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THERMAL ANALYSIS AND KINETIC CONCEPTS OF SOLID-STATE REACTIONS

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The general problems provoking widespread controversial opinions in the field of solid-sate kinetics are presented on the basis of the contributions and discussions at ESTAC 4, Jena, 1987. The main problems discussed are: a) the proper mathematical procedure in the currently used kinetic methods, b) the usefulness of the kinetic parameters calculated in the ordinary way for the description of the kinetic properties of the compounds, and c) the correlation between the real physical phenomena occurring during decomposition and the formal kinetic models.

The problems of the usefulness of the kinetic parameters, or (more generally) the purpose of the kinetic investigations, have caused much discussion in the past few years. After a rapid increase in the number of scientific papers, including the new methods of kinetic calculations, and after some kind of settlement in the competition between isothermal and non-isothermal measurements (the result of this compromise is: non-isothermal methods, yes, but only after the determination of the "mechanism" from isothermal experiments), the number of questions concerning the reliability of heterogeneous kinetics has been growing step by step. The important publications discussing this problem, i.e. those of Garn [1] and Arnold, Veress, Paulik and Paulik [2], have seemed to vanish among the hundreds of papers containing kinetic calculations. The reason for this situation is best characterized by the opinion of Prof. Flynn, the Chairman of the Kinetics Subcommittee of ICTA [3]: "...the unfortunate fact is that, since, in thermal analysis, properties of a system are measured as a function of time and temperature, all thermoanalytical results are potentially kinetic data, and many people ill grounded in kinetics feel obliged to perform a 'kinetic analysis' of them...". Fortunately, the last three International Thermal Analysis Conferences (ESTAC 3, Interlaken, 1984, the 8th ICTA, Bratislava, 1985, and ESTAC 4, Jena, 1987) have included in their scientific programmes workshops dedicated to the problem of the reliability of kinetic measurements. Such an exchange of information and different opinions is necessary, because nothing can be worse in the present situation than to be content with the actual state of affairs in this branch of science. If the results of

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the activity in the kinetic field are to be useful not only for the accumulation of new values of activation energy, then it is crucial to discuss the kinetic concepts of solid-state reactions. In a discussion of this subject, one must mention three main, still unsolved problems:

1. The proper mathematical procedure in the currently used kinetic methods, and the mutual relations between the calculations applied to the results of isothermal and non-isothermal experiments.
2. The usefulness of the kinetic parameters calculated in an ordinary way, for the description of the kinetic properties of the compounds, such as: the variation in the reaction rate during the change of the temperature or the heating rate.
3. The correlation between the real physical phenomena occurring during decomposition and the formal kinetic models.

1. Thousands of scientists each year decompose solids, and thousands of scientific papers are published in thermoanalytical journals, but each year the gap between two main groups is growing larger and larger. These are the group of scientists investigating only the kinetics of the decompositions, and the group working in the field of the reactivity of solids. It is clear that such a separation is not a natural one, but it is also clear that it exists. For scientists studying the kinetics of solid-state reactions, the properties of the products, or the real physical mechanism of the reaction are not of the utmost importance. As a result of their work, they obtain kinetic parameters, such as the activation energy E and the pre-exponential factor A, or formal equations, theoretically connected with the mechanism of the decomposition. The importance of these calculations is not questionable (at least, when speaking and writing about activation energy, one has to have correct methods for the calculation of this kinetic parameter), but from a mathematical point of view only there are many problems in this field. The problem of the derivation of the basic equation in non-isothermal kinetics is still unsolved, there still exists much controversy concerning the mathematical treatment of the "compensation effect", and (even in the commonly used kinetic equations) the integration boundaries are not correctly applied (Mălek [4]).

To discuss only the mathematical part of kinetic considerations, it is necessary to remember that the very frequently used sentence "the decomposition of x can be described by the following equation..." can be false for two reasons:

— it is usually impossible to choose which kinetic equation is the best: depending on the method used, the process can be better described by other equations (Rózycki and Maciejewski [5, 6]);

— under different experimental conditions, the same compound can have a different decomposition mechanism, i.e. from a kinetic point of view another formal equation will describe its reaction.

When only kinetic experiments are made, it is necessary to remember that the results obtained describe the reaction only from a mathematical point of view. When one tries to connect the kinetic calculations with the real course of the reaction, a knowledge of the values of E and A or the form of the function $f(\alpha)$ is not sufficient. Besides a few interesting contributions containing new methods of calculation of the kinetic parameters (mainly E) presented during ESTAC 4 (Balek, Schouten, Rozenband, Popescu, Holender, Gavrilova, Gontkovskaya, Horvath, Widmann, Grotowska and Wojciechovska), there were also written comments to the round-table discussion. In one of these, Mălek, Militky and Šesták [4] noted two important problems that are usually avoided during the evaluation of the kinetic parameters:

— First, it is necessary to take into account the boundary conditions of the respective kinetic models, i.e. $\lim g(\alpha) = 0$ (for $\alpha \to 0$) and $\lim g(\alpha) = \infty$ (for $\alpha \to 1$). The authors emphasized that these two elementary conditions did not hold for several $g(\alpha)$ functions.

