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Computational aspects of kinetic analysis. Part B: The ICTAC Kinetics Project — the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield[☆]

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Abstract

This paper is Part B (Part A, M.E. Brown, et al., Thermochim. Acta, Special Issue Toward the New Century) of a series of papers that present and discuss the results of the ICTAC Kinetic Analysis Project. This part discusses the results which participants in the project have obtained from the isothermal and non-isothermal data provided on the thermal decomposition of calcium carbonate in nitrogen and in vacuum. The data demonstrate that the kinetic description of the process depends strongly on the experimental conditions. The very limited applicability of the kinetic methods that use single-heating rate data is emphasized. To obtain reliable kinetic descriptions, one should use computational methods that employ multi-heating rate data and allow for treating multi-step processes. The importance of evaluating full kinetic triplets is illustrated for several cases when knowledge of the activation energy alone does not permit adequate interpretation of kinetic data. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Kinetic analysis; Isothermal; Non-isothermal; Decompositions; Calcium carbonate

1. Introduction

Ambiguity inescapably accompanies interpretation of kinetic data produced from thermal analysis measurements. It originates partly from the use of inadequate computational methods and partly from experimental shortcomings. In the case of frequently studied reversible reactions, such as the dehydration of calcium oxalate monohydrate or the decomposition of calcium carbonate, the effect of experimental conditions on the partial pressure of a gaseous reactant is the major source of the observed differences in kinetic parameters. Generally, direct comparison of the kinetic parameters obtained by different computational methods is very problematic because it is unclear whether the observed differences in the values originate from differences in the experimental conditions or from the differences in the computational methods. The ICTAC Kinetics Analysis Project provides a unique opportunity to compare computational methods, because different methods are applied to the same sets of experimental and simulated data. Comparison of the results obtained can highlight the weak and strong features in the applied methods and, therefore, identify the most promising of them.

[☆] The title refers to the paper by M. Brown “Steps in a minefield — some kinetic aspects of thermal analysis” [1] discussing controversial aspects in the field of solid state kinetics.

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Common sources of misinterpreting kinetic data are rooted in several rather naive beliefs:

1. That reactions that are *simple* from the stoichiometric point-of-view, such as dehydration, decompositions of carbonates, hydroxides, etc., all resulting in one well-defined product, can be represented by a *simple* kinetic description, i.e. by a single kinetic triplet (activation energy, pre-exponential factor and reaction model).
2. That a *single kinetic triplet* should uniquely characterize a 'simple' reaction. If only one solid (CaO) and one gaseous product (CO_2) are formed during the decomposition of $CaCO_3$, then the experimentally determined value of, say, the activation energy should represent the height of the energetic barrier for this process, and, therefore, should practically be a fundamental characteristic of the reaction.
3. That the "mechanism of decomposition is independent of the temperature and reaction progress". This belief is a source of a common delusion that kinetic parameters can be reliably estimated from the data of a single non-isothermal experiment. It also is a source of the perpetual inspiration for developing numerous computational methods that are usually published under the title "A Simple (or New) Method of Evaluation of…"
4. That "non-isothermal kinetics is obliged to give the same results as isothermal kinetics". The number of papers supporting this belief is comparable to the number of papers that prove that non-isothermal kinetics actually gives better (or worse) results than isothermal kinetics. Therefore, whatever the results obtained by a particular worker, he or she would not have a problem to choose proper references in its support.

Let us consider if the results obtained by the participants in the project are (in)consistent with the above assumptions.

2. Results

The summary of the results is presented in Fig. 1 (decomposition in nitrogen) and Fig. 2 (decomposition in vacuum) in the form of graphs showing the

