Special Review

PHILOSOPHY OF NON-ISOTHERMAL KINETICS

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The most debatable and discrepant viewpoints of non-isothermal kinetics are discussed in the form of twelve questions and answers. The reputation of non-isothermal kinetics when carried out by thermoanalysts; the consequences of simplified concepts transferred from the kinetics of homogeneous reactions; the physical meaning of basic kinetic parameters in solid-state processes; the kinetic compensative effect and interdependence of kinetic parameters using the Arrhenius rate constant; the mutual usefulness of differential and integral methods of kinetic data evaluation; their accuracy and correctness; the reliability of DTA measurements; non-isothermal versus isothermal investigations; equilibrium and kinetic data and their mutual effect; the extended discussion initiated by MacCallum and Tanner; non-isothermal data publication policy; and finally the use of computers.

Instead of an introduction

An article which would contain merely questions with their answers on some notoriously discussed but not yet clear topics of the fashionable kinetics of non-isothermal processes first came into my thoughts on the basis of the remarks presented at the panel discussion at the TA seminar on kinetics held in Budapest, in July 1972 (Berggren, Jesenak, Pungor, Zsakó). This idea, however, survived untouched until the meeting of Hungarian thermoanalysts in Balatonfüred in October 1976, where it matured during the round-table discussion (Dollimore, Meisel, Oswald, Rouquerol). The written form was finally encouraged by J. Simon, editor of JTA.

The problematics of description of non-isothermal processes fall into two categories. The part dealing with the more rigorous thermodynamic aspects and definitions of experimental conditions and thermophysical experiments in general was published in TCA 28/2 in 1978 in the form of a classical type of review. The present part intends to pay attention to some controversial viewpoints regarding non-isothermal kinetics, which sometimes intentionally and sometimes by mistake veil the consequences of dynamic experiments. This untraditional form for a review seeks, last but not least, for possibly better answers to those questions which are felt not to have been explained in a satisfactory manner, or which have not been taken into account as yet. This also remains a task for the reader's own consideration when studying the article.

It should further be mentioned that this approach was affected by the discussions held during the German autumn school on kinetics, in Eisenach in 1977 (Anderson, Heide, Ludwig, Schultze). My thanks are also due to my friends and co-workers, particularly V. Satava and P. Holba, for a long, cheerful, as well as most creative cooperation, and for their frank discussions on all aspects (reasonable and even crazy) of philosophy and science.

Questions and answers

(1) *Q*: *Why has non-isothermal kinetics gained so bad a reputation? Is it due to experiments carried out mainly by thermoanalysts?*

A: Any advent of commercial apparatus production sophisticated stage of automatization and even pressing development of evaluating techniques makes it easier to produce nice curves and other digital or punched output ready for further mathematical treatment. As already long ago, this has tempted many investigators to determine easily attainable parameters of processes called kinetic data [1]. The result is well known: a number of scientific reports containing information with varying degrees of reliability. It is evident that those making classical investigations of kinetics have attacked non-isothermal studies. This has consequently resulted in a rather great disrespect for non-isothermal studies, and in some restrictions with respect to the publicability of such data in some of the more recognized journals.

Let us take an example. In the literature we can find recipes on how calculate basic kinetic parameters, regardless of their true physical meaning. What is more, this is often applied to a most complicated case, i.e. DTA measurements of solid-state processes. For instance we can draw by hand a curve in the form of a DTA peak and then calculate certain numerical data: the activation energy by Piloyan's method [2] and the reaction order by Kissinger's method [3]. There is certainly something out of order, as nobody can extract the similarly important thermodynamic data so easily without some additional specifications as to the curve origin (material and experiment). The puzzle of such a non-isothermal kinetic treatment is a fairly good coincidence with the analogous data established with complementary measurements. In spite of this we can easily see some lack of logistics or, at least, the insufficiency of the physico-chemical grothwork in some branches of non-isothermal kinetics. However, I by no means want to increase any consciousness of thermoanalytical society that all non-isothermal data ought to be treated with great caution, as was felt during the 5th ICTA in Kyoto. I am aware that any critique of the present kinetic procedures because of they unsatisfactory description of the reality of e.g. heterogeneous reactions is much easier than making a new proposal how to substitute it by more suitable theory. Therefore the rejection of the present mode of the calculation of certain parameters which we want (although not always may) compare is not a solution at all.

(2) *Q: Non-isothermal kinetics, in fact, is liable to pay for the mode of its historical introductions. Where are the roots of possible misfits and where can we best learn the basis of non-isothermal treatments?*

A: Probably the first description of a non-isothermal treatment of TG data was reported by Van Krevelen, Van Heerden and Hutjens in 1951 [4]. The real progress was started by the work of Murray and White, Tsuzuki and Nagasava (for detail see [1]) Kissinger [3] and Freeman and Carroll [5] in the late fifties. The first concise reviews came in the middle sixties [6–8]. However, we should not forget the pioneering work of Akahira [9] who introduced the integration of the temperature-dependent exponential in the late twenties.

