

## REMARKS ON THE DESCRIPTION OF REACTION KINETICS UNDER NON-ISOTHERMAL CONDITIONS

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### ABSTRACT

Many fundamental problems regarding the mathematical description of non-isothermal reaction kinetics are still the subject of various considerations. In this communication an attempt is made to clarify some aspects concerned with: (1) the use of the degree of conversion in the rate equations; (2) fundamental relationships describing non-isothermal reaction kinetics; (3) the existence of the total differential of  $\alpha = f(t, T)$ ; (4) the physical meaning of Doyle's assumption; (5) the possibility of the application of non-isothermal techniques on various temperature programs to the investigation of reaction kinetics; and (6) other problems arising on examination of thermodynamics and non-isothermal kinetics of simple thermal processes.

### INTRODUCTION

Since the introduction of thermoanalytical methods to the investigation of the thermal behaviour of various systems, considerable efforts have been made to utilize experimental data for the evaluation of some important parameters characterizing the kinetics and thermodynamics of proceeding processes [1]. The originally applied isothermal techniques [2,3] made such information available, however, the full kinetic description of the process investigated was made possible by the data from several independent experimental runs [1–3]. The non-isothermal thermoanalytical methods, introduced later, soon gained many followers, resulting from the fact that all the interesting information could be obtained from just one experimental run [1,2,4]. There is still an emphasis on non-isothermal methods of investigation despite some criticism with regard to the mechanistic interpretation [5–7] and numerous difficulties arising from the mathematical description of the non-isothermal reaction kinetics [8]. The latter problem has been discussed in a previous communication [8] in which the forms of basic kinetic equations have been derived assuming that the degree of conversion is a function of both temperature and time. The soundness of this fundamental assumption has however, been questioned by Tang [9] in a recent communication.

In the same publication the author also had objection to the recent paper of MacCallum [10], who, starting from the premise of the transition state theory, derived the two-term rate expression for non-isothermal reactions.

The intention of this publication is to reconsider some of the problems concerned with the mathematical description of non-isothermal reaction kinetics in view of recently published experimental facts [11–13]. Some aspects regarding the possibilities of the application of non-isothermal methods to the examination of kinetics and thermodynamics of simple thermal processes are also discussed.

#### SOME ASPECTS REGARDING KINETICS OF NON-ISOTHERMAL PROCESSES

##### *The use of the degree of conversion in the rate equations*

The general equation describing the rate of the isothermal process represented by reaction (1)



can be expressed in the form,

$$-\frac{dc_A}{dt} = \frac{dc_B}{dt} = \frac{dc_C}{dt} = f(c_A)k(T) \quad (2)$$

where  $t$  indicates time,  $T$  is temperature, and  $c$  denotes concentration of a given reactant in the reaction system. In eqn. (2)  $f(c_A)$  represents the hypothetical model of the reaction mechanism [14]. It is generally assumed that chemical processes are the activated-type processes [14]. For such processes the  $k(T)$  function is most frequently expressed in the form of the Arrhenius equation,

$$k(T) = Z \exp(-E/RT) \quad (3)$$

although the modern theories predict more complex relationship [8,15],

$$k(T) = ZT^b \exp(-E/RT) \quad (4)$$

where  $E$  is the apparent activation energy,  $Z$  is the pre-exponential factor, and  $b$  denotes a constant. It is worthwhile to mention that  $k(T)$  simply represents the isothermal rate constant.

To describe the kinetics in homogeneous systems some intensive quantities, being directly proportional to the reaction progress, can be used in eqn. (2) instead of concentrations. For the description of the extent of reaction in heterogeneous systems involving solids (for example if  $A$  and  $B$  are solids and  $C$  is a gaseous product) the most convenient method is to use the degree of conversion ( $\alpha$ ) [14]. In the case of a simple irreversible process, e.g., given by eqn. (1),  $\alpha$  is equal to  $(c_{0A} - c_A)/c_{0A}$ ,  $c_B/c_{0A}$ , or  $c_C/c_{0A}$ , since  $c_{\infty A}$  can be assumed to be equal to 0. From the foregoing considerations we get

$$-\frac{dc_A}{dt} = \frac{dc_B}{dt} = \frac{dc_C}{dt} = c_{0A} \frac{d\alpha}{dt} \quad (5)$$