— Secondly, they pointed to the distortion of the kinetic data caused by cutting off peak ends in DTA/DSC curves. Using computer simulation, they observed that a frequent cutting-off of both peak ends, often regarded as negligible with respect to the rest of the peak, may lead to catastrophic results.

Another written contribution to the final discussion during ESTAC 4 was made by Segal and Urbanovici. Their comments are connected with a problem which has been discussed for many years and introduced to kinetic considerations by MacCallum and Tanner [7]: the derivation of the rate equations used in non-isothermal kinetics. For 17 years, this "mystery of derivations" (Šesták [8]) has not been clarified; in fact, there are two large groups of scientists having opposite opinion. The literature on the problem has more than 50 positions (see for example references 1–23 in the Šesták [8] paper, references 9–42 in Blazejewski's [9] publication, or the presentation of Kemény in Thermal Analysis Highlights, 8th ICTA, Bratislava [10]), and there are (and will be) still other published papers trying to clarify this problem. But if we cannot correctly solve one of the noteworthy problems of non-isothermal kinetics, even from the simplest, i.e. only a mathematical point of view, the frequent opinion that it is necessary to stop the discussion is not justified. All the kinetic considerations trying to solve the existing contradictions are desirable and valuable, the new methods of calculation of the kinetic parameters uder isothermal and non-isothermal conditions are needed, and well-elaborated computer programs are also necessary. However, while working hard to introduce new methods of calculation of the activation energy, one should keep in mind that one is calculating the mathematical value, which is valid only for the investigated compound under the applied experimental conditions. It is necessary to limit, step by step, the conclusions involved in the attempt to determine the mechanism of the decomposition on the basis of kinetic calculations only (see, for instance, the sentence from one abstract of the paper submitted to ESTAC 4: "the kinetic studies are therefore made on the basis of TGA results, with the mechanism of the limiting stage of the process being determined for each case..."). All that one can obtain is the selection from a few mathematical expressions of the one best describing the experimental results. This is useful information and can be used, among others, for correlations between isothermal and non-isothermal results, but one should not try to deduce the shape of the particles of the product on the basis of the fact that the Avrami–Erofeev equation with the exponent $n = 3$ is the best (see the interesting paper of Dziembaj [11] concerning the meaning of the exponents in this equation). How rightly Boldyreva [12] has written "...studying kinetics is not the quickest way of understanding the mechanism of solid-state reactions...".

The discussions presented here and in other papers, concerning the popular approach towards the common methods of treatment of kinetic calculations, can lead to the misunderstanding, best described by Šesták [13]:

"...It is obvious that the criticism of present kinetic procedures for not characterizing sufficiently precisely the reality of heterogeneous processes is much easier than the proposal of more suitable models. Therefore, rejection of the present method of calculations of kinetic parameters, which we want to (but not always can) compare, is not a solution...". These words, often heard during discussions, cannot be fully accepted. From the fact that nobody has recently proposed a new concept of a physical meaning of the kinetic parameters such as A or E (and despite the considerable progress in solid-state chemistry and physics, nobody will probably do so in the near future), it does not automatically follow that the conclusions based on the Arrhenius equation should be fully accepted. This equation has been used in thousands of scientific papers concerning solid-state reactions, in the majority of which the experimental results satisfied this equation, and it should be noted that there is, at the moment, no better mathematical expression for the correlation of the results in the coordinate rate constant *vs.* temperature. However, as pointed out by Oswald during a discussion in Jena, one very often forgets that this equation was introduced into kinetics on the basis of considerations based on relations that are valid in the gas phase, and belief in their physical meaning in a much more complicated system should be very limited.

It is obvious that nobody is against the Arrhenius equation, but this equation should lead to conclusions concerning only the kinetics of the reaction. Kinetic parameters are important, but, as constants obtained on the basis of very simplified assumption, they cannot serve as proof in a mechanism determination. The critical remarks do not refer to the advisability of the utility of the Arrhenius equation for solid-state kinetics, but they concern the real physical meaning of the kinetic parameters and the reliability of the conclusions concerning the mechanism and based only on the values of A or/and E.