Unfortunately, all the above articles carried along the basic terminology by analogy with the adopted kinetics appropriate for the description of homogeneous reactions in gases and/or liquids. However, this was an understandable result of an easy treatment of the concept of reaction-order to surmount the initial mathematical difficulties. Later on, the continuous schematic and sometimes blind transmission of such premises led to problems in the application of the non-isothermal treatments to heterogeneous processes. This has been the subject of severe criticism [1, 10], but many of these notorious oversimplifications survive. Nevertheless, I do hope never to read again introductory sentences such as "solid-state process may be represented by a simplified kinetic relation defined by reaction order . . ."

The present state still needs a monograph truly devoted to non-isothermal kinetics. The existing literature deals either with homogeneous reactions or with a formal description of heterogeneous processes* [1, 11]. Some reviews have been published in JTA [12, 13] as well as in the Proceedings of ICTA conferences [14].

Otherwise, much useful information is scattered throughout all these scientific journals which still dare to print articles on non-isothermal kinetics. The ratio of the contributions on the different kinds of kinetic analysis was searched for in two most representative TA journals (see Table 1). Although no steady trend towards a definite sort of kinetics has developed as yet, it is worth noting that the first signs of a new, actually non-isothermal approach are to be seen [15, 16].

(3) *Q: What do kinetic parameters such as activation energy and reaction-order really mean? Are these terms generally applicable, particularly assuming solid-state processes?*

A: From the textbooks we know well what these terms express, i.e. we can ascribe a definite meaning to the activation energy E, e.g. for the reaction of

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* There also was published a book by E. Koch: "Non-isothermal Reaction analysis" which unfortunately I have not seen as Plenum Press refused to provide it for reviewing. A book by K. Heide about non-isothermal kinetics of heterogeneous processes is announced to be published in Berlin. Another book including kinetics of solid state reactions is in the course of preparation by author to be published jointly by Academia and Elsevier.

gaseous iodine with hydrogen either by coordinate energy calculation or by the scholastic approach. It is, in fact, a potential barrier separating the initial and final states. At the moment when we admit one reactant to be a solid phase, the above reaction scheme presumably loses its validity; nevertheless it can still yield certain numerical values. Consequently the rate constant is affected by the choice of a kinetic model and may be found in the form of a power. Such an exponent is a function of nuclei formation, interface and mass transport, and thus the analytical formulation of the kinetic equation becomes a decisive step. The parameter E fitted to the given kinetic equation is understood as a derived constant and is of limited validity. The obligatory expressing of E in the dimension of energy per mole is retained as a practical result of multiplication by the gas constant (compare for example, phase-boundary processes). The overall (apparent) value of E is not always a primitive value for nucleation-controlled processes [17]. It is composed of partial energies associated with nuclei formation, crystal growth and diffusion, and altogether may reach a rather large value. Experimentally, such a process exhibits a very sharp, explosive-like course; its surprisingly high barrier thus does not permit the process to occur thermally until the barrier is finally surmounted the reaction then rocketing at full speed. On the other hand, the reactions which are limited by mass transport show a rather low value of E, although the diffusion seems to be a smooth process taking place within a comparatively large time-temperature interval. For metals it may be well interpreted by a defect-walk mechanism [1, etc].

In contrast to the physico-chemical approach, we must admit that the reaction-order concept may be an adequate tool for finding the most favourable conditions to control and carry out an engineering process satisfactorily. It may be assumed that not much care is directed to the reliability of the mathematical description nor to the correctness of the kinetic parameters. The aim is merely a formal fit of the experimental data using the simplest form of polynomials, to be able to compare reaction rates or energy barriers for various experimental conditions in a sensitive enough manner.

No less important is an appropriate choice of the experimental set-up and measuring conditions to match the conditions of the process in question. It is evident that the thermogravimetric investigation of micro-samples in vacuum is of little applicability to the industrial process of the burning of limestone, while the study of the decomposition of a ball-like sample at least 10 mm in diameter may provide useful data as regards not only the chemical character of the process, but more likely to its geometric aspects, mass and heat transfers, etc.

In addition one must keep in mind that a bad kinetic result either due to pure and undefined sample and/or vague experimental conditions cannot be veiled by any resonant nor ingenious mathematics. That is, "experiment does not have to agree with our theory and process never obeys our equations" [10, 14b].

(4) *Q*: *Some authors advocate either the separability or non-constancy of kinetic data. Is this true, and how is it related to the so-called kinetic compensation effect?*

A: Although this is connected with the preceding question, it is worth discussing separately. Let us first talk about the "Arrhenius" rate constant, $k_{(T)}$, itself, which has a general validity for thermally-activated processes, where either diffusion and/or phase-boundary chemical reaction are effective as basic rate-controlling processes. $k_{(T)}$ is then composed of the pre-exponential factor, A, describing the frequency of attempts to surpass an energy barrier E of the process, and the exponential, $\exp(-E/RT)$, expressing the probability of successful attempts. It was argued that the lack of an energy statistical distribution in real solids rules out the use of this concept [14b]. This certainly would deny the fifty years' work of famous scientists in the field of heterogeneous kinetics although a certain criticism of mechanically derived models upon oversimplified geometric systems is in its place. At least from a viewpoint of general relaxation processes we ought to admit that there always exist an (energetic) hinderance separating initial and final states which must be surmount if the process is to advance even it is located to certain sites.