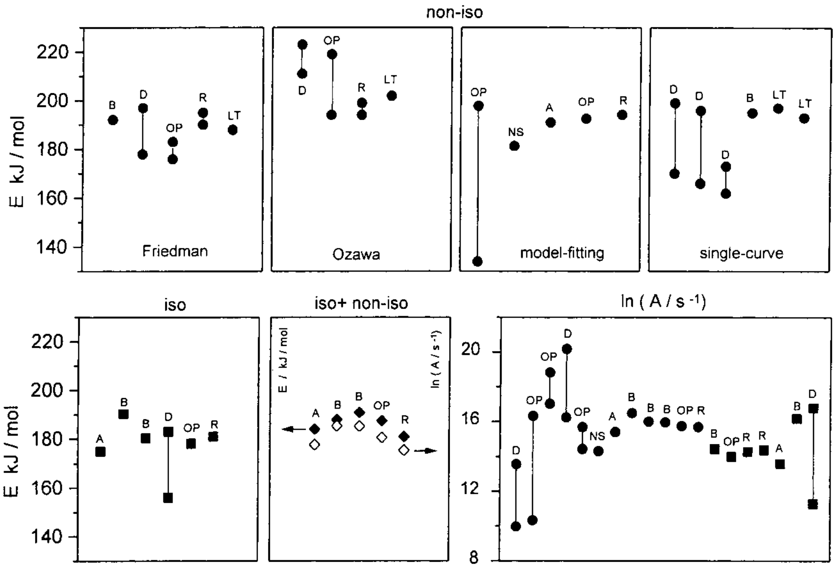

Fig. 1. Graphical presentation of the submitted Arrhenius parameters for the decomposition of $CaCO_3$ in nitrogen. The meaning of the solid lines connecting some symbols is explained in the text. The letter codes stand for the participants; A: Anderson, B: Burnham, D: Desseyn et al., LT: Li and Tang, NS: Nomen and Sempre, MM: Malek and Mitsuhatsi, O: Opfermann and R: Roduit. The top row contains the calculations from the non-isothermal data (non-iso), the bottom row both the isothermal (iso) and (iso+non-iso), as well as the values of the pre-exponential factor in the form of ln A (s^{-1}) values for both non-isothermal (●) and isothermal (■) data.

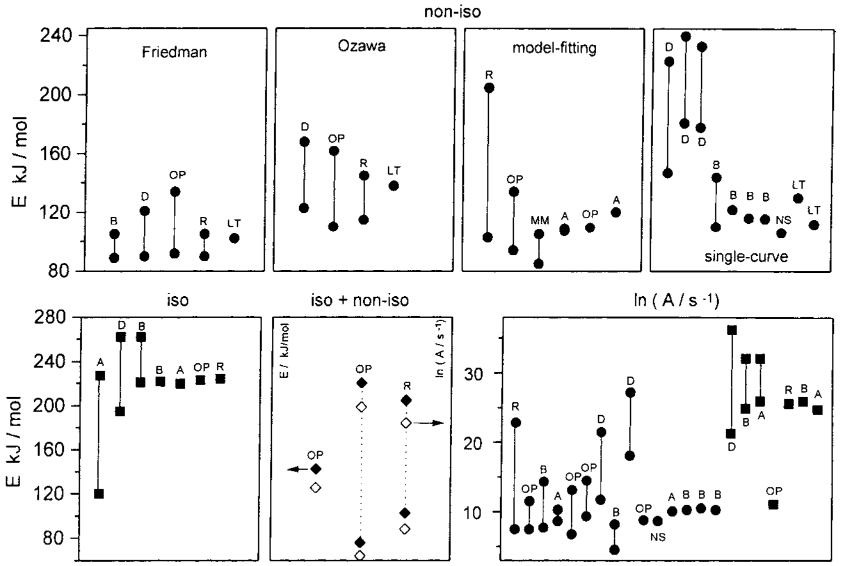

Fig. 2. Arrhenius parameters for the decomposition of $CaCO_3$ in vacuum. For the details of the caption, see Fig. 1.

values of the activation energy (E_a) calculated by the model-free isoconversional methods that use multi-heating rate data (Friedman, Flynn, Wall, Ozawa) and by the model-fitting methods that use single-heating rate data (Kofstadt, Ingraham–Marrier, Coats–Redfern, Freeman–Carroll, Sestak–Berggren). In both figures, the E_a values determined from non-isothermal experiments (denoted as 'non-iso') are presented in the top rows. The bottom rows contain the E_a values estimated from isothermal (denoted as 'iso') and from combined non-isothermal and isothermal experiments. The values of the pre-exponential factors are also given in the bottom row. If the reported results contain two values for E_a and/or for A (e.g. for low and high extent of reaction α) then both values are presented as symbols connected by a solid line. If the dependence of E_a versus α was given, the values of E_a for low and high α were taken at α=0.1 and 0.9 respectively. This way of presentation was also applied to the results obtained by fitting multi-step models, i.e. when two sets of kinetic triplets have been used to describe the process.

