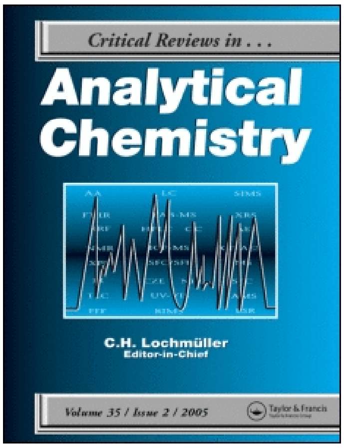
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

# Kinetic Aspects of Thermal Analysis

György Pokol; Gáor Várhegyi; David Dollimore

**To cite this Article** Pokol, György , Várhegyi, Gáor and Dollimore, David(1988) 'Kinetic Aspects of Thermal Analysis', Critical Reviews in Analytical Chemistry, 19: 1, 65 — 93

**To link to this Article: DOI:** 10.1080/10408348808542808

**URL:** http://dx.doi.org/10.1080/10408348808542808

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# KINETIC ASPECTS OF THERMAL ANALYSIS

Authors: **György Pokol**
Institute for General and Analytical Chemistry
Technical University of Budapest
Budapest, Hungary

**Gábor Várhegyi**
Research Laboratory for Inorganic Chemistry
Hungarian Academy of Sciences
Budapest, Hungary

Referee: David Dollimore
Department of Chemistry
University of Toledo
Toledo, Ohio

## I. INTRODUCTION

Roughly 20% of thermoanalytical publications deal with reaction kinetics or contain reaction kinetic evaluations.[1] Unfortunately, a great portion of these publications have presented contradictory or meaningless results, which induced a great deal of pessimism about the applicability of reaction kinetics for the evaluation of thermoanalytical curves.[2-4] In our opinion, however, the cause of the problem must be searched mainly in the application of oversimplified kinetic equations for processes composed from several chemical, physical, and physicochemical subprocesses. Careless experimental work and poor mathematical evaluation techniques have also contributed to the wrong performance of the reaction kinetics in this field. In the present review, we analyze the causes of this situation in detail. The discussion is concerned with the evaluation of nonisothermal experiments on reactions having at least one solid reactant.

Initially, however, we must clarify why one has to deal with reaction kinetics in thermal analysis. Without giving a complete list, we recount a few aims that illustrate that the development of the thermal analysis is inseparable from some sort of kinetic description or modeling of the studied processes.

The following points seem to be the most important

1. Every experimental technique needs some sort of theoretical basis to determine what can be expected if the experimental parameters are changed, etc. In thermal analysis, the nonisothermal reaction kinetics help to predict the effect of the various temperature programs on the measured thermoanalytical curves. The effect of the errors of the temperature programs and inhomogeneous temperature distributions can also be predicted, explained, or modeled by reaction kinetic deduction. In this respect, the correct description of a few simple reactions is already a great help in the same way as the idealized models, perfect gas, rectangular potential well, one-dimensional lattice, etc., help to explain the physical phenomena.
2. Some fundamental results of the nonisothermal reaction kinetics are already used in the everyday interpretation of the thermoanalytical curves. For example, if a multipeak curve is measured, everyone supposes more than one chemical reaction. This is an

implicit application of an early result of the nonisothermal reaction kinetics stating that a simple chemical reaction cannot produce multipeak curves at linear heating programs.

3. Some sort of mathematical modeling is essential to draw quantitative conclusions from experimental data. A very frequent and entirely accepted goal of thermoanalytical measurements is to investigate the so-called thermal behavior of substances or systems, i.e., to establish the transformations taking place and to characterize their temperature range and rate qualitatively. Kinetic studies can be regarded as the next step, a part of the quantitative description of thermal behavior.
4. With a suitable mathematical description, the thermoanalytical experiments can be applied in the modeling of industrial, geochemical, or other nonisothermal processes.

## II. THE REACTION RATE EQUATIONS AND THEIR PHYSICAL BACKGROUND

### A. Rate Equations and Basic Quantities

In the field of thermal analysis, the rate of transformation, especially that of thermal decompositions, is described almost exclusively by rate equations of the type

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{1}$$

where $\alpha$, t, T, and k stand for the reacted fraction, conversion, time, absolute temperature, and the rate coefficient, respectively, $f(\alpha)$ denotes an appropriate function of $\alpha$. The more generalized constitutive equations, put forward by Šesták and Kratochvil,[5,6] are also based on the assumption that the state of the system is determined by the temperature and the reacted fraction.

On rearrangement and integration of Equation 1

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{t_0}^t k(T)dt \tag{2}$$

is obtained. The $f(\alpha)$ and $g(\alpha)$ functions corresponding to the most important models are summarized in Tables 1 and 2, on the basis of the works of Šesták[6] and Brown et al.[7]

In a recent article Fatemi et al.[8] pointed out the lack of a rigorous definition of the specific rate constant k, which often caused confusion in the applications of the Avrami-Erofeev equation (for the latter, see Section II.B). In order to avoid such confusion, they suggested that k (per definitionem) should be equal to $d\alpha/dt$ at $\alpha = 0.5$, and, consistently, the $f(\alpha)$ functions shall contain a multiplicative constant to ensure $f(\alpha) = 1$ at the midpoint of the decomposition.

The source of Equation 1 is the rate law of homogeneous reactions written in the

$$-\frac{dc_i}{dt} = k(T) \cdot f(c_1, \ldots c_2, \ldots c_n) \tag{3}$$

general form, where $c_i$ is the concentration of component i. In other words, Equation 1 is based on the analogy of the concentration in the homogeneous case and the reacted fraction in the heterogeneous one. Warnings about the limitations of this analogy can be found in several works[2,3,9-11] without complete analysis.

## Table 1
## SOME KINETIC FUNCTIONS USED IN THE EVALUATION OF THERMOANALYTICAL CURVES WITH THE EQUATIONS $d\alpha/dt = k.f(\alpha)$ AND $$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$
## NUCLEATION AND GROWTH AS RATE-LIMITING PROCESSES; GROWTH RATE IS DETERMINED BY THE CHEMICAL REACTION AT THE BOUNDARY OF THE GROWING NUCLEUS[6,7]

| $f(\alpha)$ | $g(\alpha)$ |
|---|---|
| $1 - \alpha$ | $-\ln(1 - \alpha)$ |
| $\alpha$ | $\ln\alpha$ |
| $\alpha(1 - \alpha)$ | $\ln[\alpha/(1 - \alpha)]$ |
| $\alpha^{1-m}$ | $m \cdot \alpha^m$ |
| $(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$ | $\frac{1}{3}[-\ln(1 - \alpha)]^{1/3}$ |
| $(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$ | $\frac{1}{4}[-\ln(1 - \alpha)]^{1/4}$ |
| $(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$ | $\frac{1}{2}[-\ln(1 - \alpha)]^{1/2}$ |
| $(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$ | $\frac{1}{3}[-\ln(1 - \alpha)]^{1/3}$ |
| $(1 - \alpha)^{2/3}$ | $\frac{1}{3}[(1 - (1 - \alpha)^{1/3}]$ |
| $(1 - \alpha)^{1/2}$ | $\frac{1}{2}[1 - (1 - \alpha)^{1/2}]$ |
| $1$ | $\alpha$ |

[a] Random nucleation in independent particles, one nucleus per particle, very rapid growth.

[b] Branching chain reactions (autocatalytic). Linear growth of branching nuclei. Exponential rate law applies to different nucleation rates if branching dominates. Branching and terminating linear chains, Prout-Tompkins equation.

[c] Nucleation determined by a power law, different number of growth dimensions. (m depends on the exponent in the rate law of nucleation and the number of growth dimensions.)

[d] Avrami-Mampel-Erofeev equations. First-order nucleation, two-dimensional growth. First-order nucleation, three-dimensional growth. Constant number of nuclei, two-dimensional growth. Constant number of nuclei, three-dimensional growth.

[e] Contracting phase boundary equations. Rapid, dense nucleation resulting in a reacting interface, advancing toward the center of the particle. Three-dimensional advancement; two-dimensional advancement; one-dimensional advancement.

As was emphasized by Ozawa,[12] the reacted fraction determined from the mass change does not necessarily equal the quantity describing the process of chemical transformation; $\alpha$ can be of some function of the latter. He derived the form of this function for a polymer decomposition consisting of degradation and evaporation of the products with random chain scission as the rate-determining step.

It is well known that using the mass of the sample (or a component) instead of $\alpha$ in Equation 1 results in a rate coefficient depending on sample size. However, k(T) of Equation 1 itself is also a function of sample size for both homogeneous and heterogeneous reactions, except real first-order processes.[13-15] In surface- and diffusion-controlled reactions (see Sections II.C and III.B) this relationship can be easily expressed mathematically for ideal sample shapes.[6,7,14,15]

Table 2
SOME KINETIC FUNCTIONS USED IN THE EVALUATION OF THERMOANALYTICAL CURVES WITH THE EQUATIONS $d\alpha/dt = k.f(\alpha)$ AND

$$g(\alpha) = \int_o^\alpha \frac{d\alpha}{f(\alpha)}$$

GROWTH RATE IS LIMITED BY DIFFUSION FROM THE PHASE BOUNDARY TO THE SURFACE[6,7]

| $f(\alpha)$ | $g(\alpha)$ |
|---|---|
| $(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$ | $\frac{1}{2}[-\ln(1 - \alpha)]^{1/2}$ |
| $(1 - \alpha)[-\ln(1 - \alpha)]^{3/5}$ | $\frac{2}{5}[-\ln(1 - \alpha)]^{2/5}$ |
| $1 - \alpha$ | $-\ln(1 - \alpha)$ |
| $(1 - \alpha)[-\ln(1 - \alpha)]^{1/3}$ | $\frac{2}{3}[-\ln(1 - \alpha)]^{2/3}$ |
| $\alpha^{-1}$ | $\frac{1}{2}\alpha^2$ |
| $[-\ln(1 - \alpha)]^{-1}$ | $(1 - \alpha)\ln(1 - \alpha) + \alpha$ |
| $(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$ | $\frac{3}{2}[1 - (1 - \alpha)^{1/3}]^2$ |
| $[(1 - \alpha)^{-1/3} - 1]^{-1}$ | $\frac{2}{3}\left[1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}\right]$ |

*Note:* First-order nucleation, two-dimensional growth. First-order nucleation, three-dimensional growth. Constant number of nuclei, two-dimensional growth. Constant number of nuclei, three-dimensional growth. Rapid dense nucleation resulting in a reacting interface, advancing toward the center of the particle: one-dimensional growth, two-dimensional growth, three-dimensional growth, Jander equation, three-dimensional growth, Brounshtein-Ginstling equation.

The analogy between the concentration (or the reaction coordinate) in homogeneous reactions and the reacted fraction in heterogeneous ones is far from complete. In a heterogeneous process, $\alpha$ is a normalized average quantity unable to reflect the concentration differences within the reacting system. Moreover, as is discussed in Sections II.B and C, $f(\alpha)$ of Equation 1 quite often describes the changes in the number of sites suitable for reaction, while the local concentrations of the substances taking part in the reaction change abruptly. For example, in decompositions pure solid phases of reagent and product are frequently encountered. Thus, at a given site, the mole fraction of a chosen reactant equals either the unity or zero, while $\alpha$ for the whole system is a continuous function of time.

In order to eliminate these conceptual shortcomings of Equation 1, Pokol et al.[13,14] suggested a new general rate equation for simple heterogeneous reactions or a simple chemical step of a complex process. Its form resembles the laws of physical fluxes and current densities. According to this treatment, the gross rate of the transformation (W), expressing the time derivative of the amount of a chosen reactant in the whole system, related to the unit stoichiometric coefficient ($\nu$) is

$$W = \frac{1}{\nu} \cdot \frac{dN}{dt} = \int_Q k \cdot F \cdot dQ \tag{4}$$

Here N denotes the amount of the chosen species, preferably in molar units. For the explanation of the right-hand side of Equation 4, the analogy with heat conduction was used. W then corresponds to the heat flux, and k, equivalent with the common rate constant, is analogous with the thermal conductivity. F, a driving force depending on the distance of the system from thermodynamic equilibrium, corresponds to the temperature gradient in heat transfer. Q is defined as a measure of the number of situations (sites) suitable for reaction; it is called, on the basis of this analogy, the reaction cross section.

