

## KINETIC DATA FROM DTA MEASUREMENTS

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The theory of Borchardt and Daniels for the determination from the DTA curve of the fraction decomposed ( $\alpha$ ) is used. The probable mechanism, activation energy ( $E$ ) and frequency factor ( $Z$ ) can be found by the trial and error method from the plot of  $\alpha$  vs.  $T$  for a decomposition reaction which can be expressed by the equation

$$\log g(\alpha) = \log p(E/RT) + \frac{ZE}{Rq}$$

The use of tables of  $\log g(\alpha)$  for different mechanisms, and plots of the function  $\log p(E/RT_\alpha)$  vs. temperature for different activation energies is described. The influence is shown of the mechanism of the process, activation energy, frequency factor and heating rate ( $q$ ) on the shape of the DTA curve. The kinetic data for the decomposition of several solids obtained by the described method are in good agreement with those obtained from literature sources.

### Introduction

In the last ten years several methods have been developed to permit the kinetic analysis of DTA curves [1–12]. All of them apply simplifying assumptions in connection with the determination from the experimental DTA curve of the fraction decomposed ( $\alpha$ ). The most simple method is that devised by Borchardt and Daniels [1] and used by many other authors [2, 4, 12]. Borchardt and Daniels selected experimental conditions under which no temperature gradient occurred in either standard or sample, and the thermal conductivities and capacities of the sample and standard were identical independently of temperature, and heat loss could be neglected. In this case, from the heat balance for the rate of reaction it follows that

$$-\frac{dn}{dt} = \frac{n_0}{K \cdot \Delta H} \left( C \frac{dT}{dt} + k\Delta T \right) \quad (1)$$

where  $n$  = number of moles of starting material at time  $t$   
 $n_0$  = number of moles of starting material at the beginning of the process ( $t = t_0$ )

- $k$  = heat transfer coefficient for the sample (standard)  
 $C$  = heat capacity of sample (standard)  
 $\Delta T$  = temperature difference between sample and standard  
 $\Delta H$  = enthalpy change of the reaction  
 $K$  = constant.

Supposing a zero reaction rate at the beginning of the peak ( $t_0$ ), the total area under the peak ( $A_t$ ) is proportional to the heat of reaction

$$A_t = \frac{1}{K} \cdot \Delta H \quad (2)$$

Then, for the fraction reacted ( $\alpha$ ) up to time  $t$

$$\alpha = \frac{n_0 - n}{n_0} = \frac{1}{A_t} \left[ \frac{C}{K} \Delta T + a \right] \quad (3)$$

where  $a$  is a part of the area under the DTA curve up to time  $t$  (Fig. 1).

The values of  $A_t$  and  $a$  can be determined from the DTA curve by means of graphical integration, and the value of  $\frac{C}{K}$  from the cooling curve of the system,

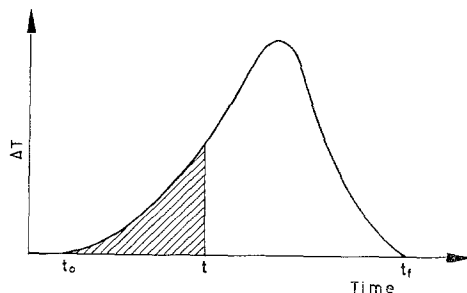


Fig. 1. Simple DTA curve

as Baumgartner and Duhant [12] have shown. When DTA curves of powdered samples are taken in a standard DTA apparatus, Borchardt's assumptions are not exactly fulfilled. It is not possible for example to eliminate entirely the temperature gradients in the sample and standard and further to provide a constant heating rate in the whole mass of the sample during a reaction. However, some authors [10, 11, 13, 15] have achieved satisfactory results in the determination of kinetic data by neglecting these effects completely.

For the description of reaction kinetics, Borchardt and Daniels used the equation

$$\frac{d\alpha}{dt} = Z \cdot e^{-\frac{E}{RT}} (1 - \alpha)^n \quad (4)$$

where  $Z$  = frequency factor  
 $E$  = activation energy  
 $n$  = apparent reaction order.