and

$$c_A = c_{0A}(1 - \alpha) \quad (6)$$

Substitution of eqns. (5) and (6) into eqn. (2) leads to the expression

$$\frac{d\alpha}{dt} = \frac{1}{c_{0A}} f[c_{0A}(1 - \alpha)] k(T) \quad (7)$$

The phenomenological description of kinetics of reactions proceeding in gaseous and homogeneous liquid phases assumes that  $f(c_A)$  is some power function of  $c_A$  and that the magnitude of the power represents the reaction order. Hence,  $f[c_{0A}(1 - \alpha)]$  can be expressed as a product,  $f(c_{0A}) f(1 - \alpha)$ , and eqn. (7) gives

$$\frac{d\alpha}{dt} = \frac{f(c_{0A})}{c_{0A}} f(1 - \alpha) k(T) \quad (8)$$

The integration of the above equation by the elementary methods [8] leads to the expression

$$g(1 - \alpha) = t \frac{f(c_{0A})}{c_{0A}} k(T) \quad (9)$$

Neither eqn. (8) nor (9) is suitable for use in the description of reaction kinetics in gaseous and homogeneous liquid solutions. As the ratio  $f(c_{0A})/c_{0A}$  is generally not equal to 1, the specific rate constants derived by any of these equations would depend on the initial concentration of substrates. For reactions involving solids the concentration of chemical species can be expressed in mole fraction units since other concentration units, applied in homogeneous kinetics, have no physical meaning [14]. Therefore,  $c_0$  is always equal to 1. In other words, there is a great number of initial states in solutions of various initial concentration but there is only one initial state for solids in which  $c_0$  is constant.

Taking into account the above facts the appropriate equations describing isothermal kinetics of reactions involving solid substrates are, respectively

$$\frac{d\alpha}{dt} = f(1 - \alpha) k(T) \quad (10)$$

and

$$g(1 - \alpha) = t k(T) \quad (11)$$

It may be noted that the dimension of the rate constant in eqns. (8)–(11) is always 1/time.

In the description of the solid-state reaction kinetics not only power functions of  $(1 - \alpha)$  are considered. It has been assumed that eqns. (10) and (11) are formally valid for more complex  $f(1 - \alpha)$  or  $g(1 - \alpha)$  functions, whose forms and physical meaning have been discussed by many authors (e.g., refs. 2, 14, 16, 17). It may be shown that any of these functions satisfy

the expression  $f[c_{0A}(1 - \alpha)] = f(1 - \alpha)$  and, thus, eqns. (10) and (11) remain valid. It is also worthwhile noting that some authors use less complicated symbols, namely  $f(\alpha)$  and  $g(\alpha)$ , instead of  $f(1 - \alpha)$  and  $g(1 - \alpha)$ .

In view of above considerations we cannot agree with the final conclusions of Fatu and Segal [18]. Only intensive quantities should be used in rate equations. Thus, the mass of the sample, being an extensive quantity, is not suitable for this purpose, unless it is used for the evaluation of  $\alpha$ . Therefore, the questions of Criado [19] regarding the accuracy of Chatterjee's method [20] seem to be fully understandable. Starting from eqn. (10) and assuming  $w = w_0(1 - \alpha)$  a relationship can be derived for evaluating the reaction order [19]

$$n = \frac{\ln\left(-\frac{dw}{dt}\right)_1 - \ln\left(-\frac{dw}{dt}\right)_2 - \ln\frac{w_{01}}{w_{02}}}{\ln\frac{w_1}{w_2} - \ln\frac{w_{01}}{w_{02}}} \quad (12)$$

Thus, only when  $w_{01} = w_{02}$  we obtain the expression proposed by Chatterjee [20]. Therefore, eqn. (12) may be used by simply taking two points from the same thermogram. This approach appears to be very similar to that proposed by Freeman and Carroll [21] for the examination of the kinetics of non-isothermal processes.

#### *Fundamental relationships describing non-isothermal reaction kinetics*

Acceptable expressions for the description of reaction kinetics under non-isothermal conditions have been derived from eqn. (10). Namely, in non-isothermal experiments time can be expressed as some function of temperature

$$t = h(T) \quad (13)$$

hence

$$dt = h'(T) dT \quad (14)$$

Substitution of relationship (14) into eqn. (10) gives

$$\frac{d\alpha}{dT} = h'(T)f(1 - \alpha)k(T) \quad (15)$$

this is the basic equation used in further considerations.