In a simple phase boundary reaction Q is related to the reacting surface of the reactant; in a nucleation step of a complex process it is equal or proportional to the number of existing germ nuclei, while in nuclei growth it corresponds to the active surface of growing nuclei.

The rate of the reaction (the volume derivative of W) is

$$w = \frac{\partial W}{\partial V} = k \cdot F \cdot \frac{\partial Q}{\partial V} = k \cdot f \cdot q \tag{5}$$

where V is the volume and q is the density of the reaction cross section. A form equivalent to the current densities of transport processes can be obtained if the gross transformation rate is related to the unity of the reaction cross section:

$$w^x = \frac{\partial W}{\partial Q} = k \cdot F \tag{6}$$

Here $w^x$ is called the fundamental rate of the reaction. In fact, this quantity is often used in surface chemistry or catalytic studies when the rate of transformation is expressed on the unit area of the reagent or catalyst surface.

The driving force of the transformation, F, is discussed in detail in Section II.D, which is devoted to the description of reversible reactions.

The rate constant or rate coefficient is usually expressed by the Arrhenius equation.

$$k = A \cdot \exp\left(-\frac{E}{RT}\right) \tag{7}$$

where A, E, R, and T stand for the preexponential factor, activation energy, gas constant, and absolute temperature, respectively. It is necessary to emphasize that if the rate equation is applied to a complex process, A and E are of a formal character.

From Equations 1 and 7

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \tag{8}$$

is obtained.

For the time being, there is no rigorous theoretical deduction of Equation 8 for condensed phase systems. Thus, we have to regard it as a semiempirical relation widely used in the various areas of chemistry. The lack of the theoretical deductions was one of the arguments in the pessimistic judgement of the kinetic evaluation of the theoretical data.[2] The physical meaning of A and E in condensed phase systems is well summarized in the work of Benson and Golden[16] through the transition state model. As they have pointed out, ln A is proportional to the entropy difference between the transition and original state. If the reaction proceeds throughout the bulk of the solid, A is about $10^{15}$ – $10^{16}$ $s^{-1}$ for a simple scission of a chemical bond, and it is considerably lower if the reaction species must go through a transition state of low geometric probability.

Function $f(\alpha)$ on the right-hand side of Equations 1 and 8 is frequently approximated by $(1 - \alpha)^n$, where n is the formal reaction order. While the reaction order in simple homogeneous processes is related to the molecularity, pure unimolecular or bimolecular, etc. reactions seldom arise in thermal analysis. The formal reaction order is frequently close to one, but this fact usually does not imply a simple unimolecular reaction. Hence, it is not surprising that the reported values of A are far from the theoretical values. The differences may be quite large.

As was discussed above, $f(\alpha)$ often represents the number of sites suitable for reaction. In a decomposition, the term "suitable for reaction" usually means that the reacting species is on a surface or interface that the reaction product can leave.

The norming of $f(\alpha)$ is arbitrarily chosen. Note that, for example, $(1 - \alpha)^n$ is equal to 1 at $\alpha = 0$, while, in reality, only a very tiny fraction of the reacting species may be on the reaction surface and in its vicinity. From this it follows that the true value of A is multiplied by a very small factor in Equation 8. Besides, the dependence of the rate constant on sample size usually manifests itself in the estimated value of the preexponential factor.[6,7,14,15]

On the other hand, A may be multiplied by factors greater than one, too, especially in polymer degradation reactions, when a given chain initiation may be followed by the depolymerization of the formed macroradicals and, in this way, the preexponential factor of the initiation is multiplied by the kinetic chain length.[17]

The values of E obtained from thermoanalytical data with Equations 1 and 8 reflect all the temperature-dependent factors not included explicitly in the rate equation and may also differ from the theoretical bond scission energies. Moreover, the measured rate of the transformation may be determined by several processes when each calculated kinetic parameter is a resultant of several factors, as is discussed in the following sections.

The more or less formal character of estimated E and A can be taken into account in two ways. The first treatment is to study the apparent activation energy and preexponential factor as functions of the reacted fraction, sample size, temperature, partial pressure, etc.[11,18-21] The other way is to expand the rate equations in order to reflect more parameters and subprocesses. This approach is of a higher theoretical level; its possibilities are discussed in different parts of this review (see Sections II and III). Finally, a few words about the so-called modified Arrhenius equations of type

$$k(T) = A'T^m e^{-E'/RT} , \tag{9}$$

where k is the rate constant and m is a constant. The transition state model leads to Equation 9 with m = 1 (16). The application of Equation 9 instead of the usual $k(T) = Ae^{-E/RT}$ does not require extra work in the evaluation of the thermoanalytical data.[22,23] Nevertheless, the temperature range in which a given reaction can be studied by thermal analysis rarely exceeds the magnitude of 100°C and in these intervals formulae $A'T^m e^{-E'/RT}$ and $Ae^{-E/RT}$ are approximately equivalent.[16]

### B. The Nonisothermal Avrami-Mampel-Erofeev Equation

Most solid-state decompositions or transformations start at lattice errors, impurities, or other irregular points of the sample (nucleation). Then the formed nuclei of the new phase grow, (acceleration), and, finally, overlap each other causing a decay of the reaction rate.[24] Under isothermal conditions, this mechanism can be approximately described by equations of type

$$-\ln(1 - \alpha) = k \cdot t^m \tag{10}$$

$$[-\ln(1 - \alpha)]^{1/m} = k_1 \cdot t \tag{11}$$

where parameter m is connected to the number of steps in the formation of stable nuclei and the number of dimensions in which the product nuclei grow.

Equations 10 and 11 are usually called Avrami-Erofeev or Avrami-Mampel-Erofeev equations though other names are also used, for example, Johnson-Mehl-Avrami eauation or Kolmogorov-Erofeev-Kazeev-Avrami-Mampel (KEKAM) equation.

In the estimation of the activation energy and preexponential coefficient confusion is caused by the lack of agreement on whether the rate constant of Equation 10 or 11 should be applied.[8] In Table 1 the special cases of the model are listed according to Equation 11.

It is important to emphasize that Equations 10 and 11 have been derived for isothermal conditions. In thermal analysis, they are usually rewritten into a nonisothermal form by rather formal means. As an example, we shall reproduce here the deduction of Criado and Morales,[25] who transformed Equation 10 in the following way:

$$[-\ln(1 - \alpha)]^{1/m} = k^{1/m}t = \int_0^t k^{1/m}dt = A^{1/m}\beta^{-1}\int_0^T e^{-E/mRT}\,dT \tag{12}$$

Here $\beta$ stands for the heating rate, i.e., $T = T_0 + \beta t$. Henderson[26] has pointed out that this widely used reasoning is erroneous, since Equations 10 and 11 had been deduced by merging a system of kinetic equations into a single equation under strictly isothermal conditions. From a physical point of view, Equations 10 and 11 describe the result of three subprocesses — nucleation, growth, and overlap — and their rate constants are composed of two physically different rate constants. The error of the deductions used in thermal analysis lies in the fact that they transformed the isothermal Equations 10 or 11 into a nonisothermal one instead of transforming the equations of the original subprocesses. This far more difficult work was later carried out by de Bruijn, Ipekoglu, de Jong, and van den Berg.[27] They emphasized, first of all, that Equation 10 or 11 may be the result of two different mechanisms:

1. The growth and overlap of a constant number of nuclei, when the nuclei already exist at the beginning of the thermal decomposition.
2. A first-order nucleation followed by the growth and overlap of the formed nuclei.

Mechanisms 1 and 2 result formally in the same equation, but the physical meaning of the parameters is different. For example, the usual three-dimensional growth of the nuclei leads to $m = 3$ and $m = 4$ at mechanisms 1 and 2, respectively. The mechanical rewriting of Equation 10 to a nonisothermal form is valid only for the simpler (1) mechanism. In the other case, a longer, tedious deduction was needed, which yielded the following approximate solution:

$$[-\ln(1 - \alpha)]^{1/m} = A'\beta^{-1}T^2\,e^{-E'/RT} \tag{13}$$

where A′ and E′ are composed from the Arrhenius parameters of the formation and growth of the nuclei ($A_f$, $E_f$, $A_g$, and $E_g$, respectively). The expression derived for E′ is the same as that arising in the isothermal kinetic evaluations by Equation 10:

$$E' = [E_f + (m - 1)E_g]/mRt \tag{14}$$

while A′ is a rather complex function of $A_f$, $E_f$, $A_g$, and $E_g$. The term $T^2$ in Equation 13 resulted from the Coats-Redfern approximation[28] of the exponential integral during the deduction. It is interesting to observe that the Coats-Redfern approximation of Equation 12 also leads to an equation formally equivalent to 13.[25] The only difference lies in the expression derived for A′. In this way, the application of the usual forms of nonisothermal Avrami-Mampel-Erofeev equations is not an error. Nevertheless, we have to emphasize that this equivalence is only approximate — the approximation of Equation 12 is equivalent to the approximation of the nonisothermal equations of nucleation, growth, and overlap.

Finally, parameter m cannot be determined from a single nonisothermal experiment.[25] This problem is discussed in detail in later sections.

### C. Surface Reactions

Phase boundaries play a crucial role in the reactions of solids. If the reactant and product phases are of definite composition, (e.g., pure) the surface or the interface may be the only place where chemical changes occur. There are many simple decomposition reactions — those of several carbonates, sulfates, etc. that fall in this category.[7,24] Let us consider a

$$\text{Solid(1)} = \text{Solid(2)} + \text{Gas} \qquad (15)$$

reaction of this type. At fixed temperature and partial pressure of the product gas, provided the diffusion or flow of the latter and heat transfer are not hindered, the overall rate of transformation is determined by the area of the moving phase boundary. In a compact particle the interface forms a contracting envelope surrounding the unchanged part, and the usual rate equation, Equation 1, is used in the

$$\frac{d\alpha}{dt} = k \cdot (1 - \alpha)^n \qquad (16)$$

form. In the ideal case, if three-, two-, or one-dimensional movement of the reacting interface takes place, the formal or apparent order of reaction n equals 2/3, 1/2, and 0, respectively. (See also Table 1.)

Equation 16 has a physical meaning with a formal order of 1 as well. It may correspond to the transformation of independent particles or crystallites, if the rate is controlled by random nucleation, (one nucleus per particle). Another case of "first-order" kinetics is related to the diffusion-limited growth of nuclei (see Table 2).[6] Equation 16 has been applied extensively in the description of thermal decompositions for a long time and has been found satisfactory in a number of cases. However, on a closer look at the structure of solids and the mechanism of their reactions, Equation 16 should be regarded as a fairly simplified model.

The dependence of the rate coefficient of the usual kinetic equation, Equation 1, on sample size has been mentioned in Section II.A. For symmetrical samples, k of Equation 16 is inversely proportional to the initial size.[6,7,14,15]

When the kinetics is governed by the area of the advancing phase boundary, a nucleation and growth mechanism is most often involved, i.e., the contiguous interface is originated from dense nuclei closely spaced on all surfaces or on specific crystallographic planes.[6,7] The acceleratory period may be very short. Evaporation or sublimation from the surface of the reactant can also bring about a surface-controlled rate of transformation.[6]

Some cases of the kinetics determined by the transport processes should also be mentioned here. First, in a compact particle, the advancement of the reacting phase boundary may be governed by heat or component transport, which is discussed in Section III. On the other hand, even in a discontinuous system, e.g., a powder contained by a sample holder, a considerable resistance to diffusion or heat transfer may result in the formation of a relatively thin reaction zone, moving toward the center of the samples.[6,13]

In addition to the one-dimensional advancement of the reacting interface, zero-order kinetics may also be observed if the rate is limited by desorption from a specific surface of the initial crystal, which follows the migration of the product from the bulk to that surface.

Generally, the formal order n obtained from thermoanalytical curves differs from the ideal values listed above, and is subject to change during reaction. In a compact particle, the shape of the contracting interface may not be constant because of the asymmetry of the particle and the dependence of the advancement rate on the crystallographic direction. Reaction zones formed around pores may also be responsible for nonideal and changing values of n.[7] If powders are considered, the apparent order depends on the distribution and the shape of the particles. This has long been regarded as a factor influencing the results computed with Equations 1 and 16.[6,7,9] Nonisothermal curves were simulated by Tonge[29] for different particle sizes and distributions. The conclusion was that reliable kinetic parameters cannot be estimated from measurements on samples of unknown and different particle size distribution.

