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HOW (UN)RELIABLE ARE KINETIC DATA OF REVERSIBLE SOLID-STATE DECOMPOSITION PROCESSES?

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ABSTRACT

Kinetic data such as activation energies, rate constants or reaction orders as well as mathematically evaluated mechanisms of reversible solid-state decomposition processes must be correlated with the experimental conditions under which any quantitative measurements have been performed. It is not only unrealistic but also impossible to describe a given decomposition process by a single activation energy and a single rate law. In particular, the omission of the effect of the partial pressure of gaseous products on the course of a solid-state decomposition, i.e., the exclusion of the pressure dependence of any experimentally and mathematically determined kinetic equation, leads to unreliable kinetic and mechanistic data. Moreover, characteristic features of the reacting solid such as its structure and morphology have to be taken into account in order to achieve reproducible results.

Why do we decompose solids and why are we interested in the course of such processes? One answer may be that the chemical and physical properties of the products obtained are somehow of greater worth to us than those of the starting materials. For example, for the last few thousand years people have been decomposing calcium carbonate; it would be rather unrealistic to pretend that the driving force for this was their desire to obtain the most accurate values for reaction orders or activation energies; the main reason is their need for calcium oxide with the desired qualities. It is well known that the properties of products obtained upon decomposition can be influenced by the experimental conditions chosen. For that matter, it is also understandable that kinetic and mechanistic data could be of great help in accurate process control and for the reproducible production of calcium oxide. The determination of such kinetic and mechanistic data, however, causes quite a lot of problems.

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From the literature it is evident that a considerable effort is required in order to grasp the complexity of solid-state decompositions [1]: within the six years from 1978 to 1984, no less than 12 500 papers were abstracted in Thermal Analysis Abstracts [2], the decomposition of solids being by far the most frequently investigated phenomenon (about 2300 publications). In a recent review article [1] it was stated that 368 papers concerning solid-state decomposition processes were published in 1981, one-third of which included kinetic data.

This interest in the evaluation of kinetic data can be explained by the following arguments:

(1) The characterization of a given process by means of quantitative data, which describe the influence of the temperature on the rate of the reaction, is certainly important from a practical and technical point of view.

(2) The conviction that the evaluation of kinetic data allows the determination or at least the recognition of the mechanism of a given decomposition process is widespread and based on the following assumption. Many years ago, theoretical models for the description of solid-state decompositions were introduced by Jander, Erofeev, Prout–Tompkins and others. If these mathematical models and kinetic equations are correlated with experimental data, the equation which gives the best fit is believed to demonstrate the validity of the mechanism theoretically described by this same equation.

During the last few years, however, the reliability of such data has frequently been questioned in articles, at congresses and at round-tables. Considering the fact that this problem affects the scientific work of approximately 1000 people each year, the establishment of reliable kinetic data and meaningful mechanistic models is of great importance.

At present, i.e., in the "age of the computer", many programs are available for the evaluation of activation energies (see, e.g., refs. 3 and 4), which, moreover, readily suggest the most probable reaction mechanism. In addition, the presence of microprocessors and computer facilities within modern thermoanalytical equipment leads inevitably to the dangerous situation where the "accurate" determination of E_a and reaction order n will be as simple as the determination of weight losses or of the temperature of onset of the process investigated. It seems an opportune time to ask: which procedures are reasonable for the evaluation of kinetic parameters? Do activation energies or mathematical equations describing a mechanism give us realistic information about the decomposition of solids?

We believe that all the computers and all the elaborate programs cannot replace morphological investigations by light and electron microscopy, structural considerations based on X-ray data or any other source of qualitative information. Such a conclusion may be trivial and well known, but it is too easily forgotten, and in the situation where "...scientific progress results not only from individual articles of outstanding merit, but also through the continual accumulation of knowledge contained in the larger number of more modest publications..." [1], we chose to repeat it.

Two simple questions have to be answered first:

(1) Is it possible to characterize a reversible solid-state decomposition by *one* value of the activation energy E_a and *one* value of the reaction order n?

(2) Is the mechanism of a reversible solid-state decomposition invariable under different experimental conditions?

In our opinion the answer to both these questions must be *no*. This means that evaluated kinetic data "...are characteristics of the experimental conditions rather than of the thermal reaction itself..." [5].

In order to support this argument, results obtained from investigations on the thermal decomposition of $CaCO_3$, the compound "...almost achieving the status of a model reactant..." [6], are presented. A few hundred experiments have been performed on a Mettler 2000-C thermoanalyser under isothermal and dynamic conditions, under vacuum conditions (10^{-5} mbar), under various partial pressures of CO_2, as well as in different inert gas atmospheres (N_2, Kr and He). An extensive publication is in preparation [7].