Under linear temperature increase conditions  $h'(T) = 1/\Phi$  ( $\Phi$  = heating rate) and assuming for  $k(T)$  relationship (4) eqn. (15) can be rearranged to the form

$$\frac{d\alpha}{dT} = \frac{Z}{\Phi} f(1 - \alpha) T^b \exp(-E/RT) \quad (16)$$

The integral expression corresponding to the above differential form is given below

$$g(1 - \alpha) = \frac{Z}{\Phi} \int_{T_0}^T T^b \exp(-E/RT) dT \quad (17)$$

The integral on the right-hand side of eqn. (17) can be solved assuming the concept of Doyle [22]. He stated that since  $T_0$  represents the initial temperature, at which the rate of reaction is equal to 0, it is easiest to assume  $T_0$  to be equal to 0 K. Then eqn. (17) can be rearranged to the form

$$g(1 - \alpha) = \frac{Z}{\Phi} \left( \frac{E}{R} \right)^{b+1} \int_x^\infty x^{-(b+2)} \exp(-x) dx \quad (18)$$

where  $x = E/RT$ .

Unfortunately, the integral appearing on the right-hand side of eqn. (18) has no exact solution and this is the most inconvenient part of this approach. Some approximate methods for evaluating this integral have been reviewed elsewhere [23].

Another possible approach, previously described [8], is to consider eqn. (11) as a primary kinetic relationship. Then, substitution of eqn. (13) into eqn. (11) gives

$$g(1 - \alpha) = h(T)k(T) \quad (19)$$

Resulting from the above equation, the differential form is

$$\frac{d\alpha}{dT} = Zf(1 - \alpha)T^b \exp(-E/RT) [h'(T) + 1/T h(T)(b + E/RT)] \quad (20)$$

where expression (4) is taken for the  $k(T)$  function.

Under linear temperature increase conditions  $h'(T) = 1/\Phi$ . For the function  $h(T)$  one may substitute the expression  $T/\Phi$  resulting from the integral  $1/\Phi \int_{T_0}^T dT$  [8], if, according to Doyle's assumption [22], the value of 0 K is taken for the lower integration limit. Then, eqns. (19) and (20) become, respectively

$$g(1 - \alpha) = \frac{T}{\Phi} ZT^b \exp(-E/RT) \quad (21)$$

$$\frac{d\alpha}{dT} = \frac{Z}{\Phi} f(1 - \alpha)(1 + b + E/RT)T^b \exp(-E/RT) \quad (22)$$

It is worthwhile noting that relationships analogous to eqns. (21) and (22) have been derived earlier with  $\alpha$  considered as a function of both  $t$  and  $T$  [8].

*Does the total differential of  $\alpha = f(t, T)$  exist?*

As mentioned earlier eqns. (21) and (22) state that the degree of conversion is a function of both temperature and time. Of course,  $\alpha$  cannot be

considered as a state function. The term state function has been introduced in thermodynamics. It represents several physical quantities such as total energy of the system, its enthalpy, entropy, etc., which are functionally dependent on certain variables determining the state of the system. If any process proceeds in the system the changes in value of the state function depend only on the initial and final values of the state variables, and not on the pathway of the process. It is well-known that a state function can be expressed as a total differential of the appropriate state variables. From this viewpoint any kinetic variables or constants cannot be considered as state functions.

Let us examine, however, whether the total differential of  $\alpha = f(t, T)$ , given by eqn. (23), exists

$$d\alpha = \left( \frac{\partial \alpha}{\partial t} \right)_T dt + \left( \frac{\partial \alpha}{\partial T} \right)_t dT \quad (23)$$

For this purpose we assume that eqn. (11) expresses the fundamental kinetic relationship, whose soundness has never been questioned. The mathematical rules concerning the existence of a total differential of a given function are described in ref. 24. The application of these rules with regard to the  $\alpha = f(t, T)$  function confirms that eqn. (23) is absolutely valid. This arises from the following facts.