Tateno [9], Reed, Weber and Gottfried [2], Reich [4–8] and others have reported different ways of estimating the values of  $E$ ,  $Z$  and  $n$  from the DTA curve. These methods have several disadvantages and often lead to uncertain or meaningless values for the order of reaction. In the solid state, only reactions with  $n = 0, 1/2, 2/3$  and  $1$  have theoretical justification, and many reactions (i.e. diffusion controlled ones) as Sharp et al. [17] have shown cannot be classified in terms of an order of reaction.

As the values of  $E$  and  $Z$  depend on the rate controlling process, the correct determination of the mechanism is an important step in the study of the kinetics of solid state reactions. If the correct mechanism is known, it is possible to estimate both the activation energy and frequency factor from a single DTA curve. A method has been described recently [21] for obtaining kinetic data from the thermogravimetric measurement without prior knowledge of the reaction mechanism, and an application of this method to DTA measurements is given in the present paper.

### Principle of the method

The rate of reaction of a process can be generally expressed by

$$\frac{d\alpha}{dt} = Z \cdot e^{-\frac{E}{RT}} \cdot f(\alpha) \left( 1 - e^{-\frac{\Delta G}{RT}} \right) \quad (5)$$

where  $\Delta G$  is the free energy change of the process and  $f(\alpha)$  depends on the type of the rate controlling process.

If the velocity of the reverse reaction can be neglected (far from the equilibrium temperature), then

$$\frac{d\alpha}{dt} = Z \cdot e^{-\frac{E}{RT}} f(\alpha) \quad (5a)$$

The heating rate  $q$  is constant during the DTA measurement

$$\frac{dT}{dt} = q \quad (6)$$

Substituting in (5) we get

$$\frac{d\alpha}{f(\alpha)} = \frac{Z}{q} e^{-\frac{E}{RT}} dT \quad (7)$$

and by integration to temperature  $T_\alpha$  at which the fraction decomposed is  $\alpha$ , the following relationship is obtained according to Doyle [19]

$$g(\alpha) = \frac{ZE}{Rq} \cdot p(x) \quad (8)$$

where  $x = \frac{E}{RT_\alpha}$  and the function  $p(x)$  is defined by

$$p(x) = \frac{e^{-x}}{x} - \int_{-x}^{\infty} \frac{e^{-u}}{u} du \quad (9)$$

where  $u = \frac{E}{RT}$ .

Eq. (8) can be written in logarithmic form

$$\log g(\alpha) - \log p(x) = \log \frac{ZE}{Rq} \quad (10)$$

As  $Z$ ,  $E$ ,  $R$  and  $q$  are independent of temperature, the difference on the left side of Eq. (10) must be independent of temperature for the whole range of  $\alpha$  as Zsakó [20] has shown. That, however, is fulfilled only for a function  $\log g(\alpha)$  that corresponds to the correct mechanism of the process studied.

The evaluation of DTA measurements has three phases:

1) Calculation of  $\alpha$  as a function of temperature. If the Borchardt equation (1) is assumed to be valid, the fraction decomposed in time  $t$  can be calculated from the DTA curve applying Eq. (3). Values of  $A_t$  and  $a$  are calculated by a graphical or numerical integration. Values of  $\frac{C}{K}$  in Eq. (3) can be most easily determined from the cooling curve of the studied system. The sample (or the product of its thermal decomposition) is mixed with powdered graphite and heated by passage of a known amount of electric current. From the plot of  $\Delta T$  vs. time the value of  $\frac{C}{K}$  is determined.

Now the fraction decomposed ( $\alpha$ ) is known as a function of temperature, and the procedure of evaluation of kinetic data is the same as in the case of thermogravimetric measurement, described earlier [21].

