Journal of Thermal Analysis, Vol. 41 (1994) 455-469

Kinetics

In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

ACCOMMODATION OF THE ACTUAL SOLID-STATE PROCESS IN THE KINETIC MODEL FUNCTION
I. Significance of the non-integral kinetic exponents

N. Koga and H. Tanaka

Chemistry Laboratory, Faculty of School Education, Hiroshima University, 3-1-33 Shinonome,
Minami-ku, Hiroshima 734, Japan

Absract

The degree of coordination between the kinetic information from the thermoanalytical measurements and the kinetic theory of the solid-state reactions was investigated through the microscopic study of the thermal dehydration of several inorganic salt hydrates. An accommodation function was applied to the conventional kinetic model functions $f(\alpha)$, in an attempt to reduce the disagreement between the actual process and the idealized one assumed in formulating $f(\alpha)$. The significance of the non-integral kinetic exponent in the kinetic model function was discussed with its physico-chemical meanings.

Keywords: kinetics, solid-state reactions

Introduction

Although thermoanalytical (TA) data are of a macroscopic nature averaged over the assemblage of sample, the experimentally resolved shape of the TA curves has widely been used as a possible source for the kinetic understanding of solid-state reactions [1, 2]. The shape of the TA curve is characterized by the kinetic model function $f(\alpha)$ derived on the basis of the physico-geometric assumption of the reaction interface movement [3], because the solid-state reaction is especially characterized by the existence of the specialized zone of locally enhanced reactivity at the reactant/product contact, i.e., reaction inter-

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

face. The kinetics are further characterized assuming the Arrhenius-type temperature dependence of the rate constant. The application of the Arrhenius equation, as well as mis-estimation and/or over-simplification of the $f(\alpha)$, are likely to be responsible for different kinetic parameters obtained under different experimental conditions for a given reaction. It is always important to recognize the deviation of the real process from the idealized process assumed in formulating the kinetic equation. The problem concerning the Arrhenius-type temperature dependence of the rate constant is related to the influence of the factors other than the measured temperature, which, in a strict sense, is not controlled in conventional TA techniques. The gradients in the temperature and gaseous pressure generated by the reaction itself seem to be important in evaluating the reliability of the TA curves as a possible source of the kinetic data [4, 5]. Controlled Transformation Rate Thermal Analysis (CRTA) [6] and/or Quasi-isothermal Quasi-isobaric Thermal Analysis (QQTA) [7] seem to be a possible solution. On the other hand, the problem concerning the $f(\alpha)$ is related to the really heterogeneous and complicated reaction behaviour which we are interested in. Scanning electron microscopy (SEM) and optical microscopy have been widely used for such morphological studies. In these techniques, however, the observation of the textural structure of the reactant/product interface is sometimes disturbed by an opaque product layer. Employing the thin-section technique [8, 9], the internal surface including the reactant/product interface can be observed under polarized light. The SEM of the replica makes it possible to observe the more detailed textural structure of the reaction interface as the replicated view [10, 11]. The systematic observation of microscopic views of the reaction morphology plays decisive roles in extending the understanding of the kinetic characteristics of the solid-state reactions and enables us to recognize the deviation of the idealized model assumed for the actual process.

In this paper, the problems of TA kinetics connected with the distortion of the actual process from the idealized model are reviewed. The complexity of the reaction morphology of the solid-state reaction is recognized through the microscopic observation of the thermal dehydration process of several inorganic salts hydrates. The possible way to accommodate the complexity of the actual process in the kinetic equation is briefly discussed by reviewing some differently oriented studies.

The kinetic equation and accommodation function

Assuming the physico-geometry based kinetic model function $f(\alpha)$ and the Arrhenius equation, the TA curves can be analyzed kinetically by the following equation:

$$\frac{d\alpha}{dt}=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where A and E are the Arrhenius parameters. Table 1 lists the kinetic model functions $f(\alpha)$ employed usually for the kinetic study of the solid-state reactions, together with their integral $G(\alpha)$ and differential $f'(\alpha)$ forms. In practice, however, the disagreement between the idealized process assumed in formulating the $f(\alpha)$ and the actual process investigated, as averaged by the TA measurements, has always to be taken into account, because the disagreement leads to the distortion of the Arrhenius parameters expressed by [12, 13]

$$\frac{E_{app}}{E}=\frac{h(\alpha_p)f'(\alpha_p)}{f(\alpha_p)h'(\alpha_p)} \tag{2}$$