(1) Continuous partial derivatives of the first order exist, namely

$$\left( \frac{\partial \alpha}{\partial t} \right)_T = f(1 - \alpha) Z T^b \exp(-E/RT) \quad (24)$$

$$\left( \frac{\partial \alpha}{\partial T} \right)_t = f(1 - \alpha) t Z (b + E/RT) T^{b-1} \exp(-E/RT) \quad (25)$$

(2) The cross differentiation gives the same result

$$\frac{\partial^2 \alpha}{\partial t \partial T} = f(1 - \alpha) Z (b + E/RT) T^{b-1} \exp(-E/RT) \quad (26)$$

$$\frac{\partial^2 \alpha}{\partial T \partial t} = f(1 - \alpha) Z (b + E/RT) T^{b-1} \exp(-E/RT) \quad (27)$$

Equations (24)–(27) were derived assuming the  $k(T)$  relationship resulting from eqn. (4).

Since it was established that relationship (23) is true, therefore, eqns. (19)–(22) also have to be valid. There is no doubt that eqns. (10) and (11) are oversimplified. Nevertheless, if these expressions are assumed to be valid for isothermal conditions then eqns. (19) and (20) are adequate forms for treating non-isothermal kinetic data.

It must be pointed out that the variation in the aforementioned variables, i.e.,  $\alpha$ ,  $t$  and  $T$ , is not completely free. The values of these parameters, having a physical meaning, are subject to the following restrictions:  $1 \geq \alpha \geq 0$ ,  $t \geq 0$  and  $T \geq 0$ .

The dependence of  $\alpha$  on  $t$  and  $T$  has been clearly shown by Holba and Sestak [25] (see fig. 6 of ref. 25), although the authors maintained in their conclusions that eqn. (23) is false. The same opinion has been expressed by Tang and Chaudhri [4,9] who emphasized that  $\alpha$  cannot be considered as a state function with  $t$  and  $T$ . The main argument of the latter authors against eqn. (23) is that  $\alpha$  cannot decrease even for negative  $dT$ . These statements require discussion. All kinetic equations hold terms described as  $f(1 - \alpha)$  or  $g(1 - \alpha)$ . These functions express the hypothetical model of the reaction mechanism or, in other words, the reaction pathway. For a chosen direction of temperature changes, e.g., for rising temperature, the forward reaction will appear. However, when the temperature decreases the reverse reaction is observed. Both these processes may proceed through different pathways. The evaluated kinetic constants  $E$  and  $Z$  are characteristic to a given reaction pathway only. The direction of temperature change may lead to different values of  $\alpha$ , hence, in this sense the degree of conversion cannot be considered as a state function. However, if the well-known reaction pathway is kept constant the same values of  $\alpha$  should be observed at a given temperature and/or at a given time of reaction. If the above statement is false it would be no sense to collect any kinetic information.

Furthermore, for some physical processes, for example, phase transitions, an increase in  $\alpha$  may be observed for positive  $dT$  and a decrease in  $\alpha$  for negative  $dT$ . For most chemical processes, however, the reverse reaction is not predictable, since some products leave the reaction zone. Moreover, very often the reverse reaction is not the subject of interest.

We also would like to comment on the recent communication of MacCallum [10]. The derivation he presented of the rate equation for non-isothermal reactions involved the basic premise of the transition state theory, namely that the population of the activated complex molecules ( $N_{A^*}$ ) is governed by the population of substrate molecules ( $N_A$ ) and the temperature ( $T$ ). Thus, the total differential of  $N_{A^*}$  would be

$$dN_{A^*} = \left( \frac{\partial N_{A^*}}{\partial N_A} \right)_T dN_A + \left( \frac{\partial N_{A^*}}{\partial T} \right)_{N_A} dT \quad (28)$$

Dividing both sides of eqn. (28) by  $dt$  and rearranging gives

$$\frac{dN_A}{dt} = \frac{dN_{A^*}/dt}{(\partial N_{A^*}/\partial N_A)_T} - \Phi \frac{(\partial N_{A^*}/\partial T)_{N_A}}{(\partial N_{A^*}/\partial N_A)_T} \quad (29)$$

where  $\Phi = dT/dt$ .