In spite of the problems and limitations outlined here, the contracting interface models can be applied for a number of reactions, and yield useful, though somewhat formal, kinetic parameters. In the background of the approximate validity of Equation 16, however, various microscopic mechanisms may act. For a detailed discussion of the types of reaction mechanisms and the difficulties of their study, the reader is referred to the book by Brown, Dollimore, and Galwey.[7]

### D. Reversible Processes

Reversible processes are quite frequent among the ones studied with thermoanalytical methods. In such a case, beyond the rate of the forward reaction that of the reverse reaction should also be taken into account, for example, in a decomposition of the

$$\text{A/pure solid/} = \text{B/pure solid/} + \text{C/gas/} \tag{17}$$

type, the rate of the reverse reaction, and, consequently, that of the overall process, depends on the activity (partial pressure) of C.

Since the pioneering works in modern thermal analysis were published,[30] it has been well known that product gas pressure has a strong effect on the temperature range and the rate of thermal decompositions. However, the reverse process is neglected in most kinetic studies; the common and convenient assumption is that the transformation in question takes place far from the equilibrium.

If the assumption is unacceptable, the formal treatment of the problem is to describe the dependence of the basic kinetic parameters E, A, and the $f(\alpha)$ function on product gas pressure. This was followed by Gallagher and Johnson,[18,19] as well as Ball and Casson,[20] in the investigation of the thermal decomposition of calcium carbonate and lead carbonate, respectively. In both cases, the formal activation energy and the preexponential factor were found to increase with increasing carbon dioxide pressure.

From the physicochemical aspect, it is more justified to enlarge the rate equations with terms reflecting the reversibility of the process. There are several theoretical and empirical ways to do this.

In a certain temperature range, some systems may have an equilibrium composition, i.e., the starting reactants cannot transform completely within that range. In such a case, according to Šesták,[31] an isothermal ($\alpha$) and a nonisothermal ($\lambda$) degree of conversion can be distinguished. The latter has an equilibrium value at every temperature ($\lambda_{eq}$) where the isothermal conversion equals the unity. Thus,

$$\alpha = \frac{\lambda}{\lambda_{eq}} \tag{18}$$

Therefore, the kinetic equations containing the two conversions ($\alpha$ and $\lambda$) have different forms. However, in a later work, Šesták points out that experimental results have not necessitated the distinction between $\alpha$ and $\lambda$.[6] He listed several reasons for this fact:

1. With common heating rates, in the main region of kinetic calculations $\lambda_{eq} = 1$, and $\alpha = \lambda$. The initial region, where $\lambda_{eq} < 1$ is considered as nonrepresentative.
2. The kinetic functions are flexible and sometimes intensitive.
3. Real experimental conditions can camouflage the effect of the equilibrium background.

It may be added that for a number of processes, see for example, types of equations like Equation 17, the equilibrium conversion is either 1 or 0, and there is but one equilibrium temperature if the pressure is fixed. A continuously changing equilibrium conversion occurs when the solid and molten reactants do not form separate phases of fixed composition.

A final conversion different from the unity is not the only effect of the equilibrium background of a reaction. Even when the products are only stable in the thermodynamic sense, the rate of transformation does depend on the distance from the state of equilibrium.

In thermal decompositions, the effect of product gas pressure is often represented by a power function,[6] and the rate coefficient then becomes

$$k = k(T) \cdot p^m \tag{19}$$

For reversible solid-solid reactions, Bradley suggested a driving force factor on the basis of thermodynamic and statistical mechanic considerations.[32] This factor (1-exp$\Delta G/RT$) contains the Gibbs free-energy change of the process. For large negative values of $\Delta G$, i.e., far from the equilibrium, this factor is close to the unity.

Šesták and Berggren,[33] as well as Šatava,[34,35] suggested to multiply the commonly used rate equation, Equation 1, by Bradley's driving force:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \cdot \left(1 - \exp\frac{\Delta G}{RT}\right) \tag{20}$$

The same factor was applied by Pokol et al.[13,14] in their general rate equation, Equations 4 to 6, discussed in Section II.A, yielding

$$W = \int_Q k \cdot F \cdot dQ = \int_Q k \cdot \left(1 - \exp\frac{\Delta G}{RT}\right) dQ \tag{21}$$

Equation 21 can describe the rate of simple, reversible homogeneous reactions as well. In that case, k is the rate constant of the forward reaction, and the reaction cross section Q contains the volume V and the activities — concentrations — of the initial components $a_i$,[14]

$$Q = V \cdot \Pi\, a_i^{n_i} \tag{22}$$

where $n_i$ is the partial order of reaction belonging to reactant i. In this way Equation 4, resembling the laws of physical fluxes (transport processes), appears to be equivalent to the Marcelin-DeDonder equation[36] used in the nonequilibrium theory of reaction kinetics.

In the evaluation of experimental data, only a few attempts have been reported to take the reverse reaction into account in a way equivalent or similar to Bradley's driving force. For the simple reversible decomposition type mentioned above, Equation 17, the

$$1 - \exp\frac{\Delta G}{RT} = 1 - \frac{p}{p_e} \qquad (23)$$

equation holds, where p and $p_e$ are the actual and the equilibrium partial pressure of the product gas, respectively. The factor at the right-hand side of Equation 23 was applied by Jüntgen and Van Heek in the description of calcium carbonate thermal decomposition.[37] The same factor was found satisfactory in characterizing the effect of water vapor pressure on the rate of the gibbsite ($Al(OH)_3$) → $\chi$-alumina reaction by Pokol et al.[38] In this case, however, the equilibrium pressure had to be replaced by a temperature-dependent empirical parameter, since thermodynamic reversibility of the reaction is questionable. This empirical parameter could not be assigned to the onset of the dehydration either.

The difference between the equilibrium and the actual pressure was applied on the right-hand side of Equation 1 by Rouquerol[39] and Wist,[40] which involves neglecting $1/p_e$, provided Equations 20 or 21 and 23 are valid.

The applicability of the driving force coefficient of Equation 20 was also confirmed by Pacewska et al.,[41] who studied the isothermal dehydration of basic ammonium aluminium sulfate in a vacuum and in atmospheres containing water vapor. If measurements belonging to the same extent of supersaturation were evaluated, i.e., the $p_e/p$ ratio for the water vapor was identical, the same activation energy was obtained as from measurements in a vacuum.

On the other hand, sometimes the $1\text{-}p/p_e$ factor was found inadequate. For the effect of the product gas pressure, a term representing its adsorption was applied in the description of the decomposition of carbonates by Criado et al.[42] and by Maciejewski and Baldiga.[43]

The authors of the present review expect that the use of equations containing some term reflecting the reverse process will become more frequent in the next years, leading to more reliable theoretical and practical kinetic information.

## III. TRANSPORT PROCESSES

In the reactions of solids, beyond chemical and physical transformations, the transport processes (heat and component transport) also play an important role. The latter can be facilitated in most homogeneous reactions taking place in the gas or liquid phase. However, if solid reactants are concerned, the transport within the individual particles is very difficult or impossible to intensify.

Thus, the rate of the reaction is usually influenced and, quite often, determined by the component and/or heat transport. From the engineering aspect, the transformation of large solid samples of defined geometry should be described by the laws of the transport processes, taking the gradients of concentrations and temperature into account.[33]

It is also important to note that during the reactions of solids, the relative weights of the steps (among others, those of the transport processes) may change. So may the morphology (specific surface area, porosity, etc.) of the solid reactants, which has a strong effect on the conditions of heat and mass transport.

### A. Heat Transport

The transformations followed by thermal analysis and temperature programming itself are always accompanied by heat effects and, consequently, heat transport. Thermal resistances exist between the heating element and the sample holder, in the wall of the sample holder, between the sample holder and the sample, and within the sample itself. Depending on the design of the apparatus and the sample holder, and the characteristics of the sample (size, thermal conductivity, etc.), any of these resistances may considerably influence the rate of the transformation. Quite frequently the rate of the whole process is determined by the heat transport.[44]

The existing thermal resistances and heat capacities result in considerable temperature gradients within the measuring system. This means that the temperature inhomogenities within the sample may not be neglected. On the other hand, the sample does not follow the temperature program accurately. For example, Flynn and Dunlap measured the temperatures in a 25.4 mm (1 in) diameter horizontal tube furnace[45] and found a 45°C difference at 400°C between the two thermocouples, one of which was situated in the tube axis, the other 0.8 cm off center. (The tube was purged by nitrogen of atmospheric pressure, with 25 mℓ/min flow rate.)

In this way, the solution of kinetic problems may require the description of the distribution of temperature and the heat fluxes within the sample-containing heat sources or drains. General mathematical methods for this purpose have been recently published by Hoff[46] and Sluzalec.[47]

Several models for the evaluation or simulation of thermoanalytical curves have been based on the laws of heat transport. The description put forward by Draper and Sveum starts from the assumption that the chemical or phase transformation proceeds in equilibrium conditions, at a constant temperature,[48] which is independent of the temperature program. A reacting interface having that constant temperature moves inward into the sample, and the rate of the process is determined solely by the heat transport. Similar starting assumptions have been in the description of the DTA curves of invariant processes (transformations with zero degree of freedom).[49-53] In the opinion of the present authors the above assumption is acceptable in the case of melting or some polymorphic transitions. However, most chemical reactions (and some phase transitions, too) are activated processes and they do require a Gibbs free-energy difference below zero.

If the thermal resistance within the sample is significant, the temperature of the reacting zone and its time derivative are different from the measured temperature and the chosen heating rate. Even in this case, usually, the measured thermoanalytical curves are evaluated with Equation 1, assuming that the sample temperature corresponds to the preselected program. From this aspect, deviations from the temperature program may be considered as source of error of estimated kinetic parameters.[54] This type of error in kinetic calculations was investigated in detail by Várhegyi.[55]

It can be shown that the various components of the temperature errors have different effects on the calculated kinetic parameters. The constant and linear components of the temperature errors only slightly disturb the evaluation of a simple thermoanalytical curve. The curvatures of the temperature-time function, however, distort the shape and width of the measured peaks and in this way result in considerable errors in the kinetic parameters.[55]

Several attempts have been reported to evaluate and model thermoanalytical curves, taking into account both the chemical reaction and heat transport. Studying the degradation of Teflon®, Reich and Stivala embedded the samples into a refractory material with only one of the base plates exposed.[56] They found that in the range of lower conversions the decomposition could be described by a mathematical model based on the rate of chemical reaction and one-dimensional heat conduction. An improvement of Kissinger's method for the estimation of kinetic parameters[57] was proposed by Shishkin,[58] taking into account the real heating rate of the sample. A way to determine the average real heating rate was also reported.

DSC curves of the cure reaction of rubber were simulated by Khoudier et al.[59] and Armand et al.,[60] considering heat transfer and the kinetics of the exothermic chemical process. The mathematical model was constructed for cylindrical samples with radial heat conduction; the thermal properties of the material were regarded as constant and a first-order reaction

### Table 3
### CALCULATED TEMPERATURES (°C) AT THE MIDDLE OF SPHERICAL SAMPLES UNDER DIFFERENT EXPERIMENTAL CONDITIONS[60]

| Sample radius (mm) | Parameter | Heating rate (°C min$^{-1}$) 2 | 5 | 10 | 20 |
|---|---|---|---|---|---|
| 2.5 | HF (max) | 182.3 | 197.3 | 211.3 | 225.9 |
| | ΔT (max) | 183 | 197 | 213 | 226 |
| 5.0 | HF (max) | 182.8 | 201.1 | 217.5 | 238.2 |
| | ΔT (max) | 185 | 201 | 221 | 246 |

*Note:* HF (max) and ΔT (max) denotes values belonging to the maximum heat flux and temperature gradient, respectively.

was assumed. The problem was solved with a numerical method with finite differences. The results included heat flux curves (as a function of time and temperature), and profiles of the temperature and the degree of cure vs. the time belonging to different sites of the sample. The heat flux curves agreed well with experimental DSC traces.

At first, the mathematical procedure was applied to samples 5 mm in diameter, leading to the conclusion that the estimation of kinetic parameters, in such a case, requires the description of the temperature distribution inside the sample.[59] In the second paper,[60] the effect of sample size and heating rate was studied on the same model. For a radius of 2.5 mm, the values of the temperature at the middle of the sample when the heat flux and the temperature gradients are maximal were found to be about the same, as shown in Table 3. For larger samples, a difference between these two temperatures became apparent and it increased with the heating rate.

