2	.108	127.3	.092	.092	.635	10.9	396	443	$16.7\cdot10^{57}$	380.4
112.6	5.6	.050	200.4	.150	.097	.464	11.0	396	476	$6.6\cdot10^{62}$	395
113	5.8	.037	235.0	.162	.100	.401	10.9	370	461	$4.7\cdot10^{60}$	424
115	6.0	0	278.0	.200	.104	.325	10.0	330	431	$3.2\cdot10^{56}$	341
118	5.6	-.049	364.0	.249	.108	.200	7.33	269.6	393	$1.4\cdot10^{51}$	247.0

and constant slope $\frac{\mathrm{d}\Delta T'}{\mathrm{d}t}$ so as to attain the equality

$$\alpha = \frac{A+\tau\Delta T_p}{A_t} = \frac{A'+\tau\Delta T'_p}{A_t} \tag{48}$$

However, for a peak with constant slope one may write

$$\int\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{K_0}{\bar{\varphi}}\int e^{-E/RT}\,\mathrm{d}t$$

since the heating rate of the sample for such a peak is a constant equal (according to [5]) to

$$\bar{\varphi} = \frac{\mathrm{d}\Delta T'_p}{\mathrm{d}t} + \varphi_0 \tag{49}$$

To construct the auxiliary peak, a straight line is drawn from the initial point of the peak to its intersection with the height (or its prolongation) so that Eq. (48) should be satisfied. Then, the ratio $\frac{a}{b} = \tan\alpha = \frac{\mathrm{d}\Delta T'_p}{\mathrm{d}t}$ is found and $\bar{\varphi}$ is determined from Eq. (49). In Fig. 2, the straight lines from the initial point of the peak are drawn so that the areas of the sectors separated by the straight line inside the peak and outside it should be equal; then $A = A'$. Actually, for a more accurate determination of $\bar{\varphi}$ one must slightly increase the slope of the straight line to satisfy the equality 48).

The described procedure can be applied for ideal reactions whose start coincides with the direct reaction calculated theoretically by means of the kinetic equation with the given values E and K_0. In reality, reactions of the dehydration type start at higher temperatures, close to the equilibrium temperature defined by the pressure of the gas phase in the calorimeter. As the result of this phenomenon (superheating), the initial stage of the reaction proceeds more rapidly and within a narrower temperature interval, leading to increased values determined for the activation energy. Subsequently, as the temperature rises and the conditions are more removed from the equilibrium conditions of dehydration, the process will be described more and more by the kinetic equation of the direct reaction and the values determined for E will decrease, approaching the true value (cf. Table 2).

One may, to a certain extent, take into account the phenomenon of superheating, and thus increase the accuracy of determining the initial activation energy values by drawing the line for constructing the auxiliary peak not from the initial point of the recorded peak, but from a point to its left, at the assumed true temperature of the start of the reaction. Thereby, all the $\frac{\mathrm{d}\Delta T'_p}{\mathrm{d}t}$ values will decrease and all the $\bar{\varphi}$ values will increase ($\bar{\varphi}\rightarrow\varphi_0$), and correspondingly all the activation energies will decrease (cf. formulae in Table 1). The $\bar{\varphi}$ values listed in Table 2 were determined by this latter method; it may be seen that the greatest differences between φ and $\bar{\varphi}$ appear in the initial and final stages of the reaction: in the initial stage $\varphi < \bar{\varphi}$, and the use of $\bar{\varphi}$ instead of φ substantially reduces the higher values of the initial activation energies. Comparing the course of changes in φ and $\bar{\varphi}$ as the reaction proceeds, one observes the φ rapidly decreases to its minimum value at the inflexion point ($T_i = 77.3°$, $\varphi_i = 0.081$ deg/s), and subsequently increases, whereas $\bar{\varphi}$ slowly decreases up to the point of maximum rate of reaction, where φ and $\bar{\varphi}$ are very close to one another, and subsequently increases or remains constant. The introduction of the mean heating rate concept and the consideration of the superheating phenomenon permitted an increase in the accuracy of the kinetic determinations. However, as may be seen from Table 2, even after these corrections the initial values of the activation energy remain high, exceeding those of the medium and final stages by a factor of 1.5 to 2. This might be explained either by the incomplete elimination of the superheating phenomenon by means of the procedure described, or by assuming that the found high values are true ones, characterizing the process of destruction of the crystal lattice of the hydrate, while the lower values of the subsequent phases are related mainly to the process of desorption of the water molecules from the surface of the sample.