It may be noted that  $N_A/N_{0A} = 1 - \alpha$ , ( $N_{0A}$  is the initial number of substrate molecules) and  $N_{A^*}/N_{0A} = 1 - \alpha^*$ . Therefore, eqn. (29) may describe the rate of non-isothermal processes involving solids. The partial derivatives can be evaluated based on the relationship resulting from the equilibrium conditions, namely  $N_{A^*} = \text{const.} \exp(-E/RT)f(N_A)$ , where  $f(N_A)$  is some func-

tion of substrate population dependent on the activation pathway. It may be noted that both terms of the right-hand side of eqn. (29) are dependent on the temperature. Hence, the substitution of the first term of the right-hand side of this equation by the isothermal rate expression does not seem to be justifiable. Therefore, the final equation derived by the author probably does not describe adequately the rate of non-isothermal reactions. In view of the conclusions resulting from this work it seems rather that eqn. (23), primarily proposed by MacCallum and Tanner [26], is suitable for this purpose.

#### *The physical meaning of Doyle's assumption*

As mentioned earlier, the growing interest with integral methods in non-isothermal kinetics has been observed since the early 1960s, when Doyle [22] stated that  $T_0 = 0$  K may be substituted for the lower integration limit of integral holding temperature (eqn. 17). To our knowledge this approximation has never been questioned, although its physical meaning has not been analysed either.

All modern theories of reaction kinetics assume that a given process may occur if some molecules in the system (activated molecules) attain a certain amount of energy exceeding an activation barrier for the process. The probability for a reaction to occur is directly proportional to the number of activated molecules present. This probability may be evaluated based on energy distribution functions. All of these have an exponential term of the type  $\exp(-E/RT)$ . As the latter expression gives a 0 value at  $T = 0$  K, the probability for reaction to occur is equal to 0 only at this temperature. For any values of  $T > 0$  K this probability gives a certain value greater than 0. Thus, the rate of reaction, being directly proportional to this probability, is equal to 0 only at  $T = 0$  K, and differs from 0 for any values of  $T > 0$  K. In view of the above considerations, the soundness of Doyle's assumption appears to be fully justifiable since the lower integration limit of integral appearing in eqn. (17) should represent the situation when the rate of reaction is equal to 0.

#### *The possibility of the application of non-isothermal techniques on various temperature programs to the investigation of reaction kinetics*

So far, the examination of kinetics of non-isothermal reactions is limited mainly to the experiments carried out under linear temperature increase conditions. This technique requires that the temperature of the system investigated changes linearly with time, i.e.,  $dT/dt = \Phi$ . Then the actual temperature of the sample is given by the equation

$$\int_{T_0}^T dT = \Phi \int_{t_0}^t dt \quad (30)$$



In the above expression the lower integration limits are chosen in accordance with the beginning of the process. Thus,  $T_0$  should correspond to the temperature at which the given process does not occur. From the viewpoint of conclusions drawn in the preceding chapter the initial temperature ( $T_0$ ) should be equal to absolute zero. This is not an arbitrary choice of  $T_0$  [25], rather it results from the fundamental behaviour of the nature of reaction.

Holba and Sestak [25] extending the conception of Bradley [27] proposed the use of the temperature of equilibrium of conversion ( $T_e$ ) instead of  $T_0$  in eqn. (30).  $T_e$  has been introduced based on the relationship derived by Bradley [27]

$$\frac{d\alpha}{dt} = f(1 - \alpha)k(T)[1 - \exp(-\Delta G/RT)] \quad (31)$$

where  $\Delta G = -RT \ln X/K$ ,  $K$  is the equilibrium constant, and  $X$  is the product of the activities of all components. The authors assumed that the change of free energy for the reaction ( $\Delta G$ ) approaches zero at the equilibrium temperature ( $T_e$ ) [14]. In our opinion the temperature of equilibrium does not actually exist. The system under investigation reaches equilibrium when  $\Delta G$  is equal to 0. It may be attained in two ways. Firstly, if at a given temperature  $T > 0$  K,  $X$  becomes equal to  $K$ . Secondly, at a temperature of absolute zero, at this temperature any system investigated remains unchanged for an infinite time. Thus, the system is in the equilibrium state. If  $\Delta G$  approaches 0 the last term of the right-hand side of eqn. (31) is equal to 1 and the rate of reaction becomes equal to 0. This statement is in accord with the conclusions of the previous chapter. For most processes investigated  $\Delta G$  reaches high positive values (the process takes place "very far" from equilibrium) and, hence, the last term in eqn. (31) can be neglected. Such processes are usually the subject of interest.