For a fixed value of the exponential, the constant ratio (E/T) must be maintained by the equal compensation of changes in both the numerator $(E + \Delta E)$ and denominator $(T + \Delta T)$. Similarly, for a fixed value of the reaction rate, the change of the whole exponential must be compensated by the change of the pre-exponential factor. For reasonable values of reaction rates, we thus cannot obtain the mutually independent values of the kinetic parameters (E and A). As consequence for high-temperature processes ($T > 1500$ K) we find greater values of E ($E > 100$ kcal) and A ($A > 10^{16}$ s^{-1}), which certainly lend to difficulties in their theoretical interpretation [18]. The interdependence of kinetic parameters can be best demonstrated through the theoretical construction of artificial TA curves with respect to their position within the T-coordinates and the magnitude of the kinetic parameters [19], which is a frequent and often recurring subject of kinetic reports of (cf. [1]). Nevertheless, it reflects sensitively any case where the rules of our kinetic game are not fulfilled. It may happen when the temperature-dependence of $A\ (=\bar{A}T^{b})$ is not accounted for and/or the inappropriate model relation $F(\alpha)$ (instead of $f(\alpha)$) is employed. In such a case the kinetic compensation effect can be understood as a misfit to be described analytically by equations: $\bar{E} = E - b\,RT \ln T$ or $\bar{E} = E - RT[\ln F(\alpha)/f(\alpha)]$. So far, it is still an open question how much the experimentally-found thermal dependence of E is an entirely physical property of it or merely a result of non-uniform experimental conditions and homogeneity of material or inadequate mathematical treatment. Adonyi [20], for example, emphasizes that the examination of the function: $\log A$ versus E, together with the motion of coordinate axes, when taking into account the measuring conditions, can only give deeper information about the kinetics.

(5) *Q*: *Which method of kinetic data evaluation is better, differential or integral?* (quite a common question!).

A: Every method has its positive merits, as well as disadvantages, associated with the mathematical treatment itself and further affected by the demand for experimental data of a certain quality and extent. The principal classification can be seen from the following scheme:

variable	model relation	rate constant	name
$\alpha, \dot{\alpha}, \ddot{\alpha}, T, \dot{T}$	$\mathrm{d}[f(\alpha)]/[\mathrm{d}\alpha f(\alpha)]$	k_T, $\mathrm{d}k_T/\mathrm{d}T$	double-differential
$\alpha, \dot{\alpha}, T$	$\Delta f(\alpha)$	$k_{\bar{T}}$	differential
$\Delta\alpha, \Delta\dot{\alpha}, \Delta T$	$\Delta f(\alpha) \Rightarrow n, m$	$\Rightarrow E$	difference-differential
α, T	$g(\alpha) = \int \mathrm{d}\alpha f(\alpha)$	$p(x) \approx \int k_{(T)}$	integral

The differential method of kinetic data evaluation can be understood as the basic method, as it utilizes the primitive form of kinetic equation, i.e., $\dot{\alpha} = k_T f(\alpha)$. It requires threefold input data sets, the reaction rate usually being the derived one. Generally, any derivation or differentiation exposes the resulting equation to its becoming more distinguishable with respect to the experimental input data, but also more time-consuming and sensitive as regards their fineness (namely $\dot{\alpha}$). A simple comparison of the results obtained by various formal forms of $f(\alpha)$ function based on an increasing number of reaction-order-like exponents may not provide any deeper information about the mechanisms involved, because the closeness of the relation between the calculated and measured data is increased to a limited extent [20].

By integrating this primitive kinetic equation, one obtains such a form of kinetic treatment where only twofold experimental data sets are needed. Such a method is then presumably less laborious as well as less sensitive to experimental errors (scatter in $\dot{\alpha}$ is avoided). This, of course, is on account of the model relation distinguishability, i.e. the analytical forms of model relations $g(\alpha)$ overlap each other for the different cases of rate-controlling processes, $f(\alpha)$ [21]. The foundation of these methods is complicated by establishing the so-called exponential-integral function $p(x)$ [9], which is obtained through the integration of the rate constant k_T within the temperature limits.* The practical evaluation by integral methods is comparatively easy, but requires certain assumptions about the behaviour of the $p(x)$ function [1]. It often results in the double-logarithm plot, because the $g(\alpha)$ function usually exhibits the logarithmic form itself, particularly for nucleation-growth processes. It is worth quoting an article in the Journal of Irreproducible Results saying that multilogarithmization is the most recommended way of all to diminish sensitivity. Certainly, this is not directed at the condemnation of the utilization of integral methods, but should rather be understood as suggesting caution in searching for the true limits of the applicability of integral methods.

In this place the uncorrect treatment based upon the derivation of Johnson–Mehl–Avrami–Kolgomorov–Yerofeev (nucleation-growth) equation is worth noting. It results from the origin of this equation as derived already by the integration at constant temperature. Introducing $p(x)$-function to this primary

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* It is worth noting that Reich [22] once accomplished such an integration by simply separating the exponential in front of the integral ($\approx \int \mathrm{d}T = \Delta T$), which was evidently subjected to severe criticism [6]. Nevertheless, recent articles showed that after long and complicated mathematical manipulations one reaches a similar result [1, 4, 6] indicating that nature always tends to simple solutions.

integration makes it correct and leads, fortunately, to the same result differing only by a constant [29].

In contradiction with the preceding methods, where a linear temperature increase is assumed, a priori, the double-derivative method (which has not been officially named as yet) permits introduction of the actual temperature increase, through T and truly instantaneous values of T. This, of course, is manually too difficult and experimentally too sensitive for elaboration, and hence is not yet popular.