The results for decomposition under vacuum show much greater scatter than those for the process under nitrogen. For vacuum, two sets of E_a values have generally been reported, (low and high extent of reaction α). After the removal of extreme results, the E_a values given for the beginning of the process lie in the range 105–240 kJ mol^{-1}, whereas those for high α are in the range 89–187 kJ mol^{-1}. When only one value of E_a was reported for the full range of conversion, it changes within the range 102–138 kJ mol^{-1}. The activation energies calculated from the isothermal experiments lie in the range 227–262 kJ mol^{-1} for low, and 120–221 kJ mol^{-1} for high α when two values of E_a are given, and between 220–224 kJ mol^{-1} when only one value of activation energy has been estimated for the whole process.

The results for the decomposition in nitrogen are more stable, and the differences between isothermal and non-isothermal experiments are much smaller. In non-isothermal experiments, the values of the activation energy change from 163 to 223 kJ mol^{-1} for the low α values to 131–211 kJ mol^{-1} for higher α. The isothermal data gave the value of E_a in the range 156–190 kJ mol^{-1}.

The data presented clearly indicate that the kinetic description of the solid state reactions is influenced not only by the complicated nature of the process but also by the method of calculation. Based on these results, we cannot choose 'the best' method, because we do not know the correct mechanism and kinetic parameters. This is possible only for simulated data for which the kinetics triplets are known exactly.

However, we can identify those methods whose use should rather be avoided, because they do not permit an adequate kinetic description of the process.

3. Comments

3.1. *Can the E_a value be used as an exclusive characteristic of a reaction? Some facts that are so self-evident that are almost always forgotten, but should not be!*

Fact 1: A lot of misunderstanding in interpreting kinetic data originates from exclusively focusing on the activation energy. However, the commonly used rate equations suggest that the dependence of the reaction rate on temperature and on the extent of reaction α includes at least three parameters (activation energy, pre-exponential factor, and reaction model). Kinetic books, reviews and articles are full of estimated values of the activation energy that are compared with the reaction enthalpies and bond energies. The values of pre-exponential factors and the types of reaction models quite often remain unreported. For instance, it is frequently claimed that if a process has a lower value of the activation energy, the substance will decompose at lower temperatures. It is often forgotten that the activation energy alone can determine the reaction rate only when the two other kinetic parameters are the same, which is rather unrealistic.

Let us consider three reactions that obey the same reaction model (‘contracting sphere’ R3) but have different Arrhenius parameters. The simulated curves of the α–T dependence for a heating rate of 10 K min^{-1} are presented in Fig. 3A for the following cases: (i) E_a=150 kJ mol^{-1}, ln A=24.0 s^{-1}; (ii) E_a=125 kJ mol^{-1}, ln A=17.0 s^{-1} and (iii) E_a=100 kJ mol^{-1}, ln A=14.0 s^{-1}. The reaction having the lowest activation energy (iii) occurs in the region of temperatures that are markedly higher than in the case of the reaction (i) having the highest activation energy. The situation can be even more confusing when not only Arrhenius parameters, but also reaction models are different. The simulated curves for the following triplets:

1. Jander (diffusion) mechanism, E_a=165 kJ mol^{-1}, ln A=19.0 s^{-1}
2. Contracting sphere R3 mechanism, E_a=145 kJ mol^{-1}, ln A=17.0 s^{-1}
3. Avrami–Erofeev (nucleation), n=4, E_a=100 kJ mol^{-1}, ln A=10.0 s^{-1}

are presented in Fig. 3B. One can see that even the relative temperature ranges of decomposition cannot be predicted when using only the values of the activation energy. The reaction (1) having the highest E_a value begins first and ends last. The reaction (3) with the smallest E_a (100 kJ mol^{-1}) starts at temperatures more than 150°C higher than reaction (1) with E_a=165 kJ mol^{-1} but finishes more quickly than the reaction with E_a=145 kJ mol^{-1} (2). By comparing the E_a values for different reactions, it is not possible to make any conclusions about the temperature regions of their occurrence.