The above considerations maintain the choice of  $T_0 = 0$  K for the lower integration limit in eqn. (30).

It is worthwhile noting that the choice of  $T_0$  for the lower integration limit in eqn. (30) has been analysed in a previous communication (table 1 of ref. 8). Indeed, the best fit of the integral equation, analogous to eqn. (21) if various  $T_0$  values have been taken for the lower integration limit, to the experimental data is obtained when the initial temperature is assumed to be absolute 0.

Time is the physical quantity for which only intervals are measurable. Since an absolute value of this quantity does not exist, the moment when timing commences for the experiment may be chosen arbitrarily. It is most convenient to assume  $t_0$  to be equal to 0.

The form of eqns. (19) and (20) is adequate for use in the description of kinetics of any non-isothermal process. The application of these expressions is, however, subject to some limitations. First, the mathematical form of expressions describing changes in temperature of the system with time, i.e.,

$h(T)$  and  $h'(T)$  functions, has to be known exactly. Secondly, from the foregoing considerations, these functions should satisfy the equation

$$\int_0^T h'(T) dT = h(T) \quad (32)$$

Finally, expression (32) requires that both  $h(T)$  and  $h'(T)$  functions are determined for  $T \geq 0$ .

In Table 1 some chosen functions of temperature changes in non-isothermal thermoanalytical experiments are listed. For  $h'(T)$  functions of general formulae  $1/(cT^m)$  the appropriate integral forms do not exist. However, any integral given by eqn. (32) may be solved if the temperature of the beginning of heating (e.g., the ambient temperature) is taken for the lower integration limit [28–30].

The approach presented in this work states that a given heating program occurs from  $T = 0$  K. Any linear temperature program meets the above requirements. Thus, the kinetic constants derived based on the latter method may be compared with those evaluated from the isothermal experiments. Instead, if the temperature program occurs from the arbitrarily chosen temperature ( $T_0$ ) then the acquired kinetic information is probably not representative for a given process. Also the question is whether there is any reason to use the more complex, rather than the linear, temperature programs in investigations of reaction kinetics. A detailed review of the literature indicates that unresolved problems regarding the mathematical description of the kinetics of non-isothermal processes, resolved only for the simplest, linear, heating program, still exist. It is, therefore, expected that the use of more complex temperature programs will create additional difficulties.

### Other problems

The very interesting question is how the kinetic constants evaluated from

TABLE 1  
Non-isothermal temperature functions

Type of temperature programming	The form of functions		Constants
	$h(T)$	$h'(T)$	
Linear	$T/\Phi$	$1/\Phi$	$\Phi$
Exponential [28]	does not exist	$1/(aT)$	$a$
Hyperbolic [28,29]	does not exist	$1/(bT^2)$	$b$
General [30]	does not exist	$1/(cT^m)$	$c, m$
Parabolic	$1/2 a'T^2$	$a'T$	$a'$
Parabolic [31]	$b'T + 1/2 c'T^2$	$b' + c'T$	$b', c'$
General	$1/(n+1)k'T^{n+1}$	$k'T^n$	$k', n$
General [32]	$1/T^2 \sum_{i=0}^i b_i T^i$	$1/T^2 \sum_{i=0}^i i b_i T^{i-1} - 2/T^3 \sum_{i=0}^i b_i T^i$	$n$ th $i$

eqns. (16) and (17) compare with those estimated by eqns. (21) and (22). Analyzing the literature data [8,11–13] brings to notice several regularities: (1) values of  $E$  resulting from the application of eqns. (21) or (22) are always higher by about  $5 \times 10^3 \text{ J mol}^{-1}$  than those derived from eqns. (16) or (17). These relatively small differences probably result from the fact that the sensitivity of kinetic expressions to temperature changes is caused mainly by the exponential term. This term, however, remains unchanged in all the kinetic equations examined; (2) values of  $Z$  are constant from eqns. (21) or (22) and are about an order of magnitude lower than those evaluated from eqns. (16) or (17). This dependence results from the fact that  $Z(1 + b + E/RT)$  (in eqn. 22) =  $Z$  (in eqn. 16); (3) generally, eqns. (21) and (22) give a better fit to the experimental data than do eqns. (16) and (17); and (4) it should be noted that differences in the values of kinetic constants resulting from the application of different types of mathematical approaches are usually lower in comparison to those caused by experimental and computational uncertainties. As shown recently by Varhegyi [33,34] only imperfect temperature programming may cause differences in the values of kinetic constants by about 20%. Also other experimental parameters may affect thermoanalytical curves and, thus, derived values of  $E$  and  $Z$  [35–38].

