Plenary lectures

ON SOME ERRORS COMMITTED IN THE STUDIES OF KINETICS OF THERMAL DISSOCIATION OF SOLIDS

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Abstract

The methods of preparing the samples for kinetic studies are critically discussed with particular consideration to the effect of granulometric characteristics and structure of the material, conditions of performing the measurements, and choice of proper kinetic equation on the reliability of the results obtained.

Keywords: kinetics, thermal dissociation of solids

Introduction

In our previous works [1–3] we have pointed to a number of internal and external factors influencing the course of thermal dissociation of solids. Some of them cannot be taken into account in kinetic studies, but there are many others that have a substantial effect on both the course of thermal dissociation and the interpretation of results obtained. These should be taken into account, otherwise substantial errors in evaluation of the results obtained in measurements are unavoidable.

A cannot mistake made as early as in the preparation of samples for the study is the lack of granulometric characteristics of the materials to be studied. The object of the study is usually a polydispersive material obtained by crystallization or naturally occurring materials mechanically disintegrated. The essential characteristics of such materials comprise the granulometric analysis and the type of grain size dispersion profile. As a rule, solid materials prepared by mechanical grinding are characterized by normal grain size distribution,

whereas those obtained by crystallization are described by the Rosin–Ramler–Stirling distribution [4].

The grain size plays an important part in thermal decomposition reactions since these processes are localied mostly on the surface of the reacting phase and thus the degree of dispersion of the solid phase has a bearing on the reaction rate [5].

Usually, the reaction rate increases with decreasing grain size of the solid, but this simple relationship between the grain size and the reaction rate is not always observed. Some cases are known where an increase of dispersion does not increase the rate of thermal dissociation or even reduces the rate of reaction.

The existence of a maximum in relationship between reaction rate and degree of dispersion has been predicted by Mampel [6]. It has been also confirmed experimentally [7, 8] both in thermal dissociation and in other reactions involving solids. These and other similar facts, known for long show that in kinetic studies involving solids the granulometric characteristics of the material must be taken into consideration.

The known kinetic equations describing the macromechanism of thermal dissociation of solids are usually based on the model of single spherical grain. If the reacting system contains W grains of identical initial dimensions the form of the kinetic equation remains unchanged since the degree of transformation (decomposition) for W identical grains is calculated in the same way as for a single grain.

In a case of a polydisperse system (of different grain size) the degree of transformation of grains with different initial dimensions (R_i) is different and can be described in terms of the following relationship:

$$\overline{\alpha} = 1 - \int\limits_{R_i = 0}^{R = R_m} [1 - \alpha\ (R_i)]\ f(R)\ dR \tag{1}$$

where: $\overline{\alpha}$ – average degree of transformation, when $0 \le \alpha(R_i) \le 1$; $\alpha(R_i)$ – degree of transformation for grain fraction of initial radius R_i; $f(R)$ – function of density for grain size distribution, which characterizes the polydispersive system; R_m – initial radius of the coarsest grains in the reaction system.

In the processes of thermal dissociation of the type $A_{solid} \rightarrow B_{solid} + C_{gas}$ the rate of migration of the border between the solid starting material and the reaction product (i.e. the zone of chemical reaction) in a single grain (or in a system composed of identical grains) can be described – at least in simple cases – by means of known equations [9–13]:

a) for the kinetic region (where the overall process rate is limited by the rate of chemical reaction):

$$1 - (1 - \alpha)^{1/3} = \frac{k_1}{R_i} t \qquad (2)$$

b) for the diffusion region (where the overall rate of the process is limited by the rate of diffusion of the gaseous product in the layer of solid product formed on the substrate grain):

$$[1 - (1 - \alpha)^{1/3}]^2 = \frac{k_2}{R_i} t \qquad (3)$$

where: k_1, k_2 – rate constants for the kinetic and the diffusion regions of the process, respectively; t – times lapse from the beginning of decomposition of the grain.