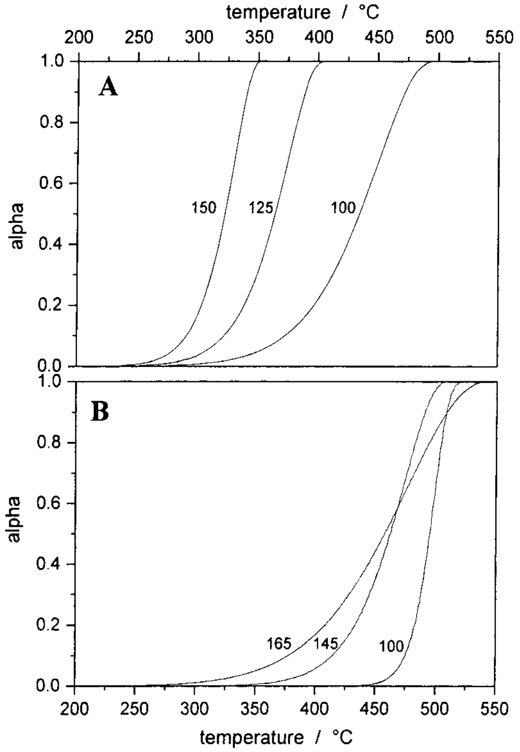

Fig. 3. Simulated α-temperature relationships for different kinetic triplets calculated for a heating rate of 10 K min^{-1}. (A) Model R3: E_a=150 kJ mol^{-1}, ln A=24 s^{-1}; E_a=125 kJ mol^{-1}, ln A=17 s^{-1}; E_a=100 kJ mol^{-1}, ln A=10 s^{-1}; (B) Jander model: E_a=165 kJ mol^{-1}, ln A=19 s^{-1}; R3 model: E_a=145 kJ mol^{-1}, ln A=17 s^{-1} and A4 model: E_a=100 kJ mol^{-1}, ln A=10 s^{-1}. The values of the activation energy are marked on the curves.

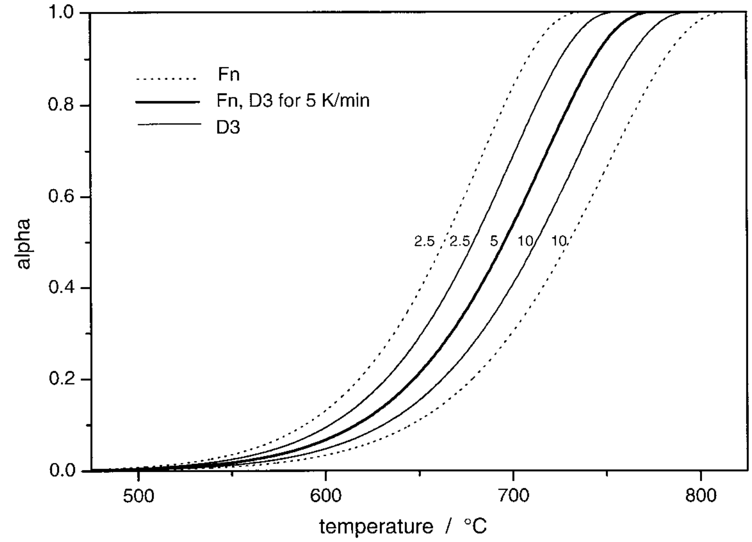

Fig. 4. The simulated α-temperature curves for the models Fn and D3 and heating rates of 2.5, 5 and 10 K min^{-1}, respectively. The values of the kinetic triplets are given in the text.

Fact 2: It has been amply reported in the literature (cf. Criado et al. [2]) that the non-isothermal data obtained at a single heating rate can be described by several different but statistically equivalent kinetic triplets. Such an example is given in Fig. 4 which depicts the simulated curves for two different reaction models: *n*-th order reaction (Fn) and three-dimensional diffusion, Jander equation (D3) at heating rates of 2.5, 5 and 10 K min^{-1}. The kinetic curves of α versus T are practically identical for the heating rate of 5 K min^{-1}. However, the Arrhenius parameters are different. For the D3 model, E_a=308 kJ mol^{-1}, ln A=29.423 s^{-1}, and for the Fn model E_a=147 kJ mol^{-1}, ln A=11.451 s^{-1}, n=0.673. This example clearly shows the danger of the application of single-heating rate methods for evaluating the Arrhenius parameters. The difference between these two data sets can be detected only from the data obtained at different heating rates (see Fig. 4). In other words, this suggests that only computational methods, which use multi-heating rate data can produce a reliable mathematical description of the reaction kinetics. The methods that use single heating rate data should simply be avoided in serious kinetic analyses. Despite this fact these methods are still used very extensively.