For successful kinetic evaluation we should always bear in mind the purpose of our kinetic analysis and the means we have at our disposal for its realization. Methods of kinetic data calculation should not be self-satisfying and nor should we be blind to their possible shortcomings.

(6) *Q*: *What about the accuracy of kinetic data calculation? Is this only a consequence of the accuracy of the experimental input data, or can it be further affected by its mathematical treatment?*

A: First of all we must distinguish not only the accuracy of the numerical values calculated, but also their correctness, i.e. the coincidence between our mathematical model (namely the $f(\alpha)$ function) and the actual process under investigation (only the data fulfilling both conditions are reliable). The diligent improving of numerical accuracy is typical evidence of how much importance is laid on mathematics and how little on logistics, as can be found in numerous articles trying to settle the accuracy after the decimal point [1]. In the light of some poorly-defined experiments such refinements are ludicrous if one imagines the possible misfit introduced by a false application of unreliable kinetic models. On the other hand, we cannot deny the definite mathematical skill and wittiness of the theoretically-oriented articles, which, however, sometimes falls beyond the range of normal kinetics, e.g. the reports refining the calculation of the $p(x)$ function. Everyone can remember that once it was fashion to search for a new rearrangement in mathematical analysis and to be frank, many of us non-isothermal kineticists must admit to the dream of discovering a new method of kinetic treatment to be named after the author. However, in most cases this ended in the knowledge that the arithmetics did not leave much space for success. As side-effect, the accuracy of different kinetic evaluations was listed mainly for different kinds of integral methods established through different ways of exponent-integral expansion. Finally there appeared the still underestimated article by Broido and Williamson [21], who diagnosed exactly what integral method yields the most accurate result by distinguishing the accuracy of individual polynomials hidden in individual kinetic treatments. For instance there are the common plots of $\log g(\alpha)$ *vs.* $\log T$, ΔT *vs.* $1/T$, the last more accurate than the first one. Nevertheless, further new such reports have very recently been published showing the notorious desire to increase the ways of deriving methods of kinetic data evaluation and to improve the numbers of resulting kinetic constants, not considering that any deviation in E under comparable conditions of the same $g(\alpha)$ always gets within the limit of ± 10 rel% of E, well accepted in all kinetic studies. This is less important than the reliability of the $g(\alpha)$ function, the correct establishment of which should be the real goal of chemical kinetics.

(7) *Q*: *There are controversial view regarding the reliability of the most popular TA method: DTA. Is it useful for kinetic studies or is it too dependent on its experimental set-up and thus more suitable for analytical applications only?*

A: As already noted in the first question, the oversimplifications of kinetic analysis of DTA data led in many reports to the popular plot of log ΔT *vs.* $1/T$ [2] to extract E from the slope. It certainly provoked much criticism [10, 24, 25] directed to all unclear and questionable aspects of DTA, going sometimes so far as to condemn completely the use of DTA in kinetic studies. This is quite understandable if we imagine the complicated relation between the measured (ΔT) and searched ($\dot{\alpha}$) properties. In this DTA equation [26] particularly the term containing $\Delta\dot{T}$ is often neglected, although it expresses the important fact that the heat cannot be delivered to the sample infinitely quickly. When searching in the classical articles about DTA (Borchard and Daniels [27], we can already observe that the Piloyan plot [2] ought to be written as log ($Cp\,\Delta T + k_{\mathrm{DTA}}\,\Delta\dot{T}$) *vs.* $1/T$, where C_p and k_{DTA} are heat capacity and DTA apparatus constant, respectively; this has been employed so far only twice [28, 29]. What is worth noting again, is the embarrassing coincidence between DTA kinetic data and those obtained under comparable conditions. Is there a real picture of a chemical process in the study, or does it report the constants of mass and/or heat transfer. All the same time, however, we must emphasize that such experimental data as those of DTA contain actual information about the non-stationarity of the system, and it is only up to the interpreter how to decipher the curves. This is not easy, as has been demonstrated in numerous articles utilizing gradient theory (Eriksson [30]), Laplace transforms (Takeo [31]), Green's functions (Akita [32]) and other high mathematics, that have not received the deserved attention. This is probably because the TA experimenter has not much time to get through high theory, and even with the aid of computers he tends to deal with easily understandable approaches like the model based on the phenomenological description of heat-exchange between two bodies of uniform temperatures [26].

DTA measurements are, in fact closely dependent on our experimental inability to maintain a strictly linear temperature increase. If we diminish the temperature deviation, the DTA peak also disappears. An increasing amount of generated heat yields a relatively higher temperature gradient and heat-exchange which may contribute to the DTA peak formation. In the first approach this may be neglected when the different heating rates affect the value of E by less than $\pm 15\%$. The different sizes of DTA peaks also have no effect in the logarithmic representation if the peaks are geometrically similar. A small deviation of the true sample temperature ($\dot{T}$) from the programmed linear increase ($\dot{T} = \emptyset$ = const) may be negligible if the temperature interval of the peak is comperatively large. A good coincidence between DTA and optical microscopy data is shown in [29] on crystallization of glass.

(8) *Q*: *If there are so many troubles with the gradients, would it be better to*

employ only isothermal methods? What, in fact, is the difference between iso- and non-iso-data?