A phase boundary reaction with at least one solid product was considered in the model of Pokol et al.[61] The basic assumptions were

1. The overall rate of the process is determined by the chemical reaction at the phase boundary and radial heat conduction within the sample. The temperature at the external surface of the sample is identical with the program value.
2. The heat flux into or out of the sample is equal to the heat effect of the reaction.

On this basis, a step-by-step procedure was worked out to simulate thermoanalytical curves for spherical samples. Calculations were carried out with various sets of input parameters (thermal conductivity, sample radius, heating rate, activation energy, and preexponential factor). The simulated curves were characterized by means of empirical parameters related to the location (temperature), the width and the assymetry of the peak, which had been applied in describing the reproducibility of thermoanalytical curves and in the estimation of kinetic constants.[62-64] Table 4 demonstrates the effect of thermal conductivity on some empirical parameters. For the given density, 3- and 1-mm sample radii correspond to initial masses of 230 and 8.4 mg.

The results were generalized by means of dimension analysis. An approximate equation was found for the maximum temperature lag ($\ell$), i.e., the maximum difference between the temperature of the linear program and that of the reacting phase boundary,

$$\ell = \text{const}\,\frac{r_0^2 \cdot H \cdot \beta}{W \cdot \lambda} \qquad (24)$$

### Table 4
### EMPIRICAL PARAMETERS CHARACTERIZING THE LOCATION,[a] THE WIDTH,[b] AND THE ASYMMETRY[c] OF THE PEAK, AND THE MAXIMUM TEMPERATURE LAG ($\ell$) FOR SAMPLES OF DIFFERENT INITIAL RADIUS $r_o$ AND THERMAL CONDUCTIVITY ($\lambda$)[61]

| $r_o$ (mm) | $\lambda$ $WK^{-1}$ $m^{-1}$ | $M_{IR}$ K | W K | R(0.6) | $\ell$ K |
|---|---|---|---|---|---|
| 3 | $\infty$ | 530.5 | 38.3 | 0.731 | — |
| | 100 | 530.7 | 38.4 | 0.730 | 0.3 |
| | 20 | 530.8 | 39.1 | 0.727 | 1.3 |
| | 5 | 531.4 | 41.3 | 0.719 | 4.4 |
| | 1 | 533.8 | 49.8 | 0.691 | 17.5 |
| | 0.2 | 542.1 | 73.1 | 0.647 | 51.6 |
| 1 | $\infty$ | 513.7 | 36.0 | 0.731 | — |
| | 5 | 513.8 | 36.3 | 0.729 | 0.6 |
| | 1 | 514.1 | 37.8 | 0.723 | 2.8 |
| | 0.2 | 515.7 | 43.5 | 0.702 | 11.2 |
| | 0.05 | 520.0 | 56.4 | 0.668 | 30.8 |

[a] $M_{IR}$ — The first relative moment, i.e., the temperature of the center of gravity of the peak.

[b]

$$W = \left(\frac{d\alpha}{dT}\right)^{-1}_{max}$$

[c]

$$R(0.6) = \frac{T(0.6)-T(0.2)}{T(0.8)-T(0.2)}$$

where $T(\alpha)$ is the temperature belonging to the given reacted fraction.

where $r_o$ is the radius of the sample, $\lambda$ and H denote the thermal conductivity and the heat of reaction in unit sample volume; W and $\beta$ represent the reciprocal of the maximum $d\alpha/dT$ and the heating rate, respectively. If SI units are used, the constant of Equation 24 is about 0.30.

Another important question concerns the possibility of specifying a range of material and experimental parameters allowing the kinetic constants of the reaction to be estimated without considering the heat transport (with a given error bound). The data of the simulated curves were also evaluated from this point of view and an approximate criterion was established with dimension analysis:

$$\frac{\lambda \cdot W^2}{r_0^2 \cdot H \cdot \beta} > \text{const}'. \tag{25}$$

where the constant of the right-hand side depends on the acceptable error limit. The decomposition of a spherical sample was chosen as an example, with an 0.1 maximum error in the estimated formal order (the correct value being 2/3). In this case, the constant of Equation 25 should equal 4.0. The heat of the reaction, density, molecular weight, and thermal conductivity were $\Delta H = 100$ kJ $mol^{-1}$, $\rho = 2000$ kg $m^{-3}$, $M = 0.1$ kg $mol^{-1}$ and $\lambda = 1$ W $K^{-1}$ $m^{-1}$, respectively; W and $\beta$ had the values of 40 K and 1/6 K $sec^{-1}$. Then, using

Equation 25, a maximum allowable sample radius of 1.1 mm was determined (corresponding to the 11 mg initial mass).[61]

All the work mentioned in this section either contain qualitative statements, use rather simplified assumptions, or deal with particular systems. The analysis of the effect of thermal resistances on the estimated kinetic constants is far from complete. However, it seems that the effect of heat transport may be neglected in chemical reactions of moderate enthalpy change and rate, if there is a good thermal contact between the heater and the surface of the sample and the sample size does not exceed the order of some milligrams. For larger amounts of material or very fast transformations, e.g., melting, heat transport is rate determining (or one of the governing processes), consequently, it should not be omitted from the kinetic description.

### B. Component Transport

Component transport in all kinds of phases may influence the rate of transformations studied with the aid of thermal analysis. The process of migration and its relationship to the mechanism of the reaction depends on the phase concerned.

In the gas phase, diffusion and flow (if the total amount of gases is changing in the reaction) are the possible means. With a proper choice of apparatus and experimental conditions (e.g., pressure regulation, purging by an inert gas), the transport of gases outside the sample are easily controlled and usually may be omitted from the description of the overall rate. However, reactions carried out in a vacuum sometimes cause pressure drops in the apparatus which are significant when compared to the total pressure.[9] On the other hand, the resistance to gas flow is extended in special experimental arrangements in order to maintain a constant rate of decomposition.[39,65,66]

A considerable resistance to diffusion or flow may be constituted by the voids among the particles of the sample and the pores in the particles. The mathematical treatment of this problem may be similar to that of heat transport, owing to the analogy between the basic laws of diffusion and heat conduction.

In condensed phases, diffusion is an activated process. Solid-state diffusion, most frequently, brings about the cessation of chemical bonds and the formation of new ones, and, consequently, it is often called chemical diffusion.[67] The temperature dependence of the diffusivity can be described by an Arrhenius type expression. A number of solid-gas and solid-melt reactions, and practically all solid-solid reactions, include diffusion in the solid state as an inherent and often rate-limiting part of the overall process.

Several diffusion models applied in the common rate equation (Equation 1) are listed in Table 2. These models reflect the cases when the overall rate of transformation is determined by diffusion from or to a reacting interface, or by nucleation and diffusion-controlled growth.[6,7] The $f(\alpha)$ and $g(\alpha)$ functions are based on quite ideal physical and geometric assumptions, thus the limitations concerning the morphology of the sample, mentioned in Section II.C, also apply here. If the rate coefficient is calculated with Equation 1 using diffusion models for $f(\alpha)$, k depends on particle size as well. In the ideal case, it is inversely proportional to the square of the size,[6] in contrast to surface reactions, where the dependence can be described by the reciprocal of the size.

In theoretical studies on the kinetics on solid-state reactions, several refinements of the diffusion models were suggested. They deal with a changing diffusion coefficient as a function of time or reacted fraction, the effect of volume mismatch between reactant and product, etc. For a detailed discussion, one can consult the monographs of Brown, Dollimore, and Galwey[7] or Schmalzried.[67] A new phenomenological model for changing the activation energy of the diffusion was worked out by Małecki and Doumerc.[68]

Solid-state reactions with diffusion control are perhaps the most sophisticated of the processes discussed in this review. The effect of the chemical changes in the narrow sense, i.e., nucleation and growth and those of the conditions of diffusion concentration of lattice defects and morphology, manifest themselves together in the apparent kinetic parameters. Therefore, this is the field where thermoanalytical research requires the most additional information for conclusions on the mechanism.

# IV. KINETIC EVALUATION METHODS

## A. Kinetic Evaluation of Single Thermoanalytical Curves

A reliable kinetic study should always be based on more than one experiment, spreading over a given domain of experimental conditions. The evaluation can be made in two different ways: either the experiments are evaluated simultaneously, looking for a set of kinetic parameters describing *all* of the experiments, or the thermoanalytical curves are evaluated one-by-one, independently from each other and the results are compared only after the evaluation. Here the term "compare" means the observation of random scattering or some systematic changes as a function of the experimental conditions. Both ways have their own merits and drawbacks. In the present section the techniques of the second way are discussed, i.e., the evaluation of single nonisothermal thermoanalytical curves.

We would like to emphasize that there are publications[3,4,69] denying more or less the correctness of the evaluation of single nonisothermal thermoanalytical curves. In the opinion of others, including the present authors,[1,6,62-64,70,71] a modest precision can surely be achieved by proper evaluation techniques. If the scattering of the obtained parameters proves to be random, the simple averaging of the parameters obtained from different experiments help to get reliable results. If the parameters depend on the experimental conditions in a systematic way, the independent evaluation of the single curves may help to find the experimental conditions where the reaction rate is controlled by chemical reactions. Note that this type of evaluation cannot be carried out without some knowledge of the f(α) function. This knowledge may be available from isothermal experiments, theoretical considerations, nonthermoanalytical experiments, etc. The number of the parameters available from the kinetic evaluation of a single thermoanalytical curve depends both on the experimental precision and the form of the kinetic equation(s) describing the process. An important delimitation was presented by Criado and Morales,[25] who showed that the approximation expressed by Equation 13 is formally equivalent with the equation of a first-order reaction. In this way, the existence of the Avrami-Mampel-Erofeev mechanism cannot be established from a single thermoanalytical curve and parameter m cannot be determined from a single experiment with a linear heating program. The deduction of this theorem is simple and well worth studying. Let us raise Equation 13 to power m:

$$-\ln(1 - \alpha) = A'^{m}\beta^{-m}T^{2m}\, e^{-mE'/RT} \tag{26}$$

As has already been mentioned at the modified Arrhenius equations (Equation 9, Section II.A), a power of T can formally be approximated by an exponential function in the limited temperature interval of a thermoanalytical peak and in this way Equation 26 is approximately equivalent to

$$-\ln(1 - \alpha) = A''\beta^{-1}T^{2}\, e^{-E''/RT} \tag{27}$$

where A″ and E″ are the parameters of the formal approximation. (E″ depends on E′ and on the temperature interval, while A″ incorporates a factor $\beta^{1-m}$ also.) On the other hand, the Coats-Redfern approximation[28] of a normal first-order reaction also leads to

$$-\ln(1 - \alpha) = A\,\beta^{-1}\,T^{2}\, e^{-E/RT} \tag{28}$$

Since Equations 27 and 28 are equivalent, there is no hope to distinguish between an Avrami-Mampel-Erofeev mechanism and a sample first-order mechanism from a single nonisothermal thermoanalytical curve at linear heating programs.

All of these deductions are based on the Coats-Redfern approximation of the exponential integral.[28] It can be shown[23] that the relative error of the Coats-Redfern approximation is on the order of $10^{-3} - 10^{-4}$. During the deduction of Equation 13, de Bruijn and coworkers[27] applied the Coats-Redfern approximation separately to each member of a product of m integrals, but this still resulted in acceptable precision. In this way the problem cannot be eliminated by the exact integration of the kinetic equations.