Fact 3: As seen from the results of the project (see also Parts A and C), the model-free isoconversional methods have shown to be successful in detecting multi-step kinetics in simulated and real data. This phenomenon is easily detectable in the form of a dependence of E_a on α. This dependence is observed when a process involves several steps that have different activation energies. There is, however, a danger of missing the multi-step character of a process in the case when different steps have practically equal activation energies, but have different pre-exponential factors and/or obey different kinetic models. This type of kinetic complexity would not show up as a dependence of E_a on α. In the case when E_a does not vary with α, fitting of multi-step heating rate data to multi-step kinetics models may be helpful in detecting this type of kinetic complexity.

3.2. Comparison of isothermal and non-isothermal kinetic parameters. Should they be the same?

Thanks to the power of modern personal computers, the approximation of the temperature integral does not present a major problem any more. Precise numerical integration eliminates the mathematical source of the difference in the kinetic parameters determined from isothermal and non-isothermal experiments. The results of the project show that many of the participants have correctly found the kinetic triplets for the simulated data for both isothermal and non-isothermal processes (Part C). In real experiments, there are two reasons that can prevent consistent kinetic triplets from isothermal and non-isothermal data being obtained: (i) the temperature ranges of isothermal and non-isothermal experiments are not the same; (ii) truly isothermal conditions cannot be accomplished for the very low and very high ranges of the reaction extent α.

Isothermal experiments cannot be carried out at temperatures when the reaction rate is too fast and significant decomposition may occur during settling of the experimental temperature at the beginning of the experiment. This undefined period depends upon the experimental conditions (applied temperature ramp, sample mass, the kind of carrier gas) and reactant properties (c_p, thermal conductivity, the mechanism of the decomposition) and makes it experimentally impossible to achieve strictly isothermal conditions over the full range of conversion. For many kinetic models the maximum rate of decomposition, under isothermal conditions, occurs at the beginning of the reaction. The simulated curves for values of E_a and A similar to those obtained for the decomposition of $CaCO_3$ under nitrogen: $E_a=193\ \mathrm{kJ\ mol^{-1}}$ and $\ln A=15.9\ \mathrm{s^{-1}}$ for the functions R3 (contracting sphere model), A4 (nucleation) and first-(F1) and zero-order reactions (F0) are plotted in Fig. 5A for the temperature of 700°C. At this temperature, a reaction progress of 0.01 is reached for the R3 function after only 0.16 min (0.05 after 0.8 min) which clearly indicates the limitations of the application of very low α values in kinetic calculations for contracting geometry models. The problem of temperature settling is of little importance for reactions where nucleation is the rate limiting step: for the A4 function a reaction progress of 0.01 is reached after 15.0 min. On the other hand, in the case of the first-order model it is difficult to determine exactly the very high progress of the reaction. For the F1 model, the change of α from 0.98 to 0.99 and 0.995 needs 33 and 32 min, respectively. The accuracy of the determination of such small mass changes over a quite long period of time is rather problematic due to the limited stability of the TG baseline. The reaction described by F1 is completed after 295 min and cannot be investigated at much higher temperatures due to the quite fast beginning — the progress 0.02 is reached in less than one minute. The above examples indicate the experimental difficulties with isothermal experiments and the problems of obtaining useful data at very low (<0.02) and very high (>0.98) reaction progresses.

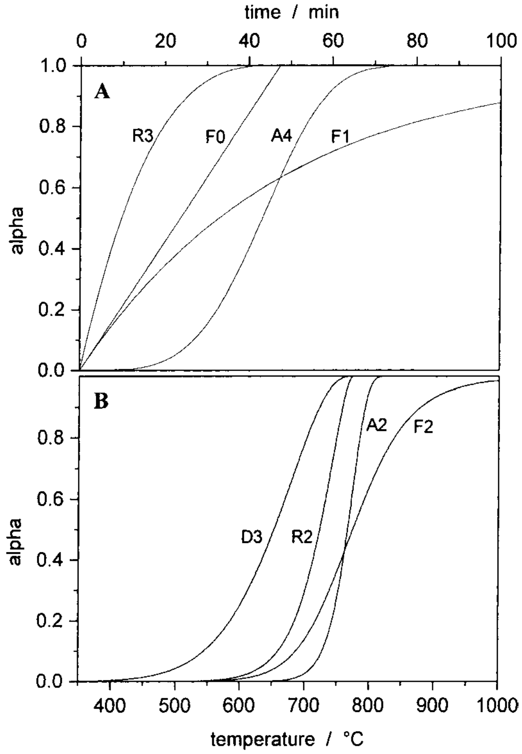

Fig. 5. Simulated α-time relationships at 700°C (A) and α-temperature relationships for a heating rate of $10\ \mathrm{K\ min^{-1}}$ (B) for the following Arrhenius parameters: $E_a=193\ \mathrm{kJ\ mol^{-1}}$, $\ln A=15.9\ \mathrm{s^{-1}}$. The models used for the calculations are marked on the curves.