In thermoanalytical journals one often encounters the following concluding remarks: "...and the value of the activation energy for the decomposition of calcium carbonate is x kcal mol^{-1}...". In many cases, the value x is close to 40 kcal mol^{-1}, but—as a result of a scrupulous literature search—one also finds rather exotic representatives among the 168 different values ranging from 11.2 kcal mol^{-1} [8] up to 915 kcal mol^{-1} [9]. A statistical survey of all the activation energies characterizing the decomposition of calcite is presented in Fig. 1. This survey is self-evident and question 1 can readily be answered. It is obvious that the experimental conditions, under which the decomposition processes have been performed, represent crucial parameters for any reasonable determination of kinetic as well as mechanistic data. Many scientists are aware of this fact and, consequently, numerous articles are concerned with the influences of the sample weight, shape of crucibles, heating rates, etc. The correlation of these variables with the evaluated kinetic data enables certain conclusions to be drawn, but does not reveal the causes of these influences.

In our opinion, one paramount reason for the observed effects and, consequently, for the differing kinetic data, is the reversibility of the decomposition process, i.e., depending on the partial pressure of CO_2, reverse reaction $CaO + CO_2 \rightarrow CaCO_3$ is enhanced or suppressed. The pressure dependence of the course of solid-state decompositions, however, has only rarely been taken into account (see, e.g., refs. 10–13).

In the situation where the experimental conditions obviously have a large influence on the kinetics, we have to concentrate on correlations of, e.g.,

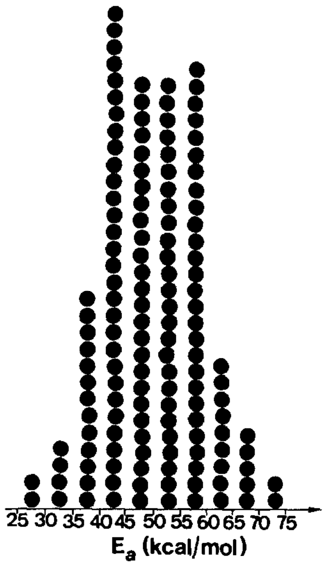

Fig. 1. Published values for the activation energy E_a characterizing the decomposition of calcite. Each dot corresponds to a published value.

heating rate, kind of atmosphere or sample weight with the quantitative kinetic data. Articles dealing with such correlations [14,15] assume, however, that the decomposition mechanism does not depend on the experimental conditions under which the measurements have been performed, i.e., the extrapolation and comparison of results obtained from experiments under vacuum or partial pressures of a few hundred millibars of CO_2 and with sample weights ranging from a few milligrams to several hundred milligrams is correct. Obviously, this problem is connected with our second question: is it possible to describe the solid-state decomposition of a given compound by one mechanism, i.e., by one equation?

Figure 2 summarizes the results obtained from isothermal measurements of the thermal decomposition of calcite as a function of the ambient atmosphere and the pressure. In order to facilitate a comparison between the results, the temperatures have been chosen in such a way that for the three measurements the fraction of decomposition α proceeded from 0 to 1 within about 40 min. Evidently, the shapes of the α vs. t curves exhibit considerable differences, which, in turn, indicates that different equations will be found for the description of the mechanism. We will not discuss the selection of the equation $g(\alpha)$ describing "the most probable mechanism" since this problem has been discussed in extenso [1,16–18]. Taking the correlation coefficient r as a proof of the validity of a particular rate equation, we evaluated the following results indicating the functions $g(\alpha)$ which best fit the experimental data:

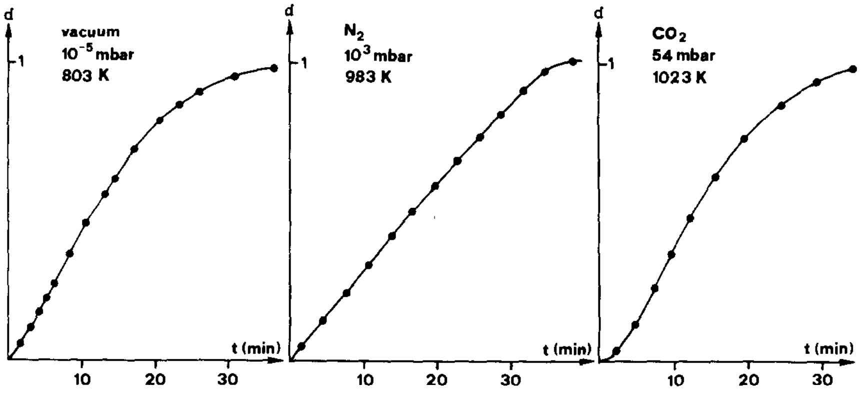

Fig. 2. α vs. t curves for the isothermal decomposition of calcite under vacuum (803 K), N_2 (983 K) and CO_2 (1023 K).