The possibility of using Eqs (2) and (3) for mathematical description of the process of thermal dissociation of solids for polydispersive systems (with non-uniform grain size) has been verified [4] for two most frequently occurring grain size distributions:

– normal distribution, for which the density function:

$$f(R) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(R - \frac{\overline{R}}{\sigma}\right)^2\right] \qquad (4)$$

and the distribuant:

$$F(R_z) = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{R_z} \exp[-B (R_z - 1)^2] \, dR_z \qquad (5)$$

where: σ – variance; $\overline{R}$ -mean value of the grain radius;

$$B = \frac{\overline{R}}{2\sigma^2} ; \quad R_z = \frac{R}{\overline{R}}$$

– Rosin, Ramler, Stirling distribution, for which the density function:

$$\varphi(R) = n \left(\frac{1}{\overline{R}}\right)^n R^{n-1} \exp\left[-\left(\frac{R}{\overline{R}}\right)^n\right] \qquad (6)$$

and distribuant:

$$\Phi(R_z) = 1 - \exp(-R_z^n) \tag{7}$$

where: n – the grain size distribution parameter; the value of n may be determined from the relationship between loglog $1/y$ and $\log R$ (weight fraction of grains with $R > R_i$).

If we insert a dimensionless variable $R_z = R/\overline{R}$ to the kinetic Eqs (2) and (3) and calculate the maximum time of transformation $(t_{m,i})$ for a fraction with grain radius R_i and determine, for the kinetic region

$$\theta_{k,i} = k_{1,i} \cdot \frac{t_{m,i}}{\overline{R}} = R_{z,i} \tag{8}$$

and for the diffusion-controlled region

$$\theta_{d,i} = k_{2,i} \cdot \frac{t_{m,i}}{\overline{R}} = R_{z,i}^2 \tag{9}$$

and we insert, also, these values to Eqs (2) and (3), respectively, we can easily note that they become identical.

A simple rearrangement of Eq. (2) or (3), insertion of $f(R)$ and $\varphi(R)$, and taking account of the fact, that $dR = \overline{R} \cdot dR_z = \overline{R} \cdot d\theta$ leads to the following relationships:

– for the normal distribution:

$$\overline{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta_m} \left(1 - \frac{\theta_1}{\theta}\right)^3 \exp\left[-B(\theta-1)^2\right] d\theta \right\} \tag{10}$$

– for the Rosin-Ramler-Stirling distribution:

$$\overline{\alpha} = 1 - \left[n \int_{\theta_1}^{\theta_m} \left(1 - \frac{\theta_1}{\theta}\right)^3 \theta^{n-1} \exp(-\theta^n) d\theta \right] \tag{11}$$

Relationships (10) and (11) have not analytical solutions; hence we have calculated numerically the values of $\overline{\alpha}$ from Eq. (10), for $B \in \langle 0.01, 1000 \rangle$ and for $\theta \in \langle \theta_1 = 0.001, \theta_m = 2 \rangle$, and the values of $\overline{\alpha}$ from Eq. (11) – for $n \in \langle 1,3 \rangle$ and for $\theta \in \langle \theta_1 = 0.001, \theta_m = 2 \rangle$. As a result we have obtained, in the system $\overline{\alpha}$ vs. θ kinetic curves for various values of B and n, respectively. Further treatment of these curves has been based on the initial kinetic Eqs (2) and (3).

The calculations have shown, that in the case of normal distribution of grain size in the material under study the process of thermal dissociation of polydispersive material may be described solely by Eq. (2) and solely for B>20. The fulfilment of the condition:

$$B = \frac{\overline{R}^2}{2\sigma^2} \geq 20 \qquad (12)$$

means, that for $\overline{R} = 1$ the means deviation can not exceed the value of 0.158 ($\sigma \leq 0.158$); hence the mathematical treatment of the process under consideration by means of Eq. (2) becomes possible, if $R \in \langle 0.5\overline{R}, 1.5\overline{R} \rangle$, i.e. where the range of R variations is relatively small.

In the case of Rosin–Ramler–Stirling distribution the process of thermal dissociation of polydispersive material can be described only by Eq. (3) and only for $n = 1$ or slightly greater than one, since the nature of the decomposition depends on the value of parameter n [14, 15]. This means, that if $n = 1$ or is slightly greater than 1, the Rosin–Ramler–Stirling distribution approaches to the exponential distribution, and in such cases a mathematical description of the process under consideration becomes possible in quite a wide range of variability of R, i.e. $R/\overline{R} \in \langle 0,4 \rangle$. For higher values: $n = 2$ or $n = 3$ the range of variability of R is also greater, as compared with the normal distribution, but with increasing value of n the utilization of Eq. (3) becomes possible for the lesser and lesser range of variability of $\overline{\alpha}$.