The simulated curves for the non-isothermal conditions presented in Fig. 5B also indicate the difficulties of the determination of the α–T dependence at the beginning of the decomposition. Due to the specific shape of this dependence for some functions, especially for the contracting geometry and diffusion models, the change of the reaction progress from 0.001 to 0.02 requires, at a heating rate of $5\mathrm{K\ min^{-1}}$, the temperature change of 63 K (R2) or 109 K (D3), respectively. Due to buoyancy effects, the determination of such small mass changes over a relatively long period of time is uncertain.

Another important factor that affects the reliability of kinetic data obtained for very low and very high α values is self-heating/cooling. The distortion of the preset temperature program is especially high at the beginning of isothermal and at the end of non-isothermal experiments due to the occurrence of the greatest thermal effects at these stages of the process. The effect of self-heating/cooling increases with increasing sample mass. The deviation of the actual T from the preset temperature may invalidate any evaluation of the kinetics triplets. This problem is largely solved by Vyazovkin [3] who developed an advanced isoconversional method which is applicable to an arbitrary heating program.

All the aforementioned remarks indicate that comparison of the kinetic parameters obtained under isothermal and non-isothermal conditions is aggravated by unavoidable experimental phenomena that affect the kinetic data. In the case of a relatively simple process, whose kinetics can be described by a single kinetic triplet (cf. the decomposition of $CaCO_3$ under nitrogen), the difference in the kinetic triplets derived from isothermal and non-isothermal data is primarily determined by these experimental phenomena, but not by computational methods (provided they are valid).

The isothermal experiments were carried out in narrower temperature ranges. The values for the calcite decomposition from α=0.01–0.99 are as follows:

- Vacuum: non-isothermal 193°C, isothermal 35°C;
- Nitrogen: non-isothermal 289°C, isothermal 73°C.

The complex nature of a multi-step process can be more easily detected when using a broader temperature range. In the narrower ranges used under isothermal conditions, the differences between different models are much less visible, which leads to a statistically acceptable description of the multi-step process by one set of kinetic parameters. The extrapolation of the α–T relationship, calculated from this triplet, for the wider temperature range (non-isothermal process) can easily show limited applicability due to its incorrect determination. The solution for avoiding these problems would seem to be the opposite procedure: determination of kinetic parameters should be done from non-isothermal experiments carried out over a wide temperature range. If a kinetic triplet is able to correctly describe the full temperature range, then it can be applied for the prediction of isothermal experiments taking place at temperatures lying inside the range of the non-isothermal experiments. This is of importance, especially in the case of multi-step processes which are accompanied by additional physical phenomena, such as melting, polymorphic transformations, sublimation, evaporation of liquid formed during melting etc. For such systems, the correct extrapolation of isothermal data to a non-isothermal process is impossible, but the reverse procedure seems, however, to be more feasible.

Let us illustrate the above remarks by the results presented in the Kinetic Project for the decomposition of $CaCO_3$ in nitrogen. In order to compare the non-isothermal and isothermal results, the set of simulated curves possessing Arrhenius parameters obtained for both heating modes were calculated for three models: zero-order (F0) and first-order (F1) and contracting sphere (R3). The results are presented in Fig. 6 for isothermal (upper row) and non-isothermal (bottom row) conditions i.e. for 680°C and 5 K min^{-1}, respectively. The following Arrhenius parameters were used: E_a=193 kJ mol^{-1}, ln A=15.9 s^{-1}, being very close to those found by the participants for non-isothermal conditions using model-fitting methods (Anderson, Opfermann, Roduit) and E_a =178 kJ mol^{-1}, ln A=14.0 s^{-1}, comparable to the isothermal values obtained by Anderson, Opfermann and Roduit. Despite the different values of the activation energies, the calculated relationships, α-time and α-temperature, are almost identical. The change of E_a values was compensated by the change of A and both sets of Arrhenius parameters could be used to predict the reaction progress under both non-isothermal and isothermal conditions. Again, these results suggest that the comparison only of the values of the activation energy can be misleading and that the experimental data could be described by the set of kinetic parameters being the same for non-isothermal and isothermal conditions. It is, however, necessary to stress that in the given example (decomposition in nitrogen) the solid state process was well described by a single kinetic triplet. This cannot be taken as a general rule, because usually solid state reactions demonstrate profoundly multi-step character. For multi-step processes, the change of the kinetic triplet during the course of the reaction has to be introduced into the calculations,