A: One of the most important problems is the extraction of appropriate information from a given set of experimental data. Let us define an isothermal process as a progress of the state of the system at constant temperature as a function of time, where the measured property Z is defined by the equations: $Z = Z(t)$, $T = \text{const}$. For the system exposed to externally-applied constant heating, the non-isothermal process is defined by time-temperature sequences of its state, i.e., $Z = Z(t)$, $\dot{T} = \text{constant} = 0$. Such resulting data are, of course, more compact and may provide a wider but also a more complicated basis for their analysis.

Numerous authors argue that the system being heated is distorted by the creation of temperature gradients, i.e. $\dot{T} \neq \text{const}$. Fortunately, such a system reaches a quasi-stationary state ($\dot{T} + \Delta = \text{const}$) under steady conditions of heating. The constant distribution of gradients makes it possible to define the state of the system by an average value of the measured property, which is in accordance with the theory of phenomenological thermodynamics and which, moreover, agrees with the single-valued data provided mostly by all TA measurements. If a thermal process occurs, the steady state becomes dependent on the time-temperature progress of the process, and thus $\dot{T} \neq \text{const}$ and $T = T(t)$. In such a case, however, the isothermal course also becomes distorted, as the sample temperature is not constant either ($T \neq \text{const}$) due to self-cooling and/or self-heating of the sample. This fact is often neglected or forgotten, although it may have the same importance as in non-isothermal measurements. The advantage of non-isothermal experiments, however, is a continuous measurement of the instantaneous sample temperature, and its deviation from a predetermined course helps us to determine not only the progress of the temperature gradients but also the entire progress of the process itself, such as in the case of DTA (see the preceding question). For ordinary measurements we may be satisfied with certain mathematical simplifications which are adequate for the simple kind of TA instrumentation; but we always have to be aware of the limits and consequences of such simplifications. Any sort of treatment can thus be tolerated if the author recognizes its shortcomings and gives to it the necessary scientific aim. An intimate correlation of iso- and non-iso-methods may then lead to refining of the true meaning of the rate constant as well as the physico-chemical aspects of the process in question.

(9) *Q*: *Can we ever speak about thermodynamics in terms of dynamic thermal experimentation, how compatible are kinetic and equilibrium data; and what then is the equilibrium background of the process?*

A: Let us first put our system investigated by TA into the scale of classical thermodynamics (thermostatics) and rational thermodynamics as limiting cases. Assuming three basic quantities, T, P, Z, we may write for theoretically quasi-stationary TA process:

$$\begin{tikzcd}
\text{class. thermodynamics} & & \text{rat. thermodynamics} \\
\begin{array}{l} T(\mathrm{d}T<) \\ P(\mathrm{d}P<) \\ Z(\mathrm{d}Z<) \end{array} \arrow[dr, shift right] & & \begin{array}{l} T(\dot{T}, \ddot{T}, \ldots) \\ P(\dot{P}, \ddot{P}, \ldots) \\ Z(\dot{Z}, \ddot{Z}, \ldots) \end{array} \arrow[dl, dashed, shift left] \\
& \begin{array}{l} \text{thermal analysis} \\ T(\Delta T, \dot{T} = \text{const}) \\ P(\Delta P, \dot{P} = 0) \\ Z(\Delta Z, \dot{Z} \approx \text{kinetics}) \end{array} \arrow[ul, shift right] \arrow[ur, dashed, shift left] &
\end{tikzcd}$$

This, in fact, is in accordance with a well-known result following from the thermodynamics of an irreversible process, which says that for systems which are not too distant from their equilibrium state and in which the processes proceed quickly enough, the ordinary thermodynamic logistics and relations may be employed. Joint and concise mathematical descriptions of the dynamic (flux) and static (equilibrium) behaviours of such systems is not yet available and, anyhow, will be too complicated for normal use. Therefore, two separate disciplines have developed: thermodynamics, where we attempt to determine the equilibrium quantities by extrapolation to equilibrium conditions ($\dot{T}$, $\dot{P}(\dot{Z}) \to 0$), and kinetics, where we try to describe the time-temperature development of the system equilibration ($\dot{Z}, \Delta T, \Delta P$). It is evident that for the system in equilibrium ($\mathrm{d}T$, $\mathrm{d}P$, ($\mathrm{d}Z<$) it is meaningless to speak about kinetics, as there is no driving force for any change (only time-temperature fluctuations). On the other hand, when the temperature of the system is continuously raised, the equilibrium conditions may also be gradually shifted, creating the so-called equilibrium background of the process. This is important for processes which proceed within a certain temperature interval (variant processes and/or diffuse first-order transformations), such as melting in a two-phase region [33]. This effect is often neglected during non-isothermal investigations, although it ought to be incorporated into the calculation in the form of the propagation of equilibrium under the idealized conditions of infinitely slow heating. High enough heating rates, however, enable us to evaluate the major part of a TA curve above the two-phase region, where ordinary kinetics is applicable again.