The results presented show, that the type and the nature of grain size distribution of the reacting material must be taken into account in the analysis of kinetic data, since they determine the possibility of using a mathematical description. Neglection of the granulometric composition leads to a situation, encountered in many references, where an equation describing kinetic data is an equation valid for the diffusion-controlled region (when the grain size distribution in the sample under study corresponds to the Rosin–Ramler–Stirling distribution), whereas the obtained value of activation energy is high and characteristic for the kinetic region.

A problem of similar importance, that should be taken into account before starting proper kinetic studies, is the behaviour of the material to be studied during the temperature increase. The state of the material may be observed in microscope, e.g. in a high-temperature microscope. The necessity of such observations arises from self-disintegration of the dissociating grains, which has considerable or even decisive bearing on the course of the decomposition and leads to erroneous interpretation of the kinetic data. Such observations are particularly important in any cases of thermal dissociation of naturally occurring materials, in which the processes of physical preparation of samples (disintegra-

tion, grinding) evoke stresses in crystal lattices. These can be, in addition to the natural effect of crystal lattice defects, a factor promoting the self-disintegration of the dissociating grains. Similar phenomena are to be expected in the studies of freshly precipitated materials, in which the ageing processes (recrystalliza-tion) have not been completed.

It is generally known [11, 12, 16] that for a spherical model of the reacting grain dissociating under isothermal conditions, i.e. in conformity with Eq. (2) the following relationship holds for equivalent rate constant (k') found experi-mentally and initial grain size (R_i):

$$k' \cdot R_i = \text{const} \tag{13}$$

but in many cases the linear relationship between k' and $1/R_i$ has not been ob-served.

In our studies of the grain size effect on thermal dissociation of several frac-tions of natural calcite [17] we have found, instead of the expected relation (13), another relation between k' and R_i:

$$\frac{k'}{R_i^{1/2}} = \text{const} \tag{14}$$

according to which the results of our studies have been linearly correlated in the system k' vs. $R_i^{1/2}$.

The reason for occurrence of the relation (14) has probably been the change of dispersion degree of the sample material, observed in microscope and result-ing from self-disintegration of the grains of starting material, which happens frequently during the dissociation of carbonates [18]. This process takes place either before the dissociation, as in the case of siderite [19], or in the course of dissociation, as in smitsonite [20].

In the case that we have observed the samples after dissociation did not ex-hibit any increase of the number of grains, as compared with the initial number, but the grains were deeply cracked with wide fissures and they crumbled easily into smaller particles. Such a specific self-disintegration occurs in the course of dissociation, and not during heating of the sample to the temperature of mea-surement.

The change of the degree of dispersion of the material under study does not usually influence the activation energy (E) of the process, but it provokes a change of the other important kinetic parameter – the pre-exponential factor (A) in the Arrhenius' equation. Taking account of the self-disintegration of sample grains enables to avoid the erroneous evaluation of that parameter.
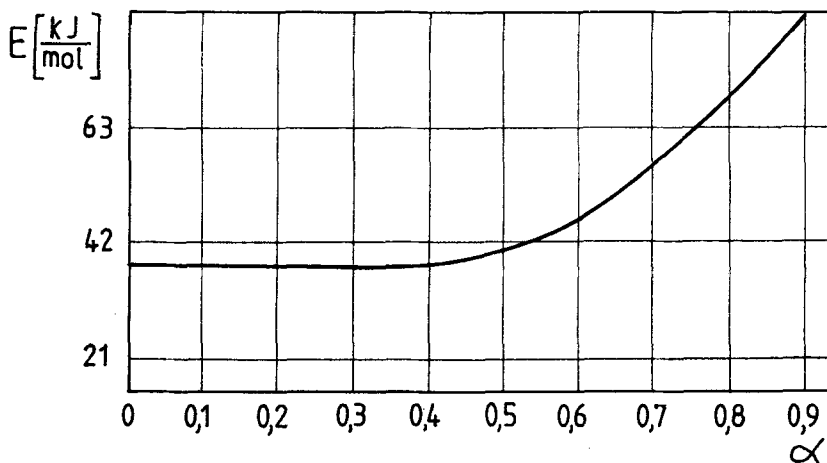
Fig. 1 Relationship between E vs. α of dehydration of $Na_3NiP_3O_{10} \cdot 12H_2O$ [21]