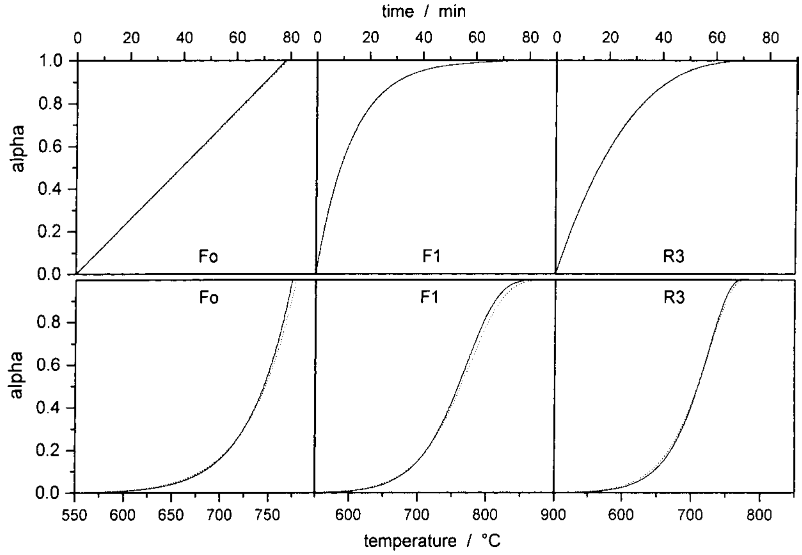

Fig. 6. The simulated α-time curves at 680°C (top row) and α-temperature curves for a heating rate of 10 K min^{-1} (bottom row), calculated for two sets of Arrhenius parameters: (—) E_a=193 kJ mol^{-1}, ln A=15.9 s^{-1}; (– – –) E_a =178 kJ mol^{-1}, ln A=14.0 s^{-1}. The models used for the calculations are marked in the respective fields.

as has been done by some of the participants (Anderson, Opfermann, Roduit), for the decomposition of calcium carbonate under vacuum.

4. The physical meaning of the kinetic triplet

What are the main reasons for investigating the kinetics of thermal decompositions of solids? Three general explanations are as follows:

1. The need for products whose properties are more valuable than those of the reactants. In the following three processes only: the production of lime, the production of alumina by the calcination of aluminium hydroxide and the production of sodium carbonate by the thermal decomposition of $NaHCO_3$ the amount of decomposed reactants exceeds 1×10^7 t a year. To carry out these industrial processes it is necessary to know the dependence of the rate of reaction on temperature and to apply the kinetics as a mathematical description of the process.
2. The need to determine thermal stability i.e. the temperature range over which a substance *does not decompose with an appreciable rate* (pharmaceuticals, polymers). Application of the kinetic parameters allows for prediction of this property.
3. The determination of the chemical processes by which the components of the crystal are transformed into the products. The application of kinetic measurements in this field provokes heated debates. The main goal of these measurements, the determination of the kind of gaseous and/or solid products, does not require kinetic measurements. The driving force for application of kinetics seems to be the belief that knowledge of the kinetic parameters can help in the elucidation of the decomposition mechanism.

Taking into account the practical purposes of evaluating the kinetic triplets, one has to choose between two opinions:

- The kinetic triplets do not have a physical meaning but can help in predicting the rate of the process for conditions when the collection of experimental data is impossible, e.g. at very low or very high reaction rates.
- The kinetic parameters do have a physical meaning and can be used to help in elucidating the solid-state reaction mechanisms.