2) The probable mechanism of the process is selected and  $\log g(\alpha)$ , calculated from known  $\alpha$  values, is plotted against the corresponding temperature values.

3) By comparing the given  $\log g(\alpha)$  vs. temperature plot with the set of  $\log p(x)$  curves for different activation energies plotted against temperature in the same scale, Eq. (10) was found to be valid over the entire range of  $\alpha$ . The curve of  $\log p(x)$  which follows an identical curvature to the given function  $\log g(\alpha)$  over the whole range of  $\alpha$  corresponds to the sought for value of the activation energy.

When an incorrect mechanism has been selected, Eq. (10) is only fulfilled partially (in a narrow range of  $\alpha$ ). The DTA curve was constructed for the process controlled by three-dimensional diffusion (function D3 in Table 1) with activation energy  $E = 20$  kcal, pre-exponential factor  $Z = 10^9 \text{ s}^{-1}$  and heating rate  $q = 1^\circ\text{C}/\text{min}$ .

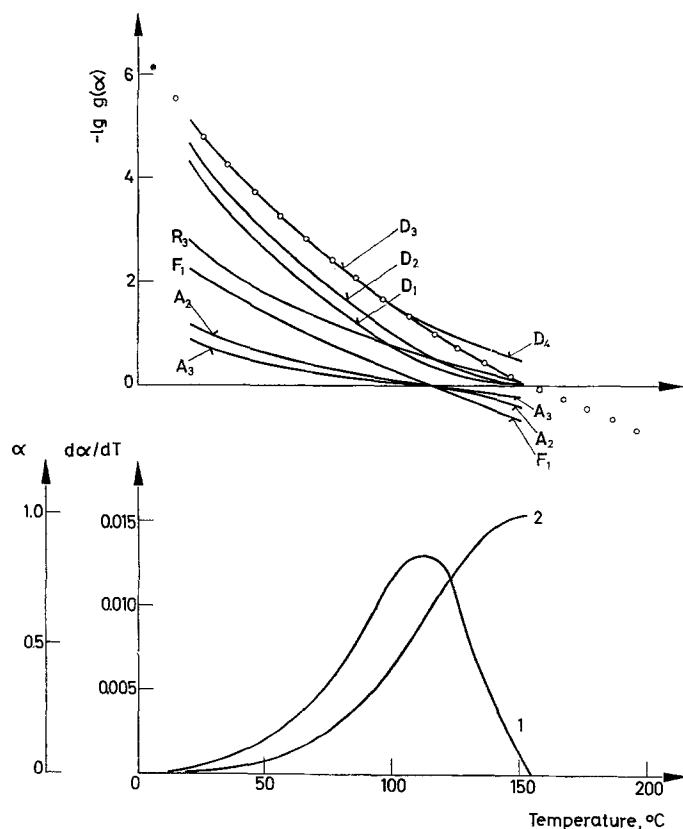


Fig. 2. Procedure for evaluating the DTA curve. Cover curve 1 complies with function  $D_3$ ;  $E = 20$  kcal/mole,  $Z = 10^9$  and  $q = 1^\circ\text{C}/\text{min}$ . Curve 2 (fraction reacted,  $\alpha$  vs.  $T$ ) calculated from the DTA curve (1). Upper curves are plots of  $\log g(\alpha)$  vs.  $T$  for the various kinetic equations. Data points are a plot of  $\log p(x)$  vs.  $T$  for  $E = 20$  kcal/mole

Curve (2) given in the lower part of Fig. 2 represents  $\alpha$  as a function of temperature calculated by means of Eq. (3). Plots of  $\log g(\alpha)$  for different assumed rate processes (Table 1) vs. temperature are given in the upper half of Fig. 2. Points marked in the diagram correspond to the function  $\log p(x)$  for  $E = 20$  kcal/mole. As can be seen in Fig. 2, only the function  $\log g(\alpha)$  calculated for Jander's equation ( $D_3$  type in Table 1) fits the  $\log p(x)$  curve just mentioned. This fitting can be achieved with other  $\log g(\alpha)$  curves only in a narrower region of  $\alpha$ .