Later, Criado and Ortega[72] tried to extend this result to the formal reaction order n of the simple surface reactions also. *They stated that thermogravimetric curves of* $n = 1, 2/3$, and $1/2$ cannot be distinguished. This result is based, however, on a rather poor kinetic evaluation technique discussed in the next section. Actually, the shape of the derivative thermoanalytical curves of these mechanisms differ so much that curves of $n = 1, 2/3$, and $1/2$ can be distinguished from each other by a mere visual inspection, as was shown by Kissinger more than 30 years ago.[57] Since then, Kissinger's classical results have been checked, reestablished, and expressed in other forms by many investigators.[64,73-75] The dependence of the shape on the formal reaction order can be expressed mathematically by various shape indexes. The simplest shape index is based on the conversion at the peak maximum.[76] The shape indexes are usually based on derivative thermoanalytical curves. In thermogravimetry, they require the numerical differentiation of the observed data. In this age of computers, the numerical differentiation is a well-established and reliable procedure, especially if the data acquisition is also computerized. Usually even the visual inspection of the peak shapes on the computer-generated plots can help to judge the complexity of the process and distinguish processes of high and low formal reaction order. Note that the reliability of the derivative thermogravimetric curves (DTG) can be checked experimentally by comparing the DTG with the result of some sort of evolved gas analysis. If the differentiation is correct, a perfect fit can be obtained.[77]

Generally speaking, a well-defined peak on a derivative type thermoanalytical curve always contains at least three independent geometric characteristics: the peak temperature, the width of the peak, and the degree of asymmetry (shape index). Hence, we can hope the evaluation of at least three independent kinetic parameters from a single thermoanalytical curve. Unfortunately, this hope is not always fulfilled in reality, as is shown by the equivalence of Equations 13 and 28. In the case of simple nth-order kinetic equations, however, there are relatively simple connections between the three kinetic parameters and three geometric characteristics,[78] and in this way one can show that a kinetic evaluation of a modest precision can easily be achieved from a single thermoanalytical curve.[64,71]

We would like to emphasize, however, that any reasoning based on Kissinger's[57] or Balarin's[75] shape indexes serve only theoretical deductions and rough estimations. The kinetic evaluation of the actual experimental data should always be based on more than a few points of the experimental curves.

## B. The Use and Misuse of Statistics

In thermal analysis, the majority of the kinetic evaluations have been based on some sort of linearization. The linearizations derived by the differentiation of the kinetic equations[79] are exact and the most frequently used approximate linearizations are of acceptable precision.[23] Nevertheless, the overwhelming majority of the publications apply these linearizations in a rather careless way, which frequently leads to wrong results and conclusions. The problem lies in the erroneous application of some sort of pseudostatistics. As an illustration, let us regard a simple first-order process. The rearrangement of its kinetic equation immediately yields a linearization suitable for the determination of E and A:

$$\ln(d\alpha/dt) - \ln(1 - \alpha) = \ln A - E/RT \tag{29}$$

An approximately equivalent equation[28] can be obtained by taking the logarithm of Equation 28:

$$\ln[-\ln(1 - \alpha)] - 2\ln T = \ln(A/\beta) - E/RT \tag{30}$$

The usual way of applying these equations is by feeding the experimental $\alpha$ and T data into a calculator and carrying out a linear regression for A and E.

This procedure contains three errors. The first is the neglecting of the uneven sensitivity of this type of equation. Note that the left-hand sides of Equations 29 and 30 tend to infinity at small and high values of $\alpha$ and in this way even small experimental errors can cause great changes there. In the central part, the sensitivity is low, hence the evaluation without some compensation of this uneven sensitivity permits relatively great alterations between the solution of the kinetic equation and the experimental values in the central part of the thermoanalytical curves. Note that the beginning and end is quite similar for a wide variety of mechanisms: flat, characterless sections on the $\alpha(t)$ function. The shape (asymmetry and width) of the thermoanalytical curves is defined by the central part of the curves.

The second error is the distinction between different mechanism models by the values of the regression coefficients obtained in this way. The general forms of Equations 29 and 30 are

$$\ln d\alpha/dt - \ln g(\alpha) = \ln A - E/RT \tag{31}$$

and

$$\ln g(\alpha) - 2\ln T = \ln(A/\beta) - E/RT \tag{32}$$

respectively, where $g(\alpha)$ is the integral of $1/f(\alpha)$. The fit between the experimental and the theoretical data should be expressed by some measure of $[\alpha^{obs}(t) - \alpha^{calc}(t)]$ or $[(d\alpha/dt)^{obs} - (d\alpha/dt)^{calc}]$. Note that $\ln g(\alpha^{obs}) - \ln g(\alpha^{calc})$ is definitely not suitable, since its actual values depend on the form of $g(\alpha)$, too. Hence the regression coefficients belonging to Equations 31 and 32 depend on the form of $g(\alpha)$ as well as on the fit of the data and they cannot be used to distinguish between different $g(\alpha)$ functions.

The third error lies in the belief of the statistical meaning of the obtained regression coefficients. Note that present-day mathematical statistics deal only with random errors. The regression coefficients, confidence intervals, and the various statistical tests are based on the supposition that the experimental errors are *random and independent from each other.* These conditions are not fulfilled in thermal analysis. Even the first electric thermobalances of the 1950s contained analogue filters to remove the *random* components of the error and this process went to a perfection in present-day computerized measurements and digital data processing. There are important experimental errors, of course, but the errors of the different points of a given thermoanalytical curve are neither random nor independent of each other.

In our opinion, the three mistakes listed above together contribute highly to the present-day confusion in the nonisothermal reaction kinetics. It should be emphasized, however, that linearized Equations 29 to 32 themselves *are suitable* for correct evaluation, too, if the uneven sensitivity is compensated by proper weight factors. Such weight factors can easily be deduced and have already been applied in thermal analysis.[80,81]

In other fields of chemistry the general means of kinetic evaluation is the nonlinear method of least squares. Regardless of its statistical background, it is usually suitable to get an optimal or near-to-optimal fit between the measured and the theoretical data. Unfortunately, the general purpose nonlinear least squares methods frequently fail to converge in nonisothermal kinetics. The numeric problems arising from the properties of the nonisothermal Arrhenius equation can be eliminated either by simple parameter transformations[78] or by the careful selection of the best available library routines for the minimization.[82] The nonlinear evaluation of the nonisothermal measurements could be carried out even on the 64 Kbyte minicomputers of the 1970s.[78,83]

We would like to emphasize, however, that the method of true, nonlinear least squares is not the best of the theoretically possible ways of kinetic evaluation.[64] It is only a well-established method to achieve a good fit between the experimental and the theoretical data. From a mathematical point of view, it is possible to elaborate better parameter evaluation methods, taking into account the special characteristics of thermoanalytical curves.

Finally, a few words about the reliability of the estimated kinetic parameters. As has been mentioned already, the usual measures of the mathematical statistics cannot be applied here since the errors are neither random nor independent. The errors of the kinetic parameters obtained by a correct evaluation method may be due to the systematic experimental errors and the application of oversimplified kinetic equations to complex processes. The analysis of these problems has started already, but it is far from any definite solution. There are papers dealing with the effects of the errors of the temperature programs on the kinetic evaluation,[55] the reproducibility of the shape of the thermoanalytical peaks and its kinetic consequences,[62-64] and well-elaborated examples on the consequences of the use of oversimplified kinetic equations.[84] But the majority of the work is still waiting for further research.

### C. Simultaneous Evaluation of Experiments Belonging to Different Heating Rates

If a single set of kinetic parameters can be used for the description of thermoanalytical curves measured at different heating rates, the evaluation becomes very simple and there is no need for the knowledge of the f(α) function.

Several similar techniques are known, due mainly to the pioneering works of Friedman[85] and Ozawa.[12,86] All of them are based on the selection of some identical points on the curves, for example, the peak maxima or the points belonging to the same α values and observing the dependence of the corresponding temperature values on the heating rate.

Let us select, for the sake of simplicity, a given α conversion on two thermoanalytical curves measured at heating rates $\beta_1$ and $\beta_2$ and let us write Equation 8 at both heating rates. Dividing the equations we immediately eliminate f(α) and A:

$$[d\alpha/dt]_1/[d\alpha/dt]_2 = \exp(-E/RT_1)/\exp(-E/RT_2) \tag{33}$$

Here subscripts 1 and 2 refer to heating rates $\beta_1$ and $\beta_2$, respectively. $[d\alpha/dt]_1$, $[d\alpha/dt]_2$, $T_1$ and $T_2$ are measured data, hence the unknown E parameter can easily be calculated from Equation 33. Equation 33 can be used for the evaluation of two isothermal measurements as well as an isothermal and nonisothermal thermoanalytical curve. Using more than two heating rates one can decrease the effects of the experimental errors. In thermal analysis, this type of evaluation has been used since 1957.[87]

Carrying out this simple calculation at several α values, E is obtained as a function of the conversion.[88] If the E vs. α function significantly differs from a random scattering, Equation 8 does not describe the process for all of the applied heating rates. One of the possible causes may be due to heat and mass transport problems arising at higher heating rates.[89]

As was discussed already, the meaning of the term "higher heating rate" depends on the experimental conditions (sample mass, carrier gas, heat conduction in the instruments, etc.) as well as on the properties of the sample and the studied reactions. There are cases in thermogravimetry when 4 K/min proved to be too high for 5 mg samples.[77] If the heat and mass transfer problems have been carefully checked and eliminated, the deviation of the E vs. $\alpha$ function from the constant may be due to a reaction mechanism more complex than the ones described by Equation 8. Antal[88] has pointed out that the shape of the E vs. $\alpha$ curves may be characteristic of the type of the true reaction mechanism and in this way this type of evaluation is suitable for reaction identification.

Thermal decomposition curves of polymers were found by Shlensky[90-92] to converge to limiting curves at very high and very low heating rates. The existence of upper limiting curves was explained by changes in the chemical characteristics of the processes, owing to the extreme shift of the temperature range of reaction.

## V. MISCELLANEOUS TOPICS

### A. The Kinetic Compensation Effect

This term is quite frequently used when different pairs of (apparent) activation energy and preexponential coefficients are obtained either from the thermoanalytical curves of similar substances, from curves of the same substance recorded under different experimental circumstances, or even from the same curve evaluated with different kinetic functions,[93-95] and the points belonging to the different $A_i$ - $E_i$ pairs fit a straight line in the log A vs. E plane,

$$\log A_i = a + b \cdot E_i \tag{34}$$

It is easy to show that Equation 34 is equivalent with the existence of an isokinetic temperature, where all the A - E pairs determine an identical rate constant (k, see Equation 7).[96-99]

In the field of thermal analysis, the concept of the kinetic compensation effect is used in a broad sense and, quite often, carelessly, since the cases listed above, when Equation 34 is approximately valid, may be attributed to entirely different causes. This topic has recently been discussed by Šesták,[100] and Lesnikovich and Levchik.[101,102]

The possible causes of apparent or real kinetic compensation effect are as follows:

1. The mathematical form and nature of the kinetic equations, especially those of the Arrhenius equation for the rate constant
2. Poor efficiency of the estimation of the kinetic parameters
3. Certain differences in the experimental conditions of the curves compared
4. Existing relationships between the characteristics of different substances having similar structure

Visibly, the first two causes are of mathematical character, the other two have physicochemical and methodical backgrounds.

Point 1 means that the estimated kinetic parameters (E, A, n or other constants of the $f(\alpha)$ function) are not independent. The extent of the interdependence of the apparent activation energy and preexponential factor may be characterized, among others, by the angle of functions E/RT and log A in the Hilbert space, as shown by Šesták.[6,100] This angle depends on the temperature range of analysis as well. By means of projection geometry, Pysiak and Sabalski arrived at the conclusion that this type of compensation effect is one of the possible appearances of the underlying relationships, and there are some other correlations, too.[99] The compensation effect was interpreted as an isoparametric relation by Lesnikovich and Levchik.[101,102]

Transformations make it possible to obtain rearranged forms of the kinetic equations, having new parameters that can be estimated independently. However, the physical meaning of such parameters is rather sophisticated, and, on returning from the independent parameters to the theoretical ones, E, A, etc., the interdependences manifest themselves again.

Owing to the interdependence between the estimated values of the activation energy and the preexponential coefficient, the confidence interval of the results, being approximately an ellipse in the log A - E diagram, is not coaxial. The longitudinal axis of the ellipse corresponds to the straight line of Equation 34, if no other sources of the compensation effect are active.

If a third kinetic parameter (the one determining the form of the α function) is also sought, its estimated value is correlated to the other two as well.[4,93,94] Starting from this fact, Adonyi derived a broader concept of the kinetic compensation effect.[93,94] When the formal order is applied in the kinetic function, i.e.,

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1 - \alpha)^n \tag{35}$$

the center line of the confidence region in the log A - E - n space was found to be approximately straight.[64]

The procedure of the estimation cannot eliminate the feature discussed here, but it can further contribute to the effect, i.e., it can make the confidence interval even more prolate. Thus, inefficient estimation procedures constitute another source of apparent compensation effect. This case corresponds to point 2 above.