The truth lies somewhere between these two opposite opinions. It seems to be acceptable for everybody that kinetic calculations may not be the most efficient means of determining a reaction mechanism, however, they can be useful for drawing reasonable mechanistic conclusions. The connection between the kinetic parameters and the reaction mechanism is usually very complex, therefore, in the general case it is difficult to ascribe clear and simple physical meaning to the effective kinetic values. It is also almost always forgotten that the kinetic calculations give us, at least, three parameters and the use of only one, generally the activation energy, for interpreting physical processes can be of little value. When trying to ascribe physical meaning to kinetic parameters obtained from thermoanalytical data, we have also to remember that a lot of assumptions introduced 40 or 50 years ago into models of solid state reactions that are still used today can hardly be explained by modern solid state chemistry or physics. Mampel's assumption that only one nucleus is generated on each particle of the decomposed reactant seems to be rather unrealistic and impossible to corroborate with electron microscopy. In addition, the physical meaning of the exponent n in the Avrami–Erofeev equation seems to be hardly understandable. The introduced concept of 'number of steps (?) involved in nucleus formation' that has to be zero or one, or the formation of one-dimensional (?) nuclei are in contradiction to the definition of the nucleus being 'the smallest and most stable particle of the product'. It is difficult to imagine a one-dimensional particle of any solid.

In our opinion, anyone who applies thermal analysis to kinetic studies has his or her own personal view concerning the physical importance of the kinetic parameters and neither this, nor other 'Kinetic Projects' will change it. The project can only help in the proper determination of these numbers and in the elimination of conclusions based on over-simplified assumptions.

5. Conclusions

1. The results of the Kinetic Project indicate that the same process cannot be characterized by the same kinetic triplet under different experimental conditions. The decomposition of calcium carbonate is, obviously, described by the different kinetic parameters in different atmospheres. This means that the kinetic triplets are not intrinsic properties of the solid. A statement that a reaction has a certain value of activation energy, without specifying the reaction conditions, should be avoided. The expression "the activation energy of the $CaCO_3$ decomposition is 180 kJ mol^{-1}" should be at least completed by the phrase 'under nitrogen'.
2. The use of single-heating rate data for the determination of kinetic parameters should be avoided. There are plenty of examples in the literature showing that a single α–T relationship can be described with very high accuracy by many different sets of kinetic triplets. At least three heating rates are necessary in order to correctly describe the course of the reaction. In specific cases, single-heating rate methods can give reasonable kinetic triplets (as in the case of the Freeman–Carroll method when applied to a reaction characterized by a function of the type 'reaction order') but they are useless when the actual reaction model differs from the assumed one, or in the case of multi-step reactions. In the latter case, an adequate kinetic description cannot be obtained by using the single heating rate model-fitting methods that assume that a single kinetic triplet holds over the full range of conversions. As a first test for reaction complexity, one should use isoconversional methods. The complexity is easily detectable as a variation of the activation energy with α.
3. From a mathematical point-of-view, model-fitting methods that use multi-heating rate data and assume a multi-step nature of the process can describe the course of a solid reaction sufficiently well. For those methods, the kinetic triplet obtained under isothermal conditions describes exactly the course of the non-isothermal experiment and vice versa. In a real system, the influence of the experimental conditions disturbs, in a different way, the course of the isothermal and non-isothermal dependencies, α-time or α-temperature, respectively, making the comparison of isothermal and non-isothermal kinetic parameters more difficult. Due to the fact that non-isothermal parameters are calculated from the data obtained in a much wider temperature range, it is logical to

use them for the prediction of isothermal runs. The opposite procedure i.e. the prediction of non-isothermal relationships based on the isothermal parameters may be erroneous.

4. The original isoconversional methods (Ozawa, Friedmann) are very sensitive to experimental noise which leads, despite their mathematical simplicity, to a great scatter of the results, as can be illustrated by the data of the $CaCO_3$ decomposition under vacuum and nitrogen. It is strongly recommended that the advanced isoconversional method proposed by Vyazovkin [3] be used. Application of this method can easily indicate the multi-step character of the process expressed by the dependence of E_a on the reaction progress. It should be kept in mind, however, that in some cases when E_a does not depend on α, the process may still involve several steps that have practically equal activation energies, but different values of pre-exponential factors and/or may follow different reaction models.
5. The physical interpretation of the kinetic triplet should be always done with extreme care. It seems to be obvious that the tendency to characterize any solid state reaction by a single kinetic triplet, or, even worse, by only one kinetic parameter (mainly E_a) is generally incorrect. The sequence of thermal stability (the beginning of the decomposition) or the temperature range of the reaction, cannot be predicted by taking only the E_a value into account. Being only one component of a kinetic triplet set, the E_a value itself should be used very carefully when describing some real physical phenomena occurring during the course of the solid state reactions.

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