There is another influential factor: proximity to equilibrium, which should often be involved in our mathematical operations. Temperature integration of the rate constant yields, in fact, the difference of two $p(x)$ functions $[p(x) - p(x_0)]$, in which the second part may be neglected only when the measurement is carried out at temperatures distant from the equilibrium temperature. This becomes important for reversible processes studied at low heating rates, so that a great portion of material reacts in the vicinity of equilibrium [34]. Inclusion of the driving force (ΔG) into the primitive form of the kinetic equation yields the rate constant in a more complex form: $k_{\mathrm{T}}(1 - k_{\mathrm{G}})$. Accordingly, the integration becomes more complicated, giving as many as four $p(x)$ functions [13]. Hence, it is evident that appropriate knowledge of the kind of process investigated, with an adequate choice of measuring conditions, particularly the heating rates [1], makes it possible to achieve reliable kinetic analysis.

(10) *Q*: *The year 1970 was full of activity in seeking the fundamentals of the correct representation of the non-isothermal kinetic equation, which was initiated by MacCallum and Tanner's article. What in fact is the essence of this problem?*

A: In principle this concerns the mathematical formulation of a basic kinetic equation valid under non-isothermal conditions. Two time-dependent variable (t and T) were put together to represent the state of the system (α). Upon a normal mathematical procedure of partial differentiation, this assumption leads to the dependence: $\dot{\alpha} = (\dot{\alpha})_T + (\partial\alpha/\partial T)_t\dot{T}$, in which the term $(\dot{\alpha})_T$ is assumed to describe the isothermal rate only. This puzzle was first raised by McCallum and Tanner [35]. The wide public reaction showed again the danger of mere mechanical application of the mathematical symbols involved [36]. Let us investigate the true physical meaning hidden in such a relation, imagining a heated container filled with water, about which we assert that the content of water (α) is dependent merely upon its instantaneous temperature (T) and the time (t) since its filling ($t = 0$), regardless of whether any water still remains in the container. It is evident that this logistic approach is wrong, as we do not describe effectively enough the actual dynamics of the boiling process in question, i.e. the volatility rate ($\dot{\alpha}$) as a function of ready-to-react material (α) at a given temperature (T) (compare question (8)).

Nevertheless, such discussion may be very instructive and such kinds of articles should from time to time, be accepted for printing. In this place the editorial policy should be noted. An example is the case of philosophically oriented reply notes [37–39] published in Nature and following the article by MacCallum and Tanner [35]. Although the problem has not been sufficiently clarified [37–39]. Nature stopped accepting additional remarks, leaving this subject to be further discussed in "local" journals [36, 40, 41], possibly regarding it as "thermoanalytical business" only. In many cases it did not touche the point as yet [41, 42]. The wide kinetic community, however, may also feel the lack of the final word [42]. On the other hand, I touched on the above problem during my 1975 lecture at the Institute of Chemical Physics in Jerevan. To my surprise I learned that this puzzle was completely evident to those people dealing with the kinetics of adiabatic gaseous reactions. Here I probably approached one of the most painful sides of kinetics and nowadays possibly all scientific work in general: the lack of an appropriate exchange of information.

(11) *Q*: *Is it worth paying such attention to non-isothermal kinetics? Is it merely good for a narrow region of interested scientists, and how about the already-mentioned publication policy?*

A: Well, it should be stressed once more that the problem associated with dynamic kinetic measurements has its significance in all branches of experimental kinetics, because truly constant experimental conditions are hard to achieve. Non-isothermal kinetics, as is obvious from recent articles printed in JTA and TCA, is primarily limited by the TA experimental technique, but is carried out

Table 1

Survey of the number (and rel. %) of kinetic articles* so far published in J. Thermal Anal. and Thermochim. Acta

Year and journals	Number of reviewed articles	The part dealing with kinetics	Theory of formal approach	Application of formal approach	Formal mechanism (stoichiometry)	Theory of mechanism and kinetics	Mechanism and kinetic applications
1970							
JTA	44	12 (27%)	4 (33%)	3 (25%)	3(25%)	1 (8%)	1 (8%)
TCA	57	12/21	1/8	5/41	5/41	1/8	2/17
1971							
JTA	43	3/7	1/33	0	1/33	0	1/33
TCA	74	17/23	5/29	2/12	5/29	3/18	2/12
1972							
JTA	39	10/26	5/50	2/20	2/20	0	1/10
TCA	78	13/17	4/31	2/15	3/23	2/15	2/15
1973							
JTA	58	23/40	8/35	5/22	2/9	2/9	6/26
TCA	106	20/19	4/20	6/30	3/15	5/20	2/10
1974							
JTA	68	15/22	3/20	6/40	4/27	1/7	1/7
TCA	101	8/8	2/25	2/25	1/20	3/30	0
1975							
JTA	120	24/20	6/25	10/42	2/8	4/17	2/8
TCA	144	35/24	20/57	2/6	2/6	5/14	6/17
1976							
JTA	91	34/37	9/26	15/44	7/21	1/3	2/6
TCA	121	21/17	3/14	5/24	7/33	1/5	5/24
1977							
JTA	77	26/34	5/19	4/15	8/31	3/12	6/23
TCA	148	26/18	2/8	7/27	5/19	5/19	7/27
1978							
JTA	67	19/28	5/26	3/16	2/11	2/11	7/37
TCA	237	49/21	12/25	15/31	8/16	5/10	14/29
Total							
JTA	521	166/32	46/28	48/30	31/19	14/9	27/16
TCA	1066	201/19	53/26	46/23	39/19	30/15	40/20