(1) Vacuum conditions (10^{-5} mbar): equation R_3, i.e., $g(\alpha) = 1 - (1 - \alpha)^{1/3}$; phase boundary reaction, spherical symmetry.
(2) Nitrogen (1000 mbar): equation P_1, i.e., $g(\alpha) = \alpha^{1/n}$; Polany–Wagner equation or power law (Mampel).
(3) CO_2 (54 mbar): equations F_1 and A_2, i.e., $g(\alpha) = -\ln(1 - \alpha)$ and $g(\alpha) = [-\ln(1 - \alpha)]^{1/2}$; nucleation is the rate-determining process (F_1, bulk growth of nuclei, one nucleus on each particle; A_2, Avrami–Erofeev equation describing a two-dimensional growth of nuclei).

These equations have been chosen from the 18 well-known equations commonly used in the literature in calculations using a conventional 48 K computer. The results show how difficult it is to declare a mathematically evaluated reaction mechanism to be the true reaction mechanism.

Summarizing these observations, we conclude that we must expect different decomposition mechanisms for different experimental conditions. As shown recently, even the shape of isolated single crystals used for the determination of kinetics and mechanism has a significant influence on the course of decomposition processes [19,20].

For solid-state decompositions with evaluated activation energies of 50–70 kcal mol^{-1}, the temperature range of the experimental measurements is usually 50–70 K and, consequently, if the range within which the reaction rates are determined is relatively narrow, deviations from the linear course of Arrhenius plots are negligible [21]. In the case where the temperature range exceeds 300 K, however, possible deviations, i.e., non-linearity of such plots, must be taken into consideration (calcite undergoes decomposition under vacuum conditions at temperatures as low as 730 K and, under partial pressure of CO_2, at temperatures as high as 1070 K!).

A further effect, which has to be kept in mind, is the influence of the temperature distribution and the heat of reaction (see, e.g., ref. 14): the actual temperature of a reacting system depends on the mass of the sample, the rate of decomposition and the heat of reaction. Even in the case of measurements using small samples (5–10 mg), differences between the actual and programmed temperatures easily reach the order of 3–5 K. For larger samples, these differences can be enhanced and one can assume that they are responsible for the observation of a decrease in the evaluated activation energies with increasing sample weights.

Apart from these effects, the main problem to be solved remains: what are the influences of the pressure of the gaseous product on the course of a reversible solid-state decomposition? In general, all equations used for the evaluation of the kinetics are based on the assumption that the rate of the reaction is a function of the temperature. This assumption, which is described by the following well-known equation

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

is only valid for experiments in an ideal vacuum. In reality, however, the measured rate of the reaction is always a function of the temperature and pressure.

Depending on the actual temperature of the decomposition as well as the actual equilibrium pressure, the possible reverse reactions play an important role inasmuch as the rate of a given decomposition varies from a maximum (vacuum conditions) to zero (under equilibrium pressure) at one and the same temperature. In Fig. 3 the mutual theoretical relationships between the reaction rate v, temperature T and pressure p are illustrated (see also refs. 21 and 22). Experimental data confirming the validity of the relation $v = f(T, p)$ have been obtained [7]. Summarizing the observations, one has

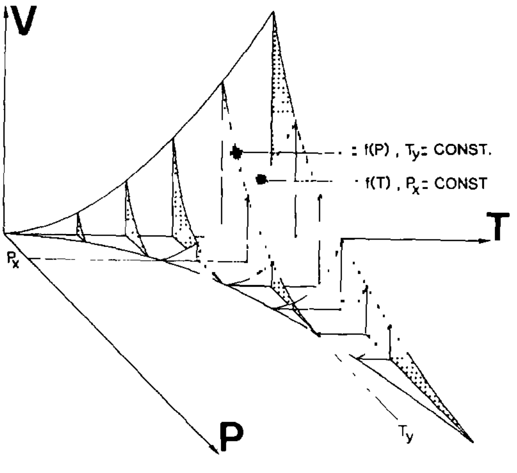

Fig. 3. Diagram representing the pressure and temperature dependence of the reaction rate v of a given decomposition process (v = reaction rate, T = temperature, p = pressure of the gaseous product).

to conclude that any change in the partial pressure of the gaseous product or for that matter in the total pressure will influence the relationships $v = f(T)$ and, consequently, that between log k and $1/T$. The problem has already been discussed [11–13,22], but its importance is still neglected.

Evidently, the (un)reliability of kinetic data evaluated with equations which only describe the dependence of the reaction rate on the temperature, must be considered carefully. Nevertheless, a review of hundreds of papers dealing with kinetics shows that the mystery of this problem is even more hidden than the mystery of the derivatives of non-isothermal rate equations [23].