The structure of the material under study can also be a factor influencing the change of kinetic parameters of the process. It concerns, first of all, the changes in activation energy with the progress of reaction. Cases are known [21], where in the initial stage of reaction the activation energy does not change with increasing degree of transformation, but it increases rapidly after the value of α has passed through a certain limit value. The increase of E value may arise from in crease of pressure of a gaseous reaction product in the reaction zone, i.e. at the interface starting material – product of reaction, provoked by increase of diffusion resistance for the gaseous product in the solid product layer accumulating in the reacting material grain. The study of relationship between E and α seems to be indispensable for avoiding erroneous determination of this important kinetic parameter.

Essential kinetic studies are carried out under highly reduced pressure (in vacuum) to avoid the impact of the reverse reaction (association) on the course of dissociation. Such measurements require the determination of the range of pressure at which the reverse reaction has no more influence on the course of the process. The differences may be considerable even within one and the same group of compounds. For example, for calcium and cadmium carbonates the effect association practically disappears at the pressure of the gaseous reaction product of the order $10^{-3} \div 10^{-4}$ hPa, whereas in the case of some rare earth carbonates the effect of reverse reaction ceases to be noticeable at as low pressures as $10^{-5} \div 10^{-6}$ hPa. Improper selection of the range of pressure may be therefore one of the factors influencing the wrong evaluation of kinetic parameters of the

process and becomes a source of considerable differences in the values of parameters of one and the same reaction found in literature.

The range of temperature, at which the studies are being carried out, is also an important factor, decisive for proper interpretation of the kinetic data. Usually it is assumed, that the limits of that range are determined by the need of securing isothermal conditions for the process during rapid transformations of the sample (upper limit) and by the possibility of steady operation of the measuring device in (sometimes) very long time of experiment (lower limit).

Experiments performed in the range of temperatures determined in this way provide a series of isothermal kinetic curves covering the whole field of the α vs. t graph. Interpretation of results obtained in such a series of experiments – unduly regarded us properly executed – meets with considerable difficulties, since it becomes impossible to describe the whole series of experiments in terms of a single kinetic equation. The reason of these difficulties lies in the change of the driving modulus of the process, which is the distance from equilibrium conditions.

Under conditions close to equilibrium (small Δp) the reaction rate is a linear function of the driving modulus [22]; the increase of the distance from equilibrium state resulting from increase of supersaturation provokes the formation greater number of nuclei of the new phase. This results in a non-linear increase of reaction rate (Fig. 2) up to a moment, at which the whole surface of the reacting material is covered with the nuclei. At this moment the reaction rate reaches its maximum. The maximum reaction rate is attained near the upper
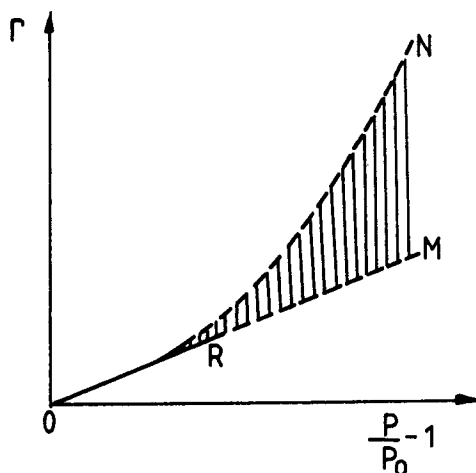

Fig. 2 Relationship between the reaction rate of thermal decomposition (r) and the deflection of state of equilibrium p/p_o-1. The line 0M designates relationship of rate of reaction occurring at the border of substrate – product. Area NRM (crossed lines) shows increase of rate due to forming nuclei of a new phase [22]

limit of temperature region, as at the large value of the driving modulus (super-saturation) the whole surface of the reacting material is rapidly covered with new phase nuclei, and the following course of the process with decreasing rate is a consequence of decreasing reaction zone (the starting material – product interface). The attempts (even successful ones) of describing three different reaction mechanisms (growth of nuclei, development of nuclei with simultaneous increase of their number, and migration of the reaction zone) in terms of a single kinetic equation can not be considered as correct, at least for the reason, that such a description does not contribute to a better knowledge of the process, though it may be, in some cases, useful for practical purposes.