Table 1  
Kinetic equations and symbols employed

Symbol	Kinetic equation	Rate controlling process
D <sub>1</sub>	$\alpha^2 = kt$	one-dimensional diffusion
D <sub>2</sub>	$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$	two-dimensional diffusion; cylindrical symmetry
D <sub>3</sub>	$[1 - (1 - \alpha)^{1/3}]^2 = kt$	three-dimensional diffusion; spherical symmetry; Jander equation
D <sub>i</sub>	$\left(1 - \frac{2}{3}\alpha\right) - (1 - \alpha)^{2/3} = kt$	three-dimensional diffusion; spherical symmetry; Ginstling and Brounstein equation
F <sub>1</sub>	$-\ln(1 - \alpha) = kt$	random nucleation; only one nucleus on each particle
A <sub>2</sub>	$\sqrt{-\ln(1 - \alpha)} = kt$	random nucleation; Avrami equation
A <sub>3</sub>	$\sqrt[3]{-\ln(1 - \alpha)} = kt$	random nucleation; Avrami equation
R <sub>2</sub>	$1 - (1 - \alpha)^{1/2} = kt$	phase boundary reaction; cylindrical symmetry
R <sub>3</sub>	$1 - (1 - \alpha)^{1/3} = kt$	phase boundary reaction; spherical symmetry

The advantage of the method described is that it is an easy procedure for evaluating the experimental data compared to the derivation methods most frequently employed [1-8, 16].

#### Influence of kinetic parameters on the shape of DTA curves

A number of factors influence the shape of the peak on a DTA curve and its position on the temperature axis. Assuming Borchardt's conditions to be fulfilled, the character of the curve is influenced by the activation energy ( $E$ ), frequency factor ( $Z$ ), heating rate ( $q$ ) and mechanism of the process studied as can be seen from Figs 3, 4a, b and c. It is obvious from Fig. 3 that the mechanism of reaction influences both the position and the shape of a peak on a DTA curve.

#### Possibilities of using DTA measurements for kinetic studies of solid-state reactions

DTA is mostly used for studies of processes in solids, but it is questionable whether kinetic data can be derived from such measurements. Even though the conditions of validity of Borchardt's equation are not exactly fulfilled, they can still be approached when measurements are suitably arranged experimentally. The temperature gradient in the solid sample can be decreased by diminishing the volume of the sample and by increasing its thermal conductivity by dilution with thermally inert well-conducting material [30], e.g. powdered corundum. When corundum is simultaneously used as a standard, the condition of identical

thermal conductivity and heat capacity is fulfilled, too. The dilution of the sample and diminution of its volume are restricted by the sensitivity of the recording apparatus, the size of the thermocouples, and a number of factors the influence of which on the accuracy of kinetic measurement is difficult to evaluate quantitatively. Hence the authors, to verify the applicability of DTA curves to studies of kinetics in solids, compared kinetic data obtained from DTA measurements by the method described with those obtained by other methods.