As may be seen from Table 2, the values of E depend on the value of n, in that with increasing n, the value of E also increases, particularly towards the end of the reaction, to the extent that the fraction $(1-\alpha)^m$ decreases. For this reason it is important to determine n as accurately as possible. Hence, the method of finding n by means of Eqs (3), (5) and (7) of Table 1 must be rendered more accurate.

Method of finding the order of reaction n, taking into account the difference between the true and mean heating rates φ and $\bar{\varphi}$

When one cannot assume that $\Phi = \bar{\Phi}$, the joint solution of the three-equation system of the m point leads to the equality

$$\frac{\varphi_m}{\bar{\varphi}_m} = \frac{n[1-(1-\alpha_m)^{n-1}]}{n-1} = 1 - \Delta_m$$

By transformation of this equation, one obtains formula (3b) in Table 1. In an analogous manner, one can obtain formulae for α_i and α_p. Figure 3 presents the relationships n *versus* α_i, α_m and α_p for the case $\varphi = \bar{\varphi}$ (curves 1, 2 and 3) and for $\Phi \neq \bar{\Phi}$ (curves 1', 2' and 3'). The values α_i, α_m and α_p were found from the data in Table 2. As seen in the Figure, taking into account that φ and $\bar{\varphi}$ are not identical and making use of the formulae (3b), (6a) and (8a) in Table 1 results in a shift of the curves for α_i towards the left, and for α_m and α_p towards the right.

The experimental values for α_i, α_m and α_p are equal to 0.18, 0.57 and 0.74, respectively. With these values, $n = 1.5$ corresponds to the corrected curves for α_i and

α_m, and $n = 1.37$ to the uncorrected curve for α_p. In this last case, the introduction of the correction into formula (8b) leads to a sharp distortion of the shape of the curve and to a substantial shift towards the right. Obviously, formula (8a) is very sensitive to experimental errors, and small errors result in sharp distortion of the shape of the

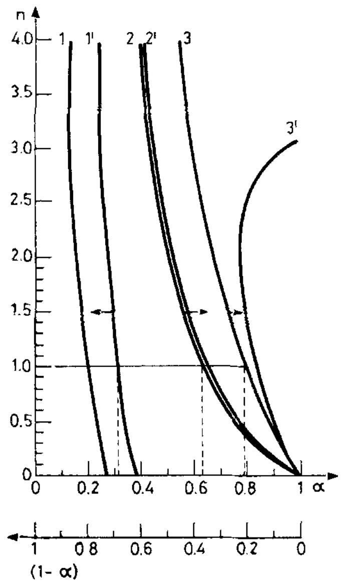

Fig. 3 Fraction reacted α *vs.* order of reaction n for the inflexion point (1, 1'), the point of maximum rate of reaction (2, 2') and the top of the peak (3, 3'). Curves 1, 2 and 3 refer to the case $\varphi = \bar{\varphi}$, and curves 1', 2' and 3' to the case $\varphi \neq \bar{\varphi}$

Table 3 Calculated kinetic data on the dehydration of $CuSO_4 . 5H_2O$ at the characteristic points of the DTA curve

	T, °C	$B \cdot 10^3$	φ, °C/s	E, kJ/mol		E, kJ/mol from Eq. (1a)	E, kJ/mol Eq. (47)
				First dehydration step			
i point	77.3	8.0	0.081	188.9	(Eq. 7a)	239.1	255.4
m point	84.0	17.5	0.174	160.9	(Eq. 4a)	158.0	188.1
p point	88.0	27.8	0.200	160.1	(Eq. 9a)	183.1	191.4
				Second dehydration step			
m point	112.6	25.7	0.097	494.1	(Eq. 4a)	476.5	395.4
p point	115.0	34.5	0.200	203.1	(Eq. 9a)	431.4	341.1