$$\ln\frac{A_{app}}{A}=\frac{E}{RT_p}\left[\frac{h(\alpha_p)f'(\alpha_p)-f(\alpha_p)h'(\alpha_p)}{f(\alpha_p)h'(\alpha_p)}\right]+\ln\frac{h(\alpha_p)}{f(\alpha_p)} \tag{3}$$

where E_{app} and A_{app} are the apparent Arrhenius parameters distorted by the use of idealized model $f(\alpha)$ instead of the function which describes the real process $h(\alpha)$. The subscript p indicates the values for the maximum of the TA peak. To avoid the distortion in Eqs (2) and (3), an empirical function $h(\alpha)$ of the Sestak-Berggren (SB) model [14] can be used.

$$h(\alpha)=\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p \tag{4}$$

Applying $h(\alpha)$ in Eq. (4) to Eq. (1) instead of $f(\alpha)$, the apparent but characteristic Arrhenius parameters can be obtained from the practical TA curves [15]. The exponents m, n and p are then understood as the kinetic parameters which precisely describe the shape of practical TA curves. In such a kinetic approach, however, the physico-geometric feature of the process as assumed in the formulation of $f(\alpha)$ is difficult to predict, because of the complicated functional dependence in Eq. (4). Prediction of the physico-geometric behaviour of the process under investigation is important, as well as the Arrhenius parameters, especially when the physical properties of the product are influenced by the geometry of the process as is seen for oxide superconductors [16] and bioglass-ceramics [17]. Introducing the accommodation function $a(\alpha)$ [18], the SB model is interpreted as the function accommodating the distortion of the actual process from the idealized model:

Table 1 The kinetic model functions $f(\alpha)$ usually employed for the kinetic analysis of solid-state reactions, together with their integral $G(\alpha)$ and differential $f'(\alpha)$ forms

Model	Symbol	$f(\alpha)$	$G(\alpha)=\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}$	$f'(\alpha)=\frac{f(\alpha)}{d\alpha}$
Phased boundery controlled reaction	R_n (n=1, 2 and3)	$n(1-\alpha)^{1-1/n}$	$1-(1-\alpha)^{1/n}$	$-\frac{n-1}{(1-\alpha)^{1/n}}$
Nucleation and growth (Avrami-Erofeev)	A_m (m=0.5, 1, 1.5, 2, 2.5, 3 and 4)	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$[-\ln(1-\alpha)]^{1/m}$	$\frac{m-1}{[-\ln(1-\alpha)]^{1/m}}-\frac{m}{[-\ln(1-\alpha)]^{1/m-1}}$
One-dimensional diffusion	D_1	$\frac{2}{\alpha}$	α^2	$-\frac{2}{\alpha^2}$
Two-dimensional diffusion	D_2	$-\frac{1}{\ln(1-\alpha)}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	$-\frac{1}{(1-\alpha)[\ln(1-\alpha)]^2}$
Three-dimensional diffusion (Jander)	D_3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$	$\frac{1/2-(1-\alpha)^{-1/3}}{[1-(1-\alpha)^{1/3}]^2}$
Three-dimensional diffusion (Ginstring-Brounshtein)	D_4	$\frac{3}{2[(1-\alpha)^{-1/3}-1]}$	$1-\frac{2\alpha}{3}-(1-\alpha)^{2/3}$	$-\frac{1}{2(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^2}$

$$h(\alpha) = f(\alpha)a(\alpha) \tag{5}$$

Then the kinetic expression of the TA curves can be taken as the distorted case of the homogeneous-like kinetics and of $f(\alpha)$. It is apparent, however, that $a(\alpha)$ is extremely difficult to formalize, based on the real physical chemistry, and is possibly expressed by the empirical (analytical) formula.

Reaction morphology and accommodation function

Contracting geometry type reaction

The kinetic model function of the contracting volume controlled by chemical reaction, i.e., R_3, is derived on the basis of an isotropic shrinkage of the cubic and/or spherical reactant with a constant rate of interface advancement. In practice, however, the shape of the reactant is usually far from cubic or spherical and the reactivity of the reaction interface shows more or less anisotropy depending on the crystallographic direction of reactant and/or product.