Most chemical reactions can be considered as a sequence of consecutive, or a set of competitive, processes. To each reaction step an adequate pathway may be ascribed and, consequently, appropriate values of kinetic constants  $E$  and  $Z$ . Usually, the rates of individual steps differ one from another. If the rate of one distinct step is much lower in comparison to the rates of other steps then the former controls the kinetics of the overall process and is named the rate determining step. Most kinetic considerations are based on the assumption that one distinct step determines the kinetics of the reaction under investigation. The description of the kinetics of consecutive [39] and competitive [40] processes presents a rather cumbersome problem.

Most considerations regard the search for an adequate reaction pathway describing the kinetics of the process. As mentioned earlier, values of kinetic constants  $E$  and  $Z$  are characteristic of a given reaction model and can be evaluated only when the latter has been established. The investigation of the reaction model however, presents a difficult problem. The currently used procedure is based on the fitting of an appropriate kinetic equation (i.e., rate equations with various  $g(1 - \alpha)$  or  $f(1 - \alpha)$  functions) to the experimental data. To examine the accuracy of the fit various statistical methods have been proposed (see for example, refs. 2, 4, 5, 8, 9, 11, 41–57). None of these methods, however, have been accepted as a standard correct procedure. There are still a lot of doubts regarding the applicability of certain methods.

The derived values of  $E$  (expressing apparent activation energy) [58], should be higher than the values of the enthalpy change corresponding to the rate determining step. If  $\Delta H_r$  for the overall reaction is known one might

expect these functions  $[g(1 - \alpha)$  or  $f(1 - \alpha)]$  to describe adequately the rate of the processes where  $E$  values are higher or, eventually, somewhat lower, than  $\Delta H_r$  values. If  $E \ll \Delta H_r$  the reaction is assumed to have a complex nature, e.g., it may result from a sequence of consecutive processes. This regularity may be helpful in the search for a suitable reaction mechanism.

Unfortunately,  $\Delta H_r$  values are not always available. Stepin et al. [59] proposed an approximate method for the evaluation of  $\Delta H_r$  from thermogravimetric traces. This method is based on the assumption that the process proceeds at equilibrium conditions. This is not always the case, however, if this did occur, then eqn. (31) should be used.

A number of questions remain regarding the real physical meaning of kinetic constants  $E$  and  $Z$  [60,61]. Some authors consider them just as empirical quantities for use in the formal mathematical description of a reaction without much true physicochemical significance [60]. It seems to be generally accepted that  $Z$  cannot be identified as a frequency factor appearing in equations describing kinetics in gases and homogeneous liquid solutions. On the other hand, values of  $E$  may be comprehended as energy barriers to the processes occurring. However, the physical interpretation of  $E$  should be handled extremely carefully.

The last point concerns the applicability of the Arrhenius model in thermal analysis. This model is widely used in the description of the solid-state reaction kinetics, although its validity has been recently questioned by several authors [6,7]. Also, the first signs of new approaches to the problem have appeared in the literature [62–64]. Doubtless, the present approach to the description of the solid-state reaction kinetics is far from perfect. Nevertheless, with the lack of a better, equally simple, general model, it will probably exist for a long time yet.

## CONCLUSIONS

In this article some problems regarding the description of non-isothermal reaction kinetics of solids were analyzed. The considerations were concerned with the form of the  $k(T)$  function in non-isothermal kinetics. It was shown that previously proposed forms of basic kinetic relationships [8] are correct from the mathematical and physical viewpoint. Both differential and integral equations are also accurate from a mathematical viewpoint. Furthermore, the proposed approach may be applied to the description of any non-isothermal data resulting from the application of various heating programs. Finally, these equations have very simple mathematical forms and are easy to work with.

The intention of this work was not to criticize the accepted solid-state reaction kinetics equations, rather to show the accuracy and advantages of the method proposed by the author.

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