Apart from those theoretical considerations, there are real phenomena which can easily be observed by, e.g., correlating pressure conditions with the kinetics and mechanism for the decomposition of calcite: high partial pressures of CO_2 shift the reaction to higher temperatures, which indicates the importance of the reverse reaction. In addition, this effect is responsible for morphological changes in the reactant (see sintering of $CaCO_3$ samples [24]) even before the actual decomposition and, as a result, the surface and the number of possible nucleation sites are altered.

It has been observed that a change in the pressure directly influences the fraction of the reaction surface covered by metastable CaO* [22,25–27]. This leads to reaction-specific, actually pressure-dependent morphologies for the product phase, as observed for polycrystalline $CaCO_3$ [24] and recently for calcite single crystals [28]. The probability of the formation of metastable CaO* has been observed to be higher under vacuum conditions. This fact may be responsible for a higher activation energy for the decomposition of $CaCO_3$ under such conditions [7,29].

All the above remarks show that we are still far from the situation where we can believe the reliability of kinetic parameters and mechanistic data obtained from the mere evaluation of thermoanalytical measurements by most elaborate fitting procedures. At a time when one expects 365 new publications each year, dealing with new and improved methods for the evaluation of the kinetics and mechanism of solid-state decompositions by computer calculations, one should remember a sentence from the very interesting paper by Carr and Galwey [1]: "...The time appears to be opportune for a general and critical reappraisal of the aims, methods and achievements of the non-isothermal methods of kinetic investigations, assessing realistically both the benefits and limitations of this approach...". In our opinion, this sentence is true for the isothermal methods as well.

The determination of kinetic and mechanistic data for a realistic description of solid-state processes is important and necessary. There is no doubt that information about the influence of the temperature or the heating rate on the course of a decomposition under given experimental conditions is also of importance. However, we have to be very careful when interpreting mathematically evaluated parameters used for the characterization of the formation of a compound, i.e., a mechanism of a decomposition. If the value of the reaction order *n* in the Avrami–Erofeev equation has been determined as three, one should not conclude that the nuclei of the product phase are perfectly spherical! More specific methods are available with which to check this.

REFERENCES

1 N.J. Carr and A.K. Galwey, Thermochim. Acta, 79 (1984) 323.
2 G. Liptay, J. Therm. Anal., 25 (1982) 235.
3 L. Reich and S.S. Stivala, Thermochim. Acta, 52 (1982) 337.
4 L. Reich and S.S. Stivala, Thermochim. Acta, 80 (1984) 185.
5 M. Arnold, G.E. Veress, J. Paulik and F. Paulik, Thermochim. Acta, 52 (1982) 67.
6 M.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
7 M. Maciejewski, to be published.
8 H. Mauras, Bull. Soc. Chim. Fr., (1960) 260.
9 P.K. Gallagher and D.W. Johnson, Thermochim. Acta, 14 (1976) 225.
10 J. Rouquerol, J. Therm. Anal., 5 (1973) 203.
11 M. Pavlutschenko and E.A. Prodan, Dokl. Akad. Nauk. USSR, 136 (1962) 651.
12 G. Bertrand, M. Lallemant and G. Watelle, J. Therm. Anal., 13 (1978) 525.
13 J. Zawadski and S. Bretsznajder, Z. Phys. Chem., Teil B, 22 (1933) 79.
14 P.K. Gallagher and D.W. Johnson, Thermochim. Acta, 6 (1973) 67.
15 J. Simon, J. Therm. Anal., 5 (1973) 271.
16 C. Różycki and M. Maciejewski, Thermochim. Acta, 96 (1985) 91.
17 M.E. Brown and A.K. Galwey, Thermochim. Acta, 29 (1979) 129.
18 Z. Smieszek, Z. Kolendo, J. Norwisz and N. Hajduk, J. Therm. Anal., 25 (1982) 377.
19 A. Reller and H.R. Oswald, J. Therm. Anal., 29 (1984) 1013.
20 A. Reller and H.R. Oswald, J. Solid State Chem., 62 (1986) 36.
21 N.Z. Lyakhov, M. Maciejewski and A. Reller, J. Solid State Chem., 58 (1985) 398.
22 M. Maciejewski and J. Batdyga, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 105.
23 J. Sestak, Thermochim. Acta, 83 (1985) 391.
24 M. Maciejewski and H.R. Oswald, Thermochim. Acta, 85 (1985) 39.
25 D. Beruto and A. Searcy, Nature (London), 263 (1976) 221; J. Chem. Soc., Faraday Trans. 1, 70 (1974) 2175.
26 J. Eving, D. Beruto and A. Searcy, J. Am. Ceram. Soc., 62 (1979) 580.
27 E.K. Powell and A. Searcy, Comm. Am. Ceram. Soc., (1982) C-42.
28 M. Maciejewski, A. Reller and H.R. Oswald, in preparation.
29 E.K. Powell and A. Searcy, Metall. Trans. B, 11 (1980) 428.