* It presents a certain (subjective) view in ranking articles as those dealing with formal determination of kinetic data (reaction order) and its formal applications, analysis of reaction stoichiometry (mechanism), theory of reaction mechanism (kinetic models) and finally the applications of kinetic models in physical-chemical studies. (The number of articles compiled must not be identical with their actual number published in the year because of some missing issues.)

by numerous workers in different fields (cf. Table 1) (question (1)). The surprisingly low citation index is probably rooted in our preoccupation which often leaves insufficient time for a patient understanding of other authors work, logistics and particularly symbolics. A good example is the series of very narrow specialized articles on the $p(x)$ function, following each other at an interval of about one year, but making little reference to the previous ones [42–49] although printed in similar journals (TCA or JTA). This, of course, is also subject to the quality of the referee's work, the importance of which is sometimes underestimated, particularly when considering the still explosive trend of kinetic publications.

Our often very sectorized specialization leads, unfortunately, to a certain type of ignorance concerning the other works on a similar theme. This results in easy self-citing, because our own past work is most simple to be understood again "usually with the little effort of one re-reading". I once read that the usefulness of our citations may be evaluated by a quotient obtained by subtracting twice the self-citations form the remainder, which should at least be positive. (Ref. 26 is not the best example.)

Another side is the efficiency of the written text. The repetition of previous results and/or theories, so obvious in kinetics articles, is sometimes powerless and so subject to severe criticism, but, on the other hand, it may help the reader to catch the point very quickly. The basic fault of most introductory lines is their dispersity and/or length. It might be a good idea to introduce a key (or code) system (similar to those employed for abstracting), making it possible to write an introduction in a standard, concise but summarized way, even avoiding redundant derivations.

Finally, I should also present a diffident comment regarding the elegance and legibility of scientific language, as recently emphasized in a very nice manner by Keatch [50]. Such discussion belongs certainly to those who possess English as their native language. Besides, the quality and amount of our work the beauty of a well-written scientific report should be a (goal and entire pleasure) of our activity, similarly to an artistic work.*

(12) *Q*: *The offensive of computing techniques in all branches of science and engineering has not certainly avoided the field of TA. Will computers be of real help in our kinetic work, or will they solve only the most painful numerical troubles?*

A: This question must be answered in a broader sense, as we must surely admit that in the near future all TA laboratories will be fully or partly equipped with computing equipment (hardware, software, microcomputers, etc.). The question hence should read: are we ready to accommodate the new methods of treatment in our everyday practice? Sophisticated sets have already appeared on the market, but their furnishing with standard programs (good for the late sixties, compare kinetic articles in TCA 1977) has brought again the danger of employing good mathematics in a rather poor physical sense. On the other hand, some terms from the computer language (slang) have become so fashionable in accelerating sales, that their real information content may be discredited.

The most important fact in data treatment is how the output signal from a TA apparatus is maintained. A typical chart record will probably persist so as to give

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* I would like to support the proposal as to create an annual prize for the best presented paper appearing in either of TA journals and or ICTA procceedings.

an immediate, first-sight feeling as to whether the curve is of good or poor quality; however, the further elaboration of the curve then requires an enormous effort: an intermediate step of usually manual and time-consuming trace reading and numerical data preparation. Another problem arises for the preparation of short algorithms and for often changing mathematical procedures, where debudgeing, data punching and mechanical transfers are sometimes too slow and immobile in computing centers. The desk or pocket calculators provide a more direct and flexible service, and should become a new "logarithmic ruler" in everyday thermoanalytic work. Nevertheless, the most serious obstacle rooted in extensive numerical and statistical data treatment has been overcome. Of course, there may appear certain inequalities, hidden in the possibility of describing the system by sets of more sophisticated equations but where we may lack a sufficient amount of physical information relating to a single point measured ($T - \alpha$ versus the sets of $\sum_{1}^{i} T_i - \sum_{1}^{i} \alpha_i$ data). At the same time, we may not be ready to know how to interpret properly a new sort of output data which may not be in the form of single-valued constants or numericals.

More work should be done in using methods of chemical and mathematical statistics, information content and capability including its theory, hypothesis testing and goodness of fit tests, etc [51–53]. It would be recommendable to all author to get acquainted with at least some books on statistics [54] prior writing an article on numerical results.

A big qualitative step is the direct digitalization of the TA apparatus signal, which will presumably become a basic requirement for all TA experimentation. Entire on-line computing systems and possible self-control of TA experiments seems to be not too effective, because it may keep the computer busy with inadequate and rather mechanical work, such as temperature control, which is more suitable for cheaper microprocessors. We should not forget the analogous computers suitable for direct comparison of the experimental curve with the master curve or for solving differential equations, both of use in theoretical kinetics, whereas a digital computer must transfer this problem to the solution by matrices.