The choice of a proper kinetic equation constitutes a fundamental problem in processing the kinetic data, since the kinetic law is a necessary condition, although by far not sufficient one, for adequate interpretation of macromechanism of the process. It is evident, that every curve, even a kinetic one, may be described, in terms of n-th order polynomial, with a satisfying accuracy. Similarly, with sufficient precision, it is possible to describe kinetic curves in terms of equations that comprise several constants free of any limitations, or ones whose interpretation has nothing common with the reality. As an example we can mention the frequently applied Kolmogorov-Erofeev-Avrami equation, in which the coefficient n is usually regarded as the order of reaction ($n = 1$ corresponds to 1st order, $n = 0.063$-2nd order) which is a pure nonsense in application to topochemical processes. The same equation with $n = 0.5$ should be reported to description of diffusion-controlled processes. Thus, only such kinetic equations should be regarded as correct ones, which involve only one constant, i.e. the rate const. The bases for introduction of such equations may be various models of the process, which does not mean, however, that a mathematical description of kinetic data may arise automatically from such a model. A correctly compiled set of kinetic equations may be found e.g. in a paper by Johnson and Gallagher [23]. A critical analysis of the values of kinetic parameters found, estimation of the trend in their variation resulting from changes in process parameters, and other observations concerning the reacting system enable, in many cases, to evaluate the adequateness of one or several models, or to confirm the existence of formal connection between $g(\alpha)$ and behaviour of the given system.

Most of thermal dissociation processes of solids are complex, multistage reactions which means, that kinetic studies should be preceded by thorough recognition of the intermediate steps of decomposition of the given compound, if a definite physical meaning should be imposed to them.

Reaction proceeding in the solid phase may be studied by thermogravimetric methods (TG, DTG, T and DTA), supplemented by X-ray diffraction and infra-

red absorption methods for determination of changes in structure and phase composition of solids. The X-ray diffraction and infrared absorption studies are carried out either for the so-called 'frozen samples' or in a high-temperature camera with programmed temperature increase. In the latter case either complete analyses are made, as frequently as possible, of the given sample at predetermined temperatures, or an appearance of a definite reflex is searched in an anticipated range of the values of θ. The changes in chemical composition are established by means of chemical analyses.

Thermogravimetric analyses should be accompanied by observation of pressure changes in the reaction space and determination of composition of the gas phase. This is possible in cases where the thermoanalytical device (e.g. a Mettler's apparatus) is coupled with a mass spectrometer.

The properly designed and performed complex studies enable to propose a scheme (and a stoichiometry) of decomposition of the given compound, i.e. the determination of temperature ranges of definite steps of the dissociation, description of the chemical and phase composition of the intermediate and end solid products, as well as the characteristic of changes in gas phase, that accompany the reactions proceeding in the solid phases. The proposed scheme of decomposition is subjected to thoroughful and detailed verification by thermodynamical analysis.

The above presented procedure is applied also in preparation of samples to be used in kinetic studies, since any studies of the kinetic of thermal dissociation require the sample material to be precisely identified. A good example of such procedure is that used in [24], where kinetic studies of synthetic alunites under isobaric and isothermic conditions were preceded by determination of stoichiometry of all the steps of dissociation. The lack of precise identification of the material studied is an object of numerous and serious reservations in the steadily increasing number of papers, where the so-called dynamic methods are applied in kinetic studies.

To summarize up one should state, that only good recognition of the object of studies and taking into account as many as possible factors that might possibly influence the course of the process, as well as the choice of a proper mathematical model may endow kinetic studies with a reliable physical meaning.

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Zusammenfassung — Vorliegend erfolgt eine kritische Betrachtung der Vorbereitung von Proben für kinetische Untersuchungen mit speziellem Augenmerk auf den Effekt granulometrischer Charakteristika und der Materialstruktur, von Messungsbedingungen und der richtigen Auswahl der kinetischen Gleichung auf die Zuverlässigkeit der erhaltenen Ergebnisse.