curve. Therefore, this formula should be used with caution. All in all, one may state that $n = 1.5$ is the most probable value for the reaction studied. The most probable value of $E = 38$ kcal/mol water for medium temperatures (80–86°) corresponds to this order of reaction. Table 3 lists the values for E calculated for the characteristic points of the DTA curve via formulae (4a), (7a) and (9a), in comparison to the corresponding values of E at these points, calculated via the formula for any single point of the curve (1a) and also via the method of several points (Eq. 47). All in all, satisfactory agreement is found between the different values of E, particularly for the m point, presumably because at this point the difference between φ and $\bar{\varphi}$ is small.

The single-point method differs from the multipoint method insofar as the heating rate φ or $\bar{\varphi}$ figures in all its formulae. Accurate determination of the values φ and $\bar{\varphi}$ is therefore of primary importance in the utilization of the single-point method. Instead of one heating rate, φ_0, figuring in the known methods of non-isothermal kinetics, a deeper and more accurate analysis demands the introduction of three heating rates, differing from one another in general case: φ_0, φ and $\bar{\varphi}$.

Relationship between the shape of the peak and the order of the reaction

It follows from the curves in Fig. 3 that with decreasing order of reaction ($n \to 0$) the difference between α_m and α_p decreases ($\alpha_m \to \alpha_p$), so that at the limit, at $n = 0$, the characteristic points of the curve will contract into one point at the top of the peak, and the top of the peak will become sharp (the exponential branch of the peak will start at the top of the peak indicating the end of the reaction, since at the top of the peak $\alpha = 1$). Hence, the sharper the top of the peak, the closer the order of the reaction to zero, and the more indistinct the top of the peak, the more probable that n is in the interval between 1 and 2. With increasing values of n, this criterion (the distance between the α_m and α_p points) becomes less and less sensitive (cf. Fig. 3).

To summarize, it may be stated that the experiments confirmed the theory satisfactorily. This agreement between theory and practice is a consequence of the satisfactory agreement of the isothermal sensor used in the experiments with the centralized parameters of its theoretical gradientless model.

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Zusammenfassung — Eine gemeinsame Erörterung der grundlegenden kinetischen Gleichung der DTA (Borchardt–Daniels-Methode) und der mathematischen Bedingungen für charakteristische Punkte der DTA-Kurve (Kissinger-Methode) ergibt ein System von drei Gleichungen mit drei Unbekannten (kinetischen Konstanten). Durch Lösung dieses Gleichungssystems werden Formeln zur Berechnung der kinetischen Konstanten von einem einzelnen Punkt der thermoanalytischen Kurve erhalten. Regeln zur Bestimmung der charackteristischen und individuellen Punkte der DTA-Kurve werden angegeben. Das Konzept der mittleren Aufheizgeschwindigkeit der Probe wird eingeführt und eine graphische Methode zur Bestimmung dieser Größe beschrieben. Die Beziehung zwischen dem am charakteristischen Punkt nicht umgesetzten Anteil (Peakform) und der Reaktionsordnung wird angegeben. Die Dehydratisierung von Kupfersulfat-Pentahydrat wurde mittels der gradientenfreien DTA-Methode untersucht und eine gute Übereinstimmung zwischen den nach verschiedenen Berechnungsmethoden erhaltenen kinetischen Konstanten festgestellt.

Резюме — Совместное рассмотрение основного кинетического уравнения ДТА (метод Борчардта–Даниельса) и метаматических условий для характерных точек кривой ДТА (метод Киссинджера) приводит к системе трех уравнений с тремя неизвестными (кинетическими константами), решая которую можно получить формулы для расчета кинетических констант по данным для одной (любой) точки термоаналитической кривой. Даны правила для определения характерных и особой точек на кривой ДТА. Введено понятие средней скорости нагревания образца и описан графический способ ее нахождения. Установлена связь между долей реагента в характерной точке (формой пика) и порядком реакции. Методом безградиентного ДТА исследована реакция дегидратации пятиводного сульфата меди и показано хорошее совпадение кинетических констант реакции, определенных различными расчетными способами.