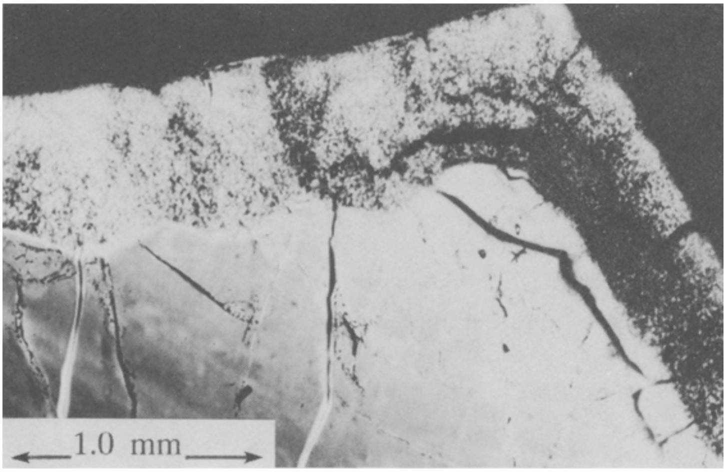

Fig. 1 Typical polarizing microscopic view of the (010) internal surface of a partially dehydrated single crystal of $Li_2SO_4{\cdot}H_2O$

Figure 1 represents the typical polarizing microscopic view of the (010) internal surface of partially dehydrated single crystalline $Li_2SO_4{\cdot}H_2O$. A wavy front is formed on the reaction front proceeding along the *c*-axis, whereas a flat front results on that advancing along the *a*-axis. This difference in the reaction fronts seems to arise from changes in the nucleation density on the corresponding original surface and in the degree of stress and/or strain at the phase boundary, depending on the crystallographic direction [19, 20]. This may lead to different reactivity at the reaction interface and consequently to different kinetic behaviour. In such a case, the reaction geometry of the overall reaction cannot be expressed using an integral value of n. Applying a non-integral value N instead of the integral value n, the kinetic equation can accommodate the distortion of the practical reaction geometry from the idealized one. A similar rate behaviour is also expected for the thermal decomposition of crushed crystals.

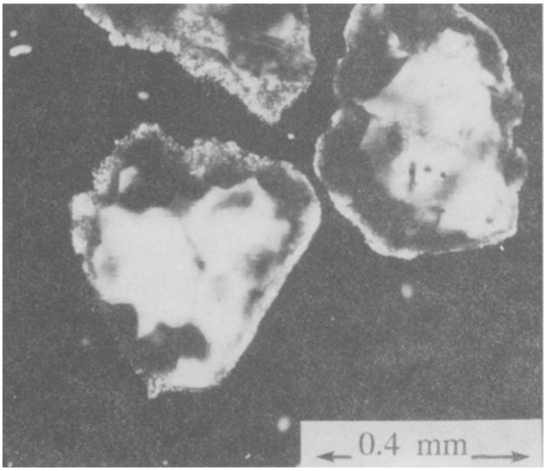

Fig. 2 Typical polarizing microscopic view of the internal surface of partially dehydrated crushed crystals of $K_2CuCl_4 \cdot 2H_2O$

Figure 2 shows a typical polarizing microscopic view of internal surfaces of partially dehydrated crushed crystals of $K_2CuCl_4 \cdot 2H_2O$. The irregularly shaped reaction interface supports the application of the non-integral values. The R_N model with non-integral values of N apparently corresponds to the specialized case of Eq. (4), i.e., $m = p = 0$. Then the accommodation function $a(\alpha)$ in Eq. (5) is expressed by

$$a(\alpha) = \frac{N}{n}(1-\alpha)^{(N-n)/nN} \tag{6}$$

The dependence of the shape of the generalized R_N function on the N value is shown in Fig. 3. This procedure has been used for describing the kinetic behaviour of isothermal decomposition and/or dehydration of solids [9, 19, 21–27], as shown in Table 2. Although the reaction geometry is also influenced by extensive factors, from a simple geometric consideration, the non-integral value of N is taken as the value corresponding to the fractal dimension [28].

Table 2 Results of kineticstudies, obtained by employing the non-integral values of *n* in the R_n law, for the isothermal decomposition and/or dehydration of inorganic solids