2. The second important problem is solid-state kinetics is the usefulness of the kinetic parameters for characterization of the properties of the solid under investigation. The kinetic parameters (mainly the activation energy) are very often used as factors giving certain information about, for instance, the energy required to break the bonds in the crystal structure, or for determination of the "thermal stability" of the compounds.

Let us forget all the previous remarks concerning the difficulties in the correct calculation of the kinetic parameters, and let us assume that all these problems have been solved properly. In this situation for the reaction under consideration (but, of course, only for actual experimental conditions), we have three kinetic parameters describing the position of the thermogravimetric (or DTA) curve in the coordinates α *vs.* temperature or α *vs.* time. These parameters are A, E and function $f(\alpha)$ (very often, instead of $f(\alpha)$, the "reaction order" n is used, the meaning of which has been borrowed from homogeneous kinetics). The main problem is that, even if all the kinetic parameters have been calculated correctly, the use of only one or two of them does not provide sufficient information about the process. The assumption that, by making experiments under "standard conditions", one can later compare the values of the activation energy in order to draw conclusions concerning the mechanism of the reaction is simply not right. Only in a completely unrealistic case, when two other kinetic parameters are equal, can the comparison of the values of the activation energies show the influence of the temperature on the rate of the reaction and the position of the curve in the coordinates α *vs.* T (or t).

At this point, it is necessary to include in the presented remarks the problem of the "compensation effect". The literature of this problem has hundreds of positions; the discussion about the mutual relation $\ln A$ *vs.* E has divided scientists into two groups: those who believe in this effect, and those who are sure that it is an artefact resulting from the mathematical form of the Arrhenius equation. All those trying to find the physical meaning of the compensation effect should remember the publication of Arnold [2] and Agrawal [14]. The latter has written rightly that a comparison of $\ln A$ *vs.* E for the parameters derived from different mathematical approximations has no physical significance. The use of the compensation effect for the extrapolation of the experimental results to other conditions or for the characterization of the investigated compound leads to such curious solutions as the use of negative values of E, or the use of the values of A and E calculated on the basis of quite different equations. Therefore, if all 15 or 20 equations based on the "theoretical models of the decomposition mechanism" give a set of 15 or 20 pairs of A and E values showing a straight-line dependence in the coordinates $\ln A$ *vs.* E, the attempts to determine the real sense of such calculations are of little value. The compound has its own decomposition mechanism under defined conditions, and only one (of any!) function $f(\alpha)$ gives the correct A and E values, and this means that in such a digram only one out of 15 or 20 points is true.

Even when comparing A and E values from only a mathematical point of view, one has to be sure that the third parameter (function $f(\alpha)$) is constant, but there are enough examples in the literature to show that the decomposition mechanism can vary under different experimental conditions. Without a knowledge of the form of the function $f(\alpha)$, all conclusions about the physical meaning of the compensation effect should be made with great care.

The need to consider all three kinetic parameters is also evident during determinations of the "thermal stability" of compounds. The problem of thermal stability has been presented in a few contributions during ESTAC 4 (Györiova, Chomič, Pielichowski and Shutov).

From the results published by the author of the present paper (Maciejewski [15–17]), one can draw the conclusion that a comparison of the temperatures at which the investigated compounds start to decompose can lead to completely false conclusions. Even for a series of compounds of similar composition, analysed under similar conditions, and even in the case when the values of A and E are similar, these compounds may have different decomposition mechanisms, which will affect the reliability of the conclusions concerning their thermal stabilities. If all three parameters are not taken into account, then the term "thermal stability" has no real physicochemical meaning (see also Logvinenko [18, 19]).

Without a knowledge of all the kinetic parameters, it is also impossible to make any correlation between isothermal and non-isothermal experiments, which indicates once more that conclusions concerning "thermal stability" determined from non-isothermal experiments can be of little value. Mathematical calculations concerning this problem are presented in paper [17] and in the one now being prepared (Maciejewski [20]).

3. The main differences in opinion concerning the usefulness of the kinetic parameters appear when kinetic procedures are considered by scientists working in the field of the "reactivity of solids". Here, by investigating all the factors influencing the course of the reaction, such as crystallographic and morphological relations and real physicochemical processes exhibited during decomposition, it is possible to find the mechanism of the reaction and a very important dependence between the experimental conditions and the properties of the product. The more direct the observations of the real phenomena occurring during decomposition, the more it becomes clear how far assumptions of the formal kinetic models used till now in solid-state kinetics are from reality. A discussion of the physical meaning of the compensation effect would be much more useful after the introduction of the results of observations on the decomposition of the solid under different conditions.