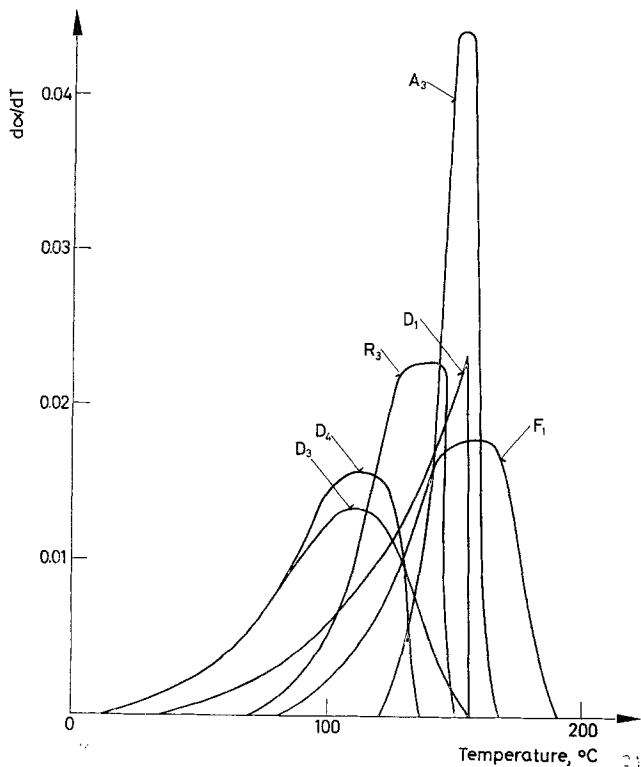


Fig. 3. Theoretical DTA curves calculated for reactions characterized by  $E = 20$  kcal/mole,  $Z = 10^9$ ,  $q = 1^\circ\text{C}/\text{mole}$ , and by different rate-controlling processes (see Table 1)

The DTA apparatus with a nickel block described earlier [22] was used. The weight of sample was 0.1 g and the sample was diluted with granulated corundum in a ratio of 1 : 2. For the determination of  $\frac{C}{K}$  values the sample (also the standard) was mixed with powdered graphite and heated by passage of alternating current between the nickel block and the thermocouple to the required temperature. The value of  $\frac{C}{K}$  was calculated from the cooling curve as follows:

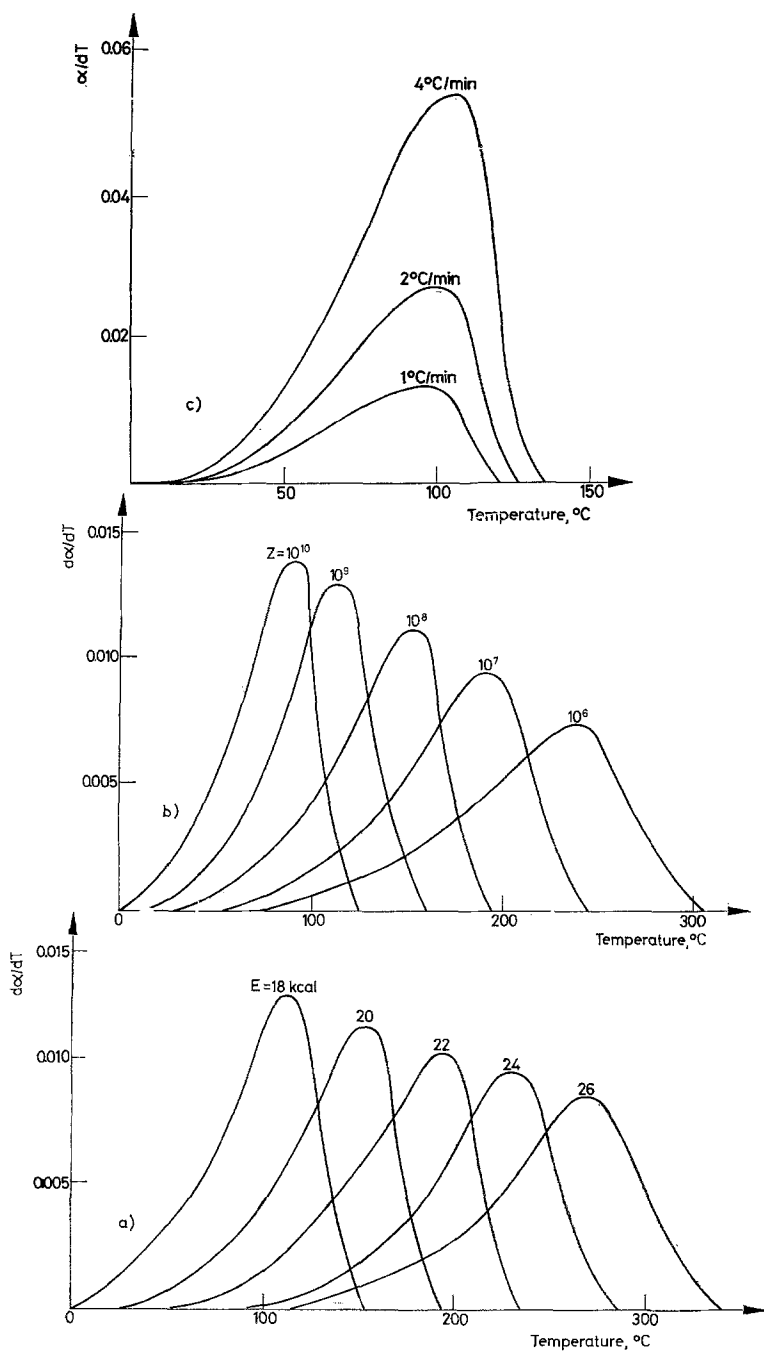


Fig. 4. Theoretical DTA curves calculated for reaction fitting function  $D_8$  (see Table 1).  
 a: for  $q = 1^{\circ}\text{C}/\text{min}$ ,  $Z = 10^9$ , various values of  $E$ ; b: for  $q = 1^{\circ}\text{C}/\text{min}$ ,  $E = 20$  kcal/mole,  
 various values of  $Z$ ; c: for  $E = 20$  kcal/mole,  $Z = 10^9$ , various values of  $q$



$$\frac{C}{K} = \left[ \left( \frac{C}{K} \right)_{\text{product}} - \left( \frac{C}{K} \right)_{\text{starting material}} \right] \cdot \alpha_{\text{uncorrected}} + \left( \frac{C}{K} \right)_{\text{starting material}} \quad (11)$$

where  $\alpha_{\text{uncorrected}} = \frac{a}{A_t}$

It follows from the experimental measurements that the term  $\frac{C}{K} \cdot \frac{d\Delta T}{dt}$  in Eq. (1) can be neglected, as Borchardt has proved [13].

An algorithm was made in Algol 60 language for an NCR Elliot 4130 computer to facilitate calculation of the fraction decomposed ( $\alpha$ ) from the DTA curves. This algorithm calculates  $\alpha$  by Eq. (3),  $\frac{C}{K}$  by Eq. (11), and also  $\log g(\alpha)$  for different rate controlling processes.

When a computer-controlled recorder is used, a plot of  $\log g(\alpha)$  vs. temperature is produced. The algorithm is available in the Joint Laboratory for Chemistry and Technology of Silicates in Prague.

Comparison of kinetic data computed from DTA measurements for decomposition of several solids with literature data (Table 2) shows the good applicability of the method described.

Table 2

Reaction	Sample		Reference		Literature
	<i>E</i> (kcal/mole)	Kinetic equation	<i>E</i> (kcal/mole)	Kinetic equation	
Ca Oxalate · 2 H <sub>2</sub> O → Ca Oxalate + + H <sub>2</sub> O (nitrogen atmosphere)	22	F <sub>1</sub>	22	F <sub>1</sub>	[16]
Mg(OH) <sub>2</sub> (brucite) → MgO + H <sub>2</sub> O	53	R <sub>3</sub>	51.4	R <sub>2</sub> , R <sub>3</sub>	[23]
ZnCO <sub>3</sub> (smithsonite) → ZnO + CO <sub>2</sub>	24	R <sub>3</sub>	22.5	R <sub>3</sub>	[24]
CaCO <sub>3</sub> → CaO + CO <sub>2</sub>	41	R <sub>3</sub>	39	R <sub>3</sub> , R <sub>2</sub>	[16]
			41.6		[25]
			39.8		[26]
			42		[27]

### Discussion

DTA curves, similarly to TG curves, provide information about the kinetics and mechanisms of processes. The advantage of DTA curves lies in the fact that they are not restricted to processes which are accompanied by changes of weight of the system. On the other hand, the temperature dependence of the fraction of reacted material is not obtained directly and the accuracy of its calculation assumes the fulfilment of several experimental conditions; this is often

difficult to attain. The conditions can be fulfilled comparatively easily for reactions proceeding in liquid systems (also heterogeneous) [28, 29] and the proposed method of evaluation of kinetic measurements has many advantages compared with those used earlier. Primarily it provides more information about the process studied and facilitates the procedure of calculating kinetic data from DTA measurements (without the need of a computer).