Reaction			Sample	Range of α	$f(\alpha)$	E / kJ·mol^{-1}	log A / s^{-1}	Ref.
$CaC_2O_4 \cdot H_2O$	→	$CaC_2O_4 + H_2O$	Powder (–170+200 mesh)	0.1–0.9	$R_{2.0}$	235	11.0	21
$MgC_2O_4 \cdot 2H_2O$	→	$MgC_2O_4 + 2H_2O$	Powder (–170+200 mesh)	0.1–0.9	$R_{1.6}$	104	8.9	22
SrC_2O_4	→	$SrCO_3 + CO_2$	Dehydration product	0.1–0.9	$R_{1.8}$	231	13.0	23
$CaCO_3$	→	$CaO + CO_2$	Decomposition poduct	0.1–0.9	$R_{1.8}$	237	10.1	24
$CuSO_4 \cdot 5H_2O$	→	$CuSO_4 \cdot 3H_2O + 2H_2O$	Single crystal	0.1–0.9	$R_{1.3}$	–	–	9
$K_2CuCl_4 \cdot 2H_2O$	→	$K_2CuCl_4 + 2H_2O$	Crushed crystals (–48+100 mesh)	0.1–0.9	$R_{1.7}$	126	16.4	25
$Li_2SO_4 \cdot H_2O$	→	$Li_2SO_4 + H_2O$	Single crystal	0.3–0.9	$R_{2.3}$	109	10.9	19
			Crushed crystals (–100+170 mesh)	0.4–0.9	$R_{2.0}$	89	9.4	19
$Cu(CH_3COO)_2 \cdot H_2O$	→	$Cu(CH_3COO)_2 + H_2O$	Single crystal	0.3–0.7	$R_{2.6}$	120	12.2	26
			Crushed crystals (–170+200 mesh)	0.1–0.9	$R_{1.5}$	86	8.6	27

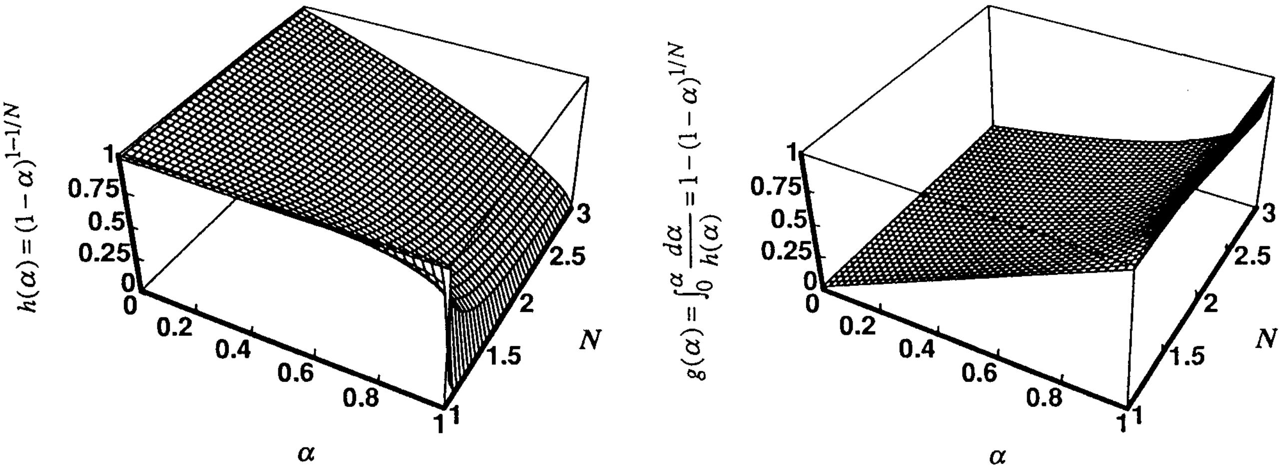

Fig. 3 Dependence of the R_N function on the non-integral kinetic exponent N

Practically, the N value does not necessary correspond directly to the fractal dimension, because of the macroscopic character of TA curves. However, the Arrhenius parameters obtained seem to be rather characteristic of the pro-cess under the condition investigated, because the distortion of the Arrhenius parameters by an inappropriate $f(\alpha)$ with an integral dimension was reduced by applying the non-integral value N, which is thought to be reasonable for the complex reaction geometry observed microscopically.

Using similar considerations, the kinetic model function of contracting geometry controlled by diffusion, i.e., the D_1, D_2, D_3 and D_4 laws, can take a non-integral exponent Q. Recently, Ozao and Ochiai derived this type of $h(\alpha)$ with a non-integral value Q [28]:

(i) $1 \leq Q < 2$

$$h(\alpha) = \frac{1}{1-(1-\alpha)^{2/Q-1}} \tag{7}$$

(ii) $2 < Q \leq 3$

$$h(\alpha) = \frac{1}{(1-\alpha)^{2/Q-1}-1} \tag{8}$$

Assuming the value $Q = 1$ and $Q = 3$, Eqs (7) and (8) correspond to the D_1 and D_4 laws, respectively.