When one makes mathematical manipulations with the values of A and E obtained for the thermal decomposition of $CaCO_3$, it is necessary to know how many real phenomena occur during the course of the reaction and how they change, for instance, the properties of the product, CaO. The sintering of $CaCO_3$ before decomposition (Maciejewski and Oswald [21]), the great influence of the pressure of CO_2 on the properties of the product and on the reaction mechanism (Maciejewski and Bałdyga [22]), and the simultaneous decomposition and polymorphic transition (in the case of vaterite, one of the polymorphs of $CaCO_3$), are all the phenomena which are not introduced into classical equations, but they really exist! It is difficult to start a discussion of the physical meaning of, let us say, the Mampel kinetic equation on the basis of the assumption that only one nucleus is formed on one particle, with someone who has used electron microscopy even only once. Many such unrealistic assumptions can be found in "classical" solid-state kinetics.

Similar remarks can be found in the interesting contributions presented by Boldyreva [23] during ESTAC 4. She has rightly reminded us that the longer the time that has passed since a formal model of "classical" kinetics was first proposed, the less are the limitations of its application taken into account. Boldyreva recalls that obvious (at first sight) and simple enough main assumptions of formal topokinetics are not always true:

— The reaction does not always start at "potential centres" and proceed via the formation and growth of nuclei of the product (Boldyreva [24]).

— If the reaction does proceed via the formation and growth of nuclei, the rate of interface advance may not be constant (Sidelnikov et al. [25]), Shachtschneider et al. [26].

— The properties of the interface between the nucleus and the parent crystal may not be equivalent at its different parts (Lyakhov [27]).

— The reactivity of the decomposed solid may not be constant, and it can change in the course of the reaction, due to the possibility of the existence of a positive or negative feed-back (Boldyrev [28], Chupakhin et al. [29]).

Classical kinetic models do not take all these phenomena into account, and they are not fully suitable for a proper treatment of various solid-state reactions—points out Boldyreva. At present, there is no good alternative to "classical" models and equations of formal topokinetics. It seems impossible to suggest such an alternative and succeed in a non-formalistic kinetic treatment of solid-state reactions without a careful study of the reactivity of solids, first at a qualitative level.

The proper way towards the solution of the described problems seems to be to use the methods proposed by Boldyrev or Oswald and their coworkers. One of these methods is the use of computer simulation as an alternative to formal topokinetics (Boldyreva [30]), and another one involves the correlation of the macroscopic morphological changes ("macroscopic reaction mechanism") with the simultaneously occurring structural rearrangements ("microscopic reaction mechanism"). As reported in the paper of Reller and Oswald [31], the evaluation of overall measurements, e.g. weight changes of powder-like samples or even isolated single-crystals as a function of time and/or temperature, cannot yield reaction-specific parameters, unless the information derived from compositional, structural and morphological studies is taken into account.

In this paper, the author has tried to survey the general problems still unsolved in the field of solid-state kinetics. There are numerous difficulties in finding the proper mathematical solution for the determination of A, E and $f(\alpha)$, in using these mathematical parameters correctly, whether they have any physical meaning or not, and in trying to correlate them with real processes occurring during decomposition. Kinetic considerations are very important, but, in the author's very personal opinion, it is much better to be more pessimistic, knowing all the limitations existing in each field, and not to be reassured and satisfied with the conviction that all methods currently used can give us reasonable results. We can solve the problems only if we know them and discuss them, and this is the main advantage of such an exchange of information as takes place during each day of such a well-organized conference as ESTAC 4 in Jena.

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Zusammenfassung — Die allgemeinen Probleme, die zahlreiche kontroverse Meinungsäusserungen auf dem Gebiet der Kinetik von Festkörperreaktionen veranlasst haben, werden auf der Grundlage von Beiträgen und Diskussionen des ESTAC-4 zusammengestellt. Hauptsächlich werden folgende Probleme diskutiert: a) die geeignete mathematische Prozedur für die gegenwärtig verwendeten kinetischen Methoden; b) die Brauchbarkeit auf herkömmliche Weise berechneter kinetischer Parameter zur Beschreibung der kinetischen Eigenschaften der Verbindungen; c) die Korrelation zwischen den tatsächlichen physikalischen Vorgängen bei der Zersetzung und formalen kinetischen Modellen.

Резюме — На основании представленных на конференцию статей и проведенных обсуждений, показаны общие проблемы, вызывающие широкораспространенные противоположные мнения относительно кинетики твердотельных реакций. Обсуждены такие основные проблемы, как соответствующий математический метод в общепринятых кинетиеских методах, непригодность вычисленных обычным путем кипетиеских параметров для описания кинетических свойств соединений и корреляция между действительным физическим явлением, протекающим во время разложения, и формальными кинетическими моделями.