If proper experimental conditions are used, the described method can also give data about the kinetics of reactions in solids. These data are in good agreement with those gained from isothermal decomposition curves. Hence it can be assumed that DTA measurements may give reliable information about the kinetics and mechanisms of reactions in solids.

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RÉSUMÉ — On utilise la théorie de Borchardt et Daniels pour déterminer la fraction décomposée ( $\alpha$ ) à l'aide de la courbe d'ATD. En traçant  $\alpha$  en fonction de  $T$ , on peut déterminer l'énergie d'activation ( $E$ ) et le facteur de fréquence ( $Z$ ), par approximations successives et pour toutes les réactions de décomposition pouvant s'exprimer par l'équation:

$$\log g(x) = \log p(E/RT) + \frac{ZE}{Rq}$$

On décrit l'utilisation de tables donnant  $\log g(x)$  pour différents mécanismes et des diagrammes donnant la fonction  $\log p(E/RT_x)$  en fonction de la température pour différentes énergies d'activation. On montre de plus l'influence du mécanisme du processus, de l'énergie d'activation, du facteur de fréquence et de la vitesse de chauffage sur la courbe d'ATD. Les données cinétiques obtenues par cette méthode dans le cas de la décomposition de plusieurs solides sont en bon accord avec les valeurs de la littérature.

ZUSAMMENFASSUNG — Zur Bestimmung der abgespaltenen Fraktion ( $x$ ) aus der DTA-Kurve wurde die Theorie von Borchardt und Daniels herangezogen. Aus dem Diagramm von  $\alpha$  in Funktion der Temperatur lassen sich der wahrscheinliche Mechanismus, die Aktivierungsenergie ( $E$ ) und der Häufigkeitsfaktor ( $Z$ ) durch Iteration für Zersetzungsreaktionen ermitteln, die durch folgende Gleichung ausgedrückt werden können

$$\log g(x) = \log p(E/RT) + \frac{ZE}{Rq}$$

Die Benutzung von Tabellen von  $\log g(x)$  für verschiedene Mechanismen und von Diagrammen der Funktion  $\log p(E/RT_x)$  gegen die Temperatur für verschiedene Aktivierungsenergien wurde beschrieben. Der Einfluß des Reaktionsmechanismus, der Aktivierungsenergie, des Häufigkeitsfaktors und der Aufheizgeschwindigkeit auf die Form der DTA Kurve wurde erörtert. Die auf diese Weise erhaltenen kinetischen Daten der Zersetzung verschiedener Festkörper stehen in guter Übereinstimmung mit den Literaturangaben.

Резюме. — Использована теория Борчарда и Даниелла для определения по кривой ДТА распавшейся фракции ( $x$ ). По зависимости кривой  $\alpha$  от  $T$  можно установить методом ошибок вероятный механизм, энергию активации ( $E$ ) и фактор частоты ( $Z$ ) для реакции распада, которую можно описать уравнением

$$\log g(x) = \log p(E/RT) + \frac{ZE}{Rq}$$

Описано применение таблицы со значениями  $\lg(x)$  для разных механизмов и кривые функции  $\log p[E/RT_x]$  от температуры для разных энергий активации ( $E$ ), фактора частоты ( $Z$ ) и скорости нагрева ( $q$ ) на ход кривой ДТА. Кинетические данные, полученные для некоторых твердых веществ описанным методом, хорошо совпадают с литературными данными.