In the calculations the thermoanalytical curve is represented by a series of points. Since the errors of subsequent points of a measured curve are not independent, the method of least squares is not necessarily optimal for the estimation of kinetic constants (for details, see Section IV.B). Least squares model fitting was compared to a method based on empirical quantities characterizing the shape of the peak by Pokol et al.[64] It was shown that if there is a significant error component in temperature measurement which is systematic within one run, but varies randomly from run-to-run, the method of true least squares is less efficient than the other one. Such errors may be caused by changes in the contact between the sample and the temperature sensor, resulting in a random displacement of the whole peak along the temperature axis.

In general, contribution to an apparent compensation effect should be an important point of view in the comparison of different methods of kinetic calculations.

Now, let us focus on the physical and chemical aspects of the problem. Earlier, Zsakó dealt with the compensation effect as a real property of the thermal processes.[97,103] However, point 3 above is related to the formal character of the kinetic parameters and the effect of factors influencing the transformation but not included in the rate equations.[100-102]

The concept of the compensation effect is often applied to the same reaction carried out under different experimental conditions. Nikolaev and Logvinenko pointed out that this is first a consequence of using physically incomplete rate equations.[104] Debating Zsakó's opinion mentioned before,[97,103] Garn described a frequent case as follows.[105,106] The temperature characteristic of the reaction, for example, that of its onset, may be determined by chemical properties; therefore, this temperature does not change, or hardly changes. On the other hand, some secondary processes may considerably influence the width of the temperature range of transformation, and the temperature dependence of the overall rate. Similar conclusions were drawn by Gallagher and Johnson from the results of a study on calcium carbonate decomposition.[19] Zmijewski and Pysiak listed several factors — supersaturation, specific surface area, etc. — affecting the appearance of the linear relationship between the logarithm of the preexponential coefficient and the apparent activation energy.[98] Certain types of nonrandom measurement errors producing similar effects cannot be excluded either.

The effect of this source of kinetic compensation effect can be diminished by using more parameters in the mathematical model, in order to reflect as much as possible of the real chemical and physical phenomena involved in the overall transformation. Some extensions of the common rate equation were discussed in Section II. This way of kinetic description requires more experimental data, and not only thermoanalytical data.

Another approach was reported by Adonyi and Körösi.[93,94] Accepting the formal use of the rate equations and the occurrence of the compensation effect, they recommended the parameters of Equation 34 be applied for the description of the effect of experimental conditions on the process in question.

The most important type of the real compensation effect, referred to in point 4, is enthalpy-entropy compensation. This phenomenon is quite often reported in the field of homogeneous and heterogeneous catalytic reactions. Using terms of the absolute reaction rate theory, this means that several similar substances react via the same type of activated complex, and so the enthalpy and the entropy change of the activation are linearly correlated. However, a profound mathematical statistical analysis of a number of homogeneous reaction types has shown that, in the majority of the cases, the observed compensation effect probably had a statistical rather than a chemical origin.[107] When the calculated isokinetic temperature lies close to the harmonic mean value of the temperature of the points involved, statistical origin cannot be ruled out.[101,102,107]

Lesnikovich considered the predominance of diffusion mechanisms and the temperature dependence of the activation energy as possible sources of the compensation effect.[102] These seem to be intermediate cases between points 3 and 4.

Finally, the importance of being aware of the different sources of the apparent or real kinetic compensation effect should be stressed again. Though physicochemical interdependence of the pre-exponential factor and the activation energy, according to point 4, may occur sometimes, it is not an inherent feature of the thermal reactions of condensed substances. Therefore, any analysis of the problem should strive to tell the origin of the compensation effect encountered.

### B. Continuous Distribution of Kinetic Parameters

A frequently underlined argument against the kinetic evaluation of the thermoanalytical curves is the emphasizing of the nondefined nature of the kinetic parameters in solid-state reactions.[2-4] In a real solid sample, the energy and entropy relations of the reacting species strongly depend on the occurrence and nature of near-by lattice errors and impurities. In surface reactions, the topology of the surface cracks, edges, etc. also plays a fundamental role. In this way, the kinetic parameters vary from point to point.

In this section we examine how this variation affects the evaluation of the kinetic curves. First of all, we should like to note that this is not a universal, ever-present problem. In many cases nature itself forms some sort of average from the distribution of the kinetic parameters. In many surface reactions, the reaction on the favorable spots produces fresh lattice errors for the neighboring species, too. As a result, the whole surface separating the reacted and the unreached part of the sample contracts together. If the contraction is irregular, some irregular empirical f(α) function will be determined in the kinetic evaluation. The kinetic parameters and f(α) function calculated from this type of thermoanalytical curve describes the macroscopic movement of the surface.

In other cases, the uneven distribution of the kinetic parameters in the sample produces a complicated reaction surface consisting of an irregular network of cavities and cracks. This again leads to some irregular f(α) function, provided that the backward reactions do not hinder the process inside the cavities and cracks. In such situations, it is possible that the parts in a favorable position for the transformation react earlier and, as a result, the activation energy will be an increasing function of the reacted mole fraction.

Independent parallel reactions with a continuous distribution of the kinetic parameters may also arise, especially in the thermal analysis of powders or reactions taking place on fixed, stationary surfaces (zeolites, etc.).

In our opinion, the above-listed complications *do not* imply that the kinetic evaluation is meaningless or hopeless in thermal analysis. Only a little bit more careful work is needed. Probably the best thing is to follow the reasoning of Antal et al.[82] and carry out the kinetic evaluation *both* by the true method of least squares and by E vs. α diagrams. Their reasoning can easily be extended to the problem of kinetic parameter distribution. The f(α) function, required for the calculations, can easily be obtained from isothermal experiment(s). If the E values calculated from single thermoanalytical curves are considerably lower than the results read from the E vs. α curves, one can assume that the distribution of the kinetic parameters broadened the thermoanalytical peaks. Broader peaks result in lower E values. If E shows a monotonous increase as a function of α, there may be domains where the energy barrier of the transformation is smaller and the reaction can proceed more easily.

For a special case, this approach has already been elaborated as far as the quantitative determination of the distribution function of the activation energy. It is the case of similar independently reacting species, each of them having the same preexponential factor but different activation energy. Originally, it was a mathematical model of the decomposition of mineral coals.[108] From a chemical point of view, this model proved to be oversimplified for the complex chemical structure of coals. From a mathematical point of view, however, the researchers in this particular field have shown that it is possible to determine the complete distribution functions from thermoanalytical curves.[109]

### C. Kinetic Resolution of Overlapping Peaks

The resolution of the multiplets is a crucial problem of analytical chemistry. There are fortunate fields in chemistry where the measured peaks can be described by simple mathematical functions (e.g., Gaussian curves) and in this way the peak resolution is a relatively easy process. In thermal analysis one has to use the various kinetic models for the description of the individual peaks, even if one is only looking for the areas of the overlapping peaks that are proportional to the amounts of the reacting species in the sample. The kinetic parameters are now only side products. Their meaningful or meaningless values help to judge the reliability of the evaluation.

So far, the problem has only been solved for independent parallel reactions by Várhegyi[78] and Boy and Böhme.[110] This type of curve resolution seems to be applicable for the thermal analysis of mixtures of powders or for reactions when the reacting species or domains decompose independently from each other. From a technical point of view, the arising convergence problems can easily be eliminated by simple parameter transformations and this type of calculation could be carried out even on the 64 Kbyte minicomputers of the 1970s.[78] Based on the experience of hundreds of kinetic curve resolutions in the DSC study of alloys[111] the following empirical rules can be formulated:

1. When the overlap is slight and the three fundamental geometric characteristics of the peaks can clearly be distinguished, it is possible to calculate four independent parameters for each peak from a single thermoanalytical curve — E, A, n (see Equation 35), and the peak area.
2. In the case of higher overlaps, n may be determined from other sources.
3. When shoulders can only be distinguished on the overlapped thermoanalytical curves, there is no unique solution.

A rather obvious way to increase the capacity of the curve resolution process is to use the kinetic parameters of the pure components in the calculations. Unfortunately, the pure components are not always available. Even if they are, they may have other kinetic parameters than in the mixture analyzed. (As was discussed already, the macroscopic kinetic parameters of the solid-state reactions strongly depend on lattice errors, impurities, and the morphology of the samples.)

Another possibility is to carry out the kinetic curve resolution for a given set of thermoanalytical experiments belonging to different heating rates or temperature programs.[78] This approach worked well in test calculations on simulated thermoanalytical curves,[78] but caused problems in the evaluation of real experiments. There is a certain fluctuation of the kinetic parameters themselves from sample to sample, and the different experimental conditions also influence the thermoanalytical curves. As a result, it is difficult to obtain a good fit with a single set of parameter values to several thermoanalytical curves. (The simple techniques of the estimation of E from the peak temperatures or other characteristic points of the curve at different heating rates are less sensitive for this type of alteration, but they cannot provide the areas of the overlapping peaks.)

The following solution seems to be advisable.[112] One should collect all the information available from chemical considerations, from the thermoanalytical curves of the pure components or samples chemically similar to the pure components, and from the shift of the peak maxima with the increase of the heating rate. On this basis one should establish those intervals or domains where the kinetic parameters may be considered meaningful. During the mathematical resolution (kinetic curve fitting) of the individual thermoanalytical curves, we can force the kinetic parameters by appropriate mathematical techniques to remain in the desired domains. In this way one can apply the information gathered from other sources without attempting to describe different experiments with exactly the same kinetic parameters. There are a large number of mathematical techniques to force the parameters into user-defined domains.[113] Some of them are quite simple, for example, to apply interval constraints during a direct minimization method or to add simple "penalty functions" to the sum minimized.

### D. The Effects of the Temperature Program on the Information Content of Thermoanalytical Curves

The effect of the temperature program on the transport processes has been treated in Section III. The applied temperature program, however, affects the kinetic evaluation also, even if the transport processes are negligible under the given experimental conditions.

Let us start with the heating rate of the linear temperature programs. It is a common belief that the proper choice of the heating rate can help, for example, in the resolution of the overlapping peaks. Ozawa[114] has examined the situation by simulated curves. His examples showed that a tenfold increase or decrease of the heating rate could merge two overlapping peaks into a single one. However, he used rather extreme kinetic parameters in his simulations. In his first "case", for example, he calculated two DTG peaks with parameters $A_1 = 10^5\ s^{-1}$, $E_1 = 20$ kcal/mol, $A_2 = 3 \times 10^{27}\ s^{-1}$(*sic*), $E_2 = 80$ kcal/mol and $n_1 = n_2 = 2$. At 10°C/min, these reactions resulted in a single DTG peak. At 1°/C, he got a wider peak on which a shoulder indicated the existence of two reactions. Considering the extremely different kinetic parameters, it is not a very convincing result. Moreover, it seems to illustrate that the change in the heating rate is a rather poor tool to obtain better peak resolution.

The situation is entirely different when the change in the heating rate facilitates or hinders the *transport processes* during the measurement. It is well known that a hindered mass transport may increase the difference between the peaks of reversible and irreversible reactions. Nevertheless, we would like to point out that there are better methods for this purpose than increasing the heating rate.[39,65,66,115,116]

Several nonlinear heating programs have been proposed but they mainly affect the simplicity of the techniques of kinetic calculations, which is a dubious aim in the present age of computers. Concerning the information content of the experiments, it is easy to show, for example, that a hyperbolic temperature program results in nearly the same $d\alpha/dt$ vs. temperature diagrams as the linear ones.[75] The nonlinear heating programs can be very helpful, however, to get optimal experimental conditions in a given apparatus, as it is achieved by the quasi-isothermal-quasi-isobaric method of the Pauliks[65,66,115] and the constant decomposition rate technique of Rouquerol.[39]

As was discussed already, the effect of the transport processes is a crucial problem and the quasi-isobaric or constant rate method is an ingenious technique in this respect. If there are no transport problems at a given reaction under the given experimental conditions, however, there is no need for a nonlinear temperature program. The instrument can be switched simply to a lower heating rate or to an isothermal section in those temperature domains where lower reaction rates are required. Let us regard, for example, two parallel reactions. If we insert a long isothermal section at the starting temperature of the first peak, we can reach a nearly lone peak for the second process. Test calculations have shown[78] that this simple process does not increase the information content of a *single* thermoanalytical curve. It may add, however, some extra information to an evaluation based on several experiments.