Looking back to the literature, probably the first computer polynomial fit was applied to a thermocouple signal [55]. It was followed by different tabulations, efforts either to make precise or list different functions, e.g. the $p(x)$ function. The pioneering work in non-isothermal kinetics was probably that by Anderson [56], who solved three simultaneous equations for different heating rates. Main activity, however, was focused on the evaluation of reaction orders and activation energies by using different simplified models [57, 58]. Only the most recent years finally brought up the problem of selection of appropriate mechanisms by fitting different analytical forms of $f(\alpha)$ and $g(\alpha)$ functions. This included correlation coefficients between the experimentally-determined and theoretical master curves as well as built in subroutines to evaluate the $p(x)$ function. No heavy-capacity algorithm, however, could give a direct and unambiguous answer to the basic kinetic question what the true reaction kinetics and mechanism involved. They merely classified the output data to a list of more or less probable kinetic models for a given sort and quality of experimental data. Complementary information, additional analysis of their physical meaning or more sophisticated criteria are needed.

In conclusion, more space should be given to computing treatments in existing TA books such as [1, 60, 53]. Seminars should bring together specialists from computers and TA to teach other the ways and means of analogies and digital data elaboration and the process control in thermophysical experiments, the numerical treatment (derivation, integration, etc.), fitting and smoothing of experimental curves and the actual aim of analysis of TA data in order to face our new tasks. The first attempt was made by the Czech group on thermal analysis in Prague, at the meeting directed to the digital treatment and conversion of the TA output signal, numerical evaluation and information property of experimental data, and the theoretical basis of TA with regard to general problems of the extraction of physico-chemical quantities when using computers [59].

In concluding I would like to re-employ the generally oriented words that V. Šatava used in his introductory lecture on theory and experiment [59]. If we ask a laic what is the progress in natural science he would probably answer that it consists in the gradual growth of results of observations and experiments. But who is actually dealing with research knows that a mere data collection is of little value, and what more, would not be self-satisfactory because of the lack of excitement. The real aim of science is different; it seeks the knowledge about the rules which control the nature i.e. the understanding and consequent description of observed phenomena. The logistics and mathematics of facts with respect to their ordering is thus the most important procedure [61–64]. Complicated mathematics, however, is not alway the only way how to reach the answers. Philosophically oriented thoughts are sometime equally important if we can afford them in the present busy world. So that I personally much appreciate such aspects in our field of science: non-isothermal kinetics, as we can trace in the work of e.g. Boldyrev, Flynn, Garn, Ozawa Šatava or Segal etc. We also may remember not often cited words of some famous scientists as "when I ever had some success in mathematical physics it was because I was able to avoid mathematical difficulties" (Gibbs) and/or "do not disturb such a nice thing like science by mathematics" (Fermi). But would it be ever said in our age of computers?

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Résumé — Les aspects les plus discutables de la cinétique non-isotherme sont traités sous forme de douze questions et réponses, en particulier: réputation de la cinétique non-isotherme appliquée par les thermoanalystes, conséquences des concepts simplifiés déduits de la cinétique des réactions en phase homogène, signification physique des paramètres cinétiques fondamentaux dans les processus en phase solide, effet de compensation cinétique et interdépendance des paramètres cinétiques lors de l'utilisation de la constante de vitesse d'Arrhenius, utilité mutuelle des méthodes différentielles et intégrales d'évaluation des données cinétiques, leur exactitude et leur degré de justesse, fiabilité des mesures par ATD, études non-isothermes vis-à-vis des méthodes isothermes, données à l'équilibre et en régime dynamique et leurs effets mutuels, extension de la discussion engagée par MacCallum et Tanner, politique de publication des données non-isothermes et finalement utilisation des ordinateurs et aide apportée par ceux-ci.

Zusammenfassung — In der Form von zwölf Fragen und Antworten werden die meist umstrittenen und auseinandergehenden Aspekte der nicht-isothermen Kinetik diskutiert. Insbesondere das Ansehen der nicht-isothermen Kinetik bei Durchführung durch Thermoanalytiker, die Konsequenzen der vereinfachten von der Kinetik homogener Reaktionen übertragenen Konzepte, die physikalische Bedeutung der kinetischen Grundparameter in Festphasenprozessen, der kinetische Kompensationseffekt und die gegenseitige Abhängigkeit der kinetischen Parameter bei Anwendung der Geschwindigkeitskonstante nach Arrhenius, die gegenseitige Nützlichkeit der Differential- und Integralmethoden der Auswertung kinetischer Daten, ihre Genauigkeit und Richtigkeit, die Zuverlässigkeit der DTA-Messungen, nichtisotherme gegenüber von isothermen Untersuchungen, Gleichgewichts- und kinetische Daten und ihre gegenseitige Wirkung, die Ausbreitung der von MacCallum und Tanner initierten Diskussion Politik der Veröffentlichung nicht-isothermer Angaben und, endlich, Einsatz und Hilfeleistung der Computer.

Резюме — В форме двенадцати вопросов и ответов обсуждены наиболее спорные и противоречивые точки зрения неизотермической кинетики. В частности рассматриваются известность неизотермической кинетики, когда она проводится термоаналитиками, послед-

ствия концепций упрощения, переносимых из кинетики гомогенных реакций, физический смысл основных кинетических параметров в процессах, протекающих в твердых телах, кинетический компенсационный эффект и взаимосвязь кинетических параметров при использовании константы скорости Аррениуса, взаимная полезность дифференциальных и интегральных методов выделения кинетических данных, их точность и корректность, надежность ДТА измерений, неизотермические исследования в сравнении с изотермическими, равновесие и кинетические данные и их взаимное влияние, расширенная дискуссия, начатая МакКэллум и Теннером, публикация неизотермических данных и, конечно, помощь и использование компьютеров.