Finally, it is well worth mentioning the cyclic temperature jump methods proposed by Rouquerol.[39] They are based on temperature jumps sufficiently quick to regard the sample identical before and after the jump and so allowing the calculation of the activation energy or an activation-energy-like quantity even if the studied process is too complex to be described by a known rate equation.

## VI. CONCLUSION

From measurements with any experimental technique, qualitative and quantitative conclusions may be drawn. In the case of thermal analysis, the way of further development is certainly connected to the increase of the proportion of quantitative information. In this respect, the description of kinetics is not only a natural application of thermal analysis, but it is essential for the quantitative interpretation of the effect of different structural and experimental parameters and for some analytical applications as well (resolution of overlapping peaks).

To satisfy these requirements the mathematical models of kinetics should be extended to include more of the chemical and nonchemical parameters and subprocesses, and to take the inhomogeneities, concentration, and temperature gradients within the system into account. On the other hand, these factors should be considered in the design of the experiments and controlled during measurements as much as possible.

The proper choice of a mathematical evaluation technique is also indispensable, and one has to be aware of the fact that poor statistics may cause a severe loss or distortion of information provided by a sound experiment.

Relevant and reliable thermoanalytical data are very useful in the elucidation of the reaction mechanism as one of the information sources. However, the demand for other information (on structure, intermediate products, etc.) is expected to increase in this field of use.

In our opinion, the activity of recent years reviewed here is a valuable contribution to the basis of a higher level kinetic application of thermal analysis.

## REFERENCES

1. **Šesták, J.**, Phylosophy of non-isothermal kinetics, *J. Therm. Anal.*, 16, 503, 1979.
2. **Garn, P. D.**, Kinetic parameters, *J. Therm. Anal.*, 13, 581, 1978.
3. **Arnold, M., Veress, G. E., Paulik, J., and Paulik, F.**, The applicability of the Arrhenius model in thermal analysis, *Anal. Chim. Acta*, 124, 341, 1981.

4. **Arnold, M., Veress, G. E., Paulik, J., and Paulik, F.**, A critical reflection upon the application of the Arrhenius model to non-isothermal thermogravimetric curves, *Thermochim. Acta*, 52, 67, 1982.
5. **Šesták, J. and Kratochvíl, J.**, Rational approach to thermodynamic processes and constitutive equations in isothermal and non-isothermal kinetics, *J. Therm. Anal.*, 5, 193, 1973.
6. **Šesták, J.**, Thermophysical properties of solids. Their measurements and theoretical thermal analysis, in *Wilson and Wilson's Comprehensive Analytical Chemistry*, Vol. 12, Part D, Svehla, G., Ed., Elsevier/North Holland, Amsterdam, 1984, chap. 8 and 9.
7. **Brown, W. E., Dollimore, D., and Galwey, A. K.**, *Reactions in the Solid State. Comprehensive Chemical Kinetics*, Vol. 22, Bamford, C. H. and Tipper, C. F. H., Eds., Elsevier/North Holland, Amsterdam, 1987, chap. 3 to 5.
8. **Fatemi, N., Whitehead, R., Price, D., and Dollimore, D.**, Some comments on the use of Avrami-Erofeev expressions and solid state decomposition rate constants, *Thermochim. Acta*, 104, 93, 1986.
9. **Garn, P. D.**, *Thermoanalytical Methods of Investigation*, Academic Press, New York, 1965.
10. **Sharp, J. H.**, Reaction kinetics, in *Differential Thermal Analysis*, Vol. 2, Mackenzie, R. C., Ed., Academic Press, London, 1972, chap. 28.
11. **Simon, J., Buzágh-Gere, É., and Gál, S.**, Contribution to the field of kinetic thermal studies, in *Proceedings of the 3rd International Conference on Thermal Analysis*, Vol. 2, Wiedemann, H. G., Ed., Birkhaeuser, Basel, 1972, 393.
12. **Ozawa, T.**, Kinetic analysis of derivative curves in thermal analysis, *J. Therm. Anal.*, 2, 301, 1970.
13. **Pokol, G., Gál, S., Sztatisz, J., Domonkos, L., and Pungor, E.**, Description of solid-gas reactions, in *Proceedings of the 8th International Symposium on Reactivity of Solids*, Wood, J., Lindqvist, O., Helgesson, C., and Vannerberg, N. G., Eds., Plenum Press, New York, 1977, 209.
14. **Pokol, G., Gál, S., and Pungor, E.**, Description of the rate of heterogeneous chemical reactions, *Thermochim. Acta*, 33, 259, 1979.
15. **Pokol, G.**, Can a rate constant independent of sample size be obtained from the rate equation generally used in thermal analysis?, *J. Therm. Anal.*, 23, 235, 1982.
16. **Benson, S. W. and Golden, D. M.**, Methods for the estimation of rate parameters of elementary processes, in *Physical Chemistry*, Vol. 7, Eyring, H., Henderson, D., and Jost, W., Eds., Elsevier/North Holland, Amsterdam, 1975, chap. 2.
17. **David, C.**, Thermal degradation of polymers, in *Comprehensive Chemical Kinetics*, Vol. 14, Bamford, C. H. and Tipper, C. F. H., Eds., Elsevier/North Holland, Amsterdam, 1975, chap. 1.
18. **Gallagher, P. K. and Johnson, D. W.**, The effect of sample size and heating rate on the kinetics of the thermal decomposition of $CaCO_3$, *Thermochim. Acta*, 6, 67, 1973.
19. **Gallagher, P. K. and Johnson, D. W.**, Kinetics of thermal decomposition of $CaCO_3$ in $CO_2$ and some observations on the kinetic compensation effect, *Thermochim. Acta*, 14, 255, 1976.
20. **Ball, M. C. and Casson, M. J.**, Thermal studies of lead(II) salts. VI. Kinetics of decomposition of lead(II) carbonate and lead(II) hydroxide carbonate (white lead), *J. Therm. Anal.*, 28, 371, 1983.
21. **Krishnan, K., Ninan, K. N., and Madhusudanan, P. M.**, Computation of activation energy spectrum — a new approach, *Thermochim. Acta*, 101, 365, 1986.
22. **Gorbachev, V. M.**, Algorithm for the solution of the exponential integral in non-isothermal kinetics at linear heating, *J. Therm. Anal.*, 10, 447, 1976.
23. **Várhegyi, G.**, Integration of the rate constant and linearization of the kinetic equations in non-isothermal reaction kinetics, *Thermochim. Acta*, 25, 201, 1978.
24. **Young, D. A.**, *Decomposition of Solids*, Pergamon Press, Oxford, 1966.
25. **Criado, J. M. and Morales, J.**, Defects of thermogravimetric analysis for discerning between first order reactions and those taking place through the Avrami-Erofeev's mechanism, *Thermochim. Acta*, 16, 382, 1976.
26. **Henderson, D. W.**, Experimental analysis of non-isothermal transformations involving nucleation and growth, *J. Therm. Anal.*, 15, 325, 1979.
27. **de Bruijn, T. J. W., Ipekoglu, A. N., de Jong, W. A., and van den Berg, P. J.**, Kinetic parameters in Avrami-Erofeev type reactions from isothermal and non-isothermal experiments, *Thermochim. Acta*, 45, 315, 1981.
28. **Coats, A. W. and Redfern, J. W.**, Kinetic parameters from thermogravimetric data, *Nature (London)*, 201, 68, 1964.
29. **Tonge, K. H.**, Particle size effects in temperature programmed topochemical reactions, *Thermochim. Acta*, 74, 151, 1984.
30. **Duval, C.**, *Inorganic Thermogravimetric Analysis*, 2nd ed., Elsevier, Amsterdam, 1963, chap. 5.
31. **Šesták, J.**, Non-isothermal kinetics, in *Proceedings of the 3rd International Conference on Thermal Analysis*, Vol. 2 and 3, Wiedemann, H. G., Ed., Birkhaeuser, Basel, 1972.
32. **Bradley, R. S.**, The energetics and statistical mechanics of the kinetics of solid-solid reactions, *J. Phys. Chem.*, 60, 1347, 1956.

33. **Šesták, J. and Berggren, G.,** Study of the kinetics of the mechanism of solid state reactions at increasing temperatures, *Thermochim. Acta,* 3, 1, 1971.
34. **Šatava, V.,** Mechanism of solid state reactions from thermal analysis measurements, in *Proceedings of 3rd International Conference on Thermal Analysis,* Vol. 2, Wiedemann, H. G., Ed., Birkhaeuser, Basel, 1972, 373.
35. **Šatava, V.,** Fundamental principles of kinetic data evaluation from thermal analysis curves, *J. Therm. Anal.,* 5, 217, 1973.
36. **Van Rysselberghe, P.,** *Thermodynamics of Irreversible Processes,* Hermann, Paris, 1963.
37. **Jüntgen, H. and Van Heek, K. H.,** Non-isothermal kinetics of reversible reactions taking as an example the thermal decomposition of $CaCO_3$, in *Proceedings of the 3rd International Conference on Thermal Analysis,* Vol. 2, Wiedemann, H. G., Ed., Birkhaeuser, Basel, 1972, 423.
38. **Pokol, G., Várhegyi, G., and Várady, L.,** Studies on the kinetics of the gibbsite → $\chi$-alumina reaction, *Thermochim. Acta,* 76, 237, 1984.
39. **Rouquerol, J.,** Critical examination of several problems typically found in the kinetic study of thermal decomposition under vacuum, *J. Therm. Anal.,* 5, 203, 1973.
40. **Wist, A. O.,** Determination of the activation energy changes of $CaCO_3$ under influence of various environmental gases, in *Proceedings of the 2nd International Conference on Thermal Analysis,* Vol. 2, Schwenker, R. F. and Garn, P. D., Eds., Academic Press, New York, 1969, 1095.
41. **Pacewska, B., Pysiak, J., and Klepańska,** The influence of the pressure of gaseous reaction products on the rate of dissociation of basic ammonium aluminum sulfate and generalities of the process, *Thermochim. Acta,* 92, 113, 1985.
42. **Criado, J. M., González, F., and González, M.,** Influence of the $CO_2$ pressure on the kinetics of thermal decomposition of manganese carbonate, *J. Therm. Anal.,* 24, 59, 1982.
43. **Maciejewski, M. and Baldiga, J.,** The influence of the pressure of the gaseous product on the reversible thermal decomposition of solids, *Thermochim. Acta,* 92, 105, 1985.
44. **Paulik, F. and Paulik, J.,** Investigations under quasi-isothermal and quasi-isobaric conditions by means of the Derivatograph, *J. Therm. Anal.,* 5, 253, 1973.
45. **Flynn, J. H. and Dunlap, L. A.,** Temperature gradients in horizontal tube furnaces, *Thermochim. Acta,* 105, 215, 1986.
46. **Hoff, H.,** Numerical calculation of the three dimensional transport of heat by conduction, *Thermochim. Acta,* 69, 45, 1983.
47. **Słuzalec, A.,** A new finite element approach to heat flow analysis in 3D developable structures, *J. Therm. Anal.,* 30, 1063, 1985.
48. **Draper, A. L. and Sveum, L. K.,** The analysis of thermal data, *Thermochim. Acta,* 1, 345, 1970.
49. **Seybold, K., Meisel, T., and Cserfalvi, T.,** A model for quantitative DTA apparatus, in *Proceedings of the 5th International Conference on Thermal Analysis,* Chihara, H., Ed., Kagaku Gijutsu-Sha, Tokyo, 1977, 416.
50. **Seybold, K., Meisel, T., and Cserfalvi, T.,** Modelling of quantitative DTA equipment. I. Electric analog approach, *J. Therm. Anal.,* 15, 93, 1979.
51. **Egunov, V. P.,** Quantitative thermal analysis. VI. Initial conditions of the mathematical description of thermal curves (gradient theory), *J. Therm. Anal.,* 30, 649, 1985.
52. **Saito, Y., Saito, K., and Atake, T.,** Base line drawing for the determination of the enthalpy of transition in classical DTA, power-compensated DSC and heat flux DSC, *Thermochim. Acta,* 104, 275, 1986.
53. **Saito, Y., Saito, K., and Atake, T.,** Theoretical analysis of peak height in classical DTA, power-compensated DSC and heat flux DSC, *Thermochim. Acta,* 107, 277, 1986.
54. **Šesták, J.,** Errors of kinetic data obtained from thermogravimetric curves at increasing temperature, *Talanta,* 13, 567, 1966.
55. **Várhegyi, G.,** The effects of imperfect temperature programming on the kinetic evaluation of thermoanalytical curves. I. A simple mathematical example, *Thermochim. Acta,* 59, 31, 1982; II. Concave and convex curvatures on the actual temperature-time functions, *Thermochim. Acta,* 59, 43, 1982; III. Error bounds for the activation energy and the formal reaction order, *Thermochim. Acta,* 65, 333, 1983.
56. **Reich, L. and Stivala, S. S.,** Heat transfer effects during Teflon degradation by TGA, *Thermochim. Acta,* 1, 65, 1970.
57. **Kissinger, H. E.,** Reaction kinetics in differential thermal analysis, *Anal. Chem.,* 29, 1702, 1957.
58. **Shishkin, L. Yu,** Reaction kinetics calculated by the single point method. A synthesis of the Borchardt-Daniels theory and the Kissinger theory of differential thermal analysis, *J. Therm. Anal.,* 30, 557, 1985.
59. **Khoudier, A., Bouzon, J., and Vergnaud, J. M.,** Modelization of the DSC technique by considering heat transfer and kinetics of reaction in the case of rubber cure, *Thermochim. Acta,* 98, 285, 1986.
60. **Armand, J. Y., Bourgois, J., Touchard, M., and Vergnaud, J. M.,** Effect of sample size and heating rate on cure reaction of rubber in DSC, *Thermochim. Acta,* 108, 345, 1986.
61. **Pokol, G., Gál, S., and Pungor, E.,** The effect of heat transport within the sample on the shape of thermoanalytical curves, *Thermochim. Acta,* 105, 313, 1986.

62. **Pokol, G. and Gál, S.,** Description of the shape of thermoanalytical curves. I. Empirical parameters for the characterization of peaks in differential scanning calorimetry, *Anal. Chim. Acta,* 167, 183, 1985.
63. **Pokol, G., Gál, S., and Pungor, E.,** Description of the shape of thermoanalytical curves. II. Simulation of peak shape from kinetic equations, *Anal. Chim. Acta,* 167, 193, 1985.
64. **Pokol, G., Gál, S., and Pungor, E.,** Description of the shape of thermoanalytical curves. III. A method for estimating kinetic constants from parameters characterizing peak shape, *Anal. Chim. Acta,* 175, 289, 1985.
65. **Paulik, F. and Paulik, J.,** Quasi-isothermal and quasi-isobaric thermogravimetry, *Anal. Chim. Acta,* 60, 127, 1972.
66. **Paulik, J. and Paulik, F.,** Simultaneous thermoanalytical examinations by means of the Derivatograph, in *Wilson and Wilson's Comprehensive Analytical Chemistry,* Vol. 12, Part A, Svehla, G., Ed., Elsevier, Amsterdam, 1981, chap. 7.
67. **Schmalzried, H.,** *Solid State Reactions,* 2nd ed., Verlag Chemie, Weinheim, 1981, chap. 5.
68. **Małecki, A. and Doumerc, J. P.,** Extension of the diffusional kinetics. Models involving changes in activation energy, *J. Therm. Anal.,* 31, 567, 1986.
69. **Reading, M., Dollimore, D., Rouquerol, J., and Rouquerol, F.,** The measurement of meaningful activation energies using thermoanalytical methods, *J. Therm. Anal.,* 29, 775, 1984.
70. **Galwey, A. K.,** The interpretation of solid state kinetics, in *Proceedings of the 7th International Conference on Thermal Analysis,* Vol. 1, Miller, B., Ed., John Wiley & Sons, New York, 1982, 38.
71. **Várhegyi, G. and Székely, T.,** Reaction kinetics in thermal analysis. The sensitivity of kinetic equations to experimental errors, *Thermochim. Acta,* 57, 13, 1982.
72. **Criado, J. M. and Ortega, A.,** Remarks on the discrimination of the kinetics of solid state reactions from a single nonisothermal trace, *J. Therm. Anal.,* 29, 1225, 1984.
73. **Koch, E.,** *Non-Isothermal Reaction Analysis,* Academic Press, London, 1977.
74. **Koch, E.,** Reaction kinetics at linearly increased temperature. I. Comparative characterization of reactions in solution and solid phase in a unique "mechanistic diagram", *Thermochim. Acta,* 56, 1, 1982.
75. **Várhegyi, G.,** The shape of the thermoanalytical curves at hyperbolic temperature programs, *Thermochim. Acta,* 57, 247, 1982.
76. **Balarin, M.,** Is Kissinger's rule true?, *Thermochim. Acta,* 33, 341, 1979.
77. **Székely, T., Várhegyi, G., Till, F., Szabó, P., and Jakab, E.,** The effects of heat and mass transport on the results of thermal decomposition studies. I. The three reactions of calcium oxalate monohydrate. II. Polystyrene, polytetrafluoroethylene, polypropylene, *J. Anal. Appl. Pyrol.,* in press.
78. **Várhegyi, G.,** Kinetic evaluation of non-isothermal thermoanalytical curves in the case of independent reactions, *Thermochim. Acta,* 28, 367, 1979.
79. **Šesták, J., Šatava, V., and Wendlandt, W. W.,** The study of heterogeneous processes by thermal analysis, *Thermochim. Acta,* 7, 333, 1973.
80. **Várhegyi, G.,** An alternative calculation method to that of Judd, *J. Therm. Anal.,* 5, 503, 1973.
81. **Boy, S. and Böhme, K.,** Contribution to the kinetics of solid reactions under non-isothermal conditions, *Thermochim. Acta,* 20, 195, 1977.
82. **Antal, M. J., Jr., Mok, W. S. L., Roy, J. C., Raissi, A. T., and Anderson, D. G. M.,** Pyrolytic sources of hydrocarbons from biomass, *J. Anal. Appl. Pyrol.,* 8, 291, 1985.
83. **Altorfer, R.,** Estimation of kinetic parameters from conversion curves, determined at constant heating rate, *Thermochim. Acta,* 24, 17, 1978.
84. **Criado, J. M.,** Influence of the pressure on the shape of DTA and DTG curves of reversible reactions of thermal decomposition solids, *Thermochim. Acta,* 19, 129, 1977.
85. **Friedman, H. L.,** Thermal degradation of plastics. I. The kinetics of polymer chain degradation, *J. Polym. Sci.,* 45, 119, 1960.
86. **Ozawa, T.,** The peak of the derivative thermoanalytical curves of diffusion, *J. Therm. Anal.,* 6, 401, 1974.
87. **Doyle, C. D.,** Quantitative calculations in thermogravimetric analysis, in *Techniques and Methods of Polymer Evaluation,* Vol. 1, Slade, Ph. E. and Jenkins, L. T., Eds., Marcel Dekker, New York, 1966, chap. 4.
88. **Antal, M. J., Jr.,** Thermogravimetric signatures of complex solid phase pyrolysis mechanisms and kinetics, in *Proceedings of the 7th International Conference on Thermal Analysis,* Vol. 2, Miller, B., Ed., John Wiley & Sons, London, 1982, 1490.
89. **Antal, M. J., Jr.,** Biomass pyrolysis, in *Advances in Solar Energy,* Böer, K. W. and Duffie, J. A., Eds., Plenum Press, New York, 1985, chap. 4.
90. **Shlensky, O. F.,** Thermal decomposition of polymeric materials: characteristics of kinetics at non-isothermal heating, *J. Therm. Anal.,* 28, 421, 1983.
91. **Shlensky, O. F.,** Polymer thermodecomposition. Characteristic features of non-isothermal kinetics by rapid heating, *Thermochim. Acta,* 92, 145, 1985.

92. **Shlensky, O. F., Matyukhin, A. A., and Vayshteyn, E. F.,** Limiting temperatures of the thermal decomposition of polymers and their determination by rapid thermal analysis, *J. Therm. Anal.*, 31, 107, 1986.
93. **Adonyi, Z.,** Quantitative method for comparing thermogravimetric data under various measuring circumstances, *Thermochim. Acta*, 55, 269, 1982.
94. **Adonyi, Z. and Körösi, G.,** Experimental study of non-isothermal kinetic equations and compensation effect, *Thermochim. Acta*, 60, 23, 1983.
95. **Lesnikovich, A. I. and Levchik, S. V.,** A method of finding invariant values of kinetic parameters, *J. Therm. Anal.*, 27, 89, 1983.
96. **Gorbachev, V. M.,** Criterion of the existence of compensation relationship for non-isothermal kinetics, *J. Therm. Anal.*, 8, 585, 1975.
97. **Zsakó, J.,** The kinetic compensation effect, *J. Therm. Anal.*, 9, 101, 1976.
98. **Zmijewski, T. and Pysiak, J.,** Compensation effect in thermal dissociation processes, in *Proceedings of the 4th International Conference on Thermal Analysis*, Vol. 1, Buzás, I., Ed., Akadémiai Kiadó, Budapest, 1974, 205.
99. **Pysiak, J. and Sabalski, B.,** Compensation effect and isokinetic temperature in thermal dissociation reactions of the type $A_{solid} \rightleftharpoons B_{solid} + C_{gas}$. Interpretation of the Arrhenius equation as a projection correlation, *J. Therm. Anal.*, 17, 287, 1979.
100. **Šesták, J.,** Kinetic compensation effect: facts and fiction of linear plots using Arrhenius law, in *Proceedings of the 6th International Conference on Thermal Analysis*, Vol. 1, Wiedemann, H. G., Ed., Birkhaeuser, Basel, 1980, 29.
101. **Lesnikovich, A. I. and Levchik, S. V.,** Isoparametric kinetic relations for chemical transformations in condensed substances. I. Theoretical fundamentals, *J. Therm. Anal.*, 30, 237, 1985.
102. **Lesnikovich, A. I. and Levchik, S. V.,** Isoparametric kinetic relations for chemical transformations in condensed substances. II. Reactions involving the participation of solid substances, *J. Therm. Anal.*, 39, 677, 1985.
103. **Zsakó, J.,** Kinetic analysis of thermogravimetric data. VI. Some problems of deriving kinetic parameters from TG curves, *J. Therm. Anal.*, 5, 239, 1973.
104. **Nikolaev, A. V. and Logvinenko, V. A.,** Compensation effect in solid-state reactions. Thermoanalysis of one substance under different experimental conditions, *J. Therm. Anal.*, 10, 363, 1976.
105. **Garn, P. D.,** The kinetic compensation effect, in *Proceedings of the 4th International Conference on Thermal Analysis*, Vol. 1, Buzás, I., Ed., Akadémiai Kiadó, Budapest, 1975, 25.
106. **Garn, P. D.,** The kinetic compensation effect, *J. Therm. Anal.*, 10, 99, 1976.
107. **Krug, R. R., Hunter, W. G., and Grieger, R. A.,** Enthalpy-entropy compensation. I. Some fundamental statistical problems associated with the analysis of Van't Hoff and Arrhenius data, *J. Phys. Chem.*, 80, 2335, 1976. II. Separation of the chemical from the statistical effect, *J. Phys. Chem.*, 80, 2341, 1976.
108. **Pitt, G. J.,** The kinetics of the evolution of volatile products from coal, *Fuel*, 41, 267, 1962.
109. **Gavalas, G. R.,** *Coal Pyrolysis*, Elsevier, Amsterdam, 1982.
110. **Boy, S. and Böme, K.,** Kinetic analysis of additively overlapping peaks, *Thermochim. Acta*, 75, 263, 1984.
111. **Várhegyi, G., Groma, G., and Lengyel, M.,** DSC examination of alloys, *Thermochim. Acta*, 30, 311, 1979.
112. **Várhegyi, G.,** A basic problem in mathematical modelling in pyrolysis: the number of the unknown parameters, *J. Anal. Appl. Pyrol.*, 2, 1, 1980.
113. **Fletcher, R.,** Methods for solving non-linearly constrained optimization problems, in *The State of Art in Numerical Analysis*, Jacobs, D., Ed., Academic Press, London, 1977, 365.
114. **Ozawa, T.,** Some demonstration of the effect of the heating rate on thermoanalytical curves, *J. Therm. Anal.*, 9, 217, 1976.
115. **Paulik, F. and Paulik, J.,** Thermoanalytical examinations under quasi-isothermal-quasi-isobaric conditions, *Thermochim. Acta*, 100, 23, 1986.
116. **Smykatz-Kloss, W.,** Application of differential thermal analysis in mineralogy, *J. Therm. Anal.*, 23, 15, 1982.