Figure 4 shows a typical polarizing microscopic view of the (010) internal surface of partially dehydrated single crystalline $Cu(CH_3COO)_2 \cdot H_2O$. An optically different layer can be observed on the reactant side adjacent to the reaction front. This layer provides us with evidence of a strain zone of appreciable thickness within the reactant extending beyond the interface, which is in accordance with the demonstration of a metastable structure resulting from water loss near the crystalline product phase [26, 29–31]. It is suggested that the kinetic behaviour of the interface reaction is very complicated and consists of several stages, e.g., the chemical act of breaking of bonds, followed by destruction of the reactant crystal lattice, formation of nuclei of the solid product and growth of these nuclei, adsorption and desorption of gaseous products, diffusion of gases, and heat transfer. It is very possible that the rate of interface advancement changes during the course of reaction, affected by the self-generated reaction condition at the reaction interface. In this case, the preliminary assumption of the constant rate of advancement of the reaction interface in the R_n model can no longer hold. It is assumed here that the rate behaviour of interface advancement could by described by the p-th order law:

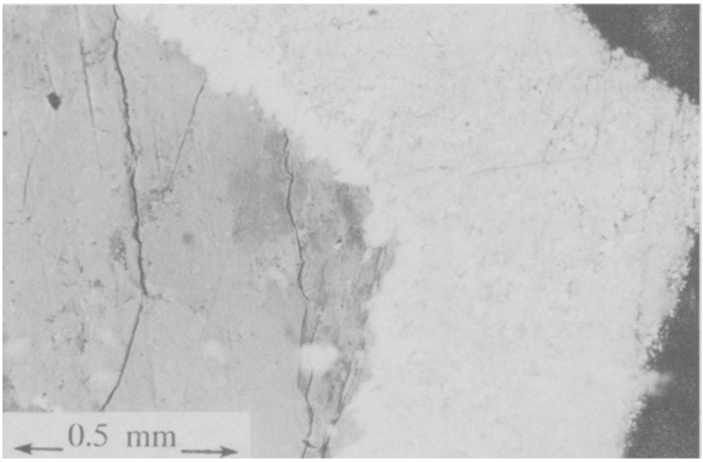

Fig. 4 Typical polarizing microscopic view of the (010) internal surface of a partially dehydrated single crystal of $Cu(CH_3COO)_2{\cdot}H_2O$

$$(r_o - r)^p = kt \tag{9}$$

where r_o and r are the radii of reactant at $t = 0$ and at $t = t$ respectively, and k refers to the apparent rate constant. Taking account of the reaction geometry, the kinetic model function can be expressed as

$$h(\alpha) = \frac{n(1-\alpha)^{1-1/n}}{p[1-(1-\alpha)^{1/n}]^{p-1}} \tag{10}$$

and

$$g(\alpha) = \int_{o}^{\alpha} \frac{d\alpha}{h(\alpha)} = [1-(1-\alpha)^{1/n}]^{p} \tag{11}$$

Thus the case described above is accommodation by the kinetic model function with the accommodation function $a(\alpha)$:

$$a(\alpha) = \frac{1}{p[1-(1-\alpha)^{1/n}]^{p-1}} \tag{12}$$

The effect of the exponent p on the shape of R_3 function is shown in Fig. 5. Having the value $p = 1$ and $p = 2$, the shapes of the model function correspond to those of the R_3 and D_3 laws, respectively. With $p = 2$ and $n = N$, the equation is also regarded as the fractal description based on the Jander equation, i.e., D_3 law.

Nucleation and growth type reaction

The nucleation-and-growth model known as that of Johnson-Mehl-Avrami-Erofeyev-Kolgomorov [2], is obtained by assuming the following topokinetic features [32]:

(i) The existence of a potential site for nucleation.

(ii) The nucleation rate can be expressed by a constant or linear law.

(iii) The nuclei grow isotropically.

(iv) The advancement rate of the reaction interface is controlled by chemical reaction, i.e., the linear law, or diffusion, i.e., the parabolic law.

(v) The reaction interface is simple reactant-product contact and the rate equation of interface advancement does not change during the course of reaction.

The kinetic model function A_m can be expressed as [1, 2]

$$f(\alpha) = \left(\beta + \frac{\lambda}{\chi}\right)(1-\alpha)[-\ln(1-\alpha)]^{[(\beta\chi+\lambda-\chi)/(\beta\chi+\lambda)]} \qquad (13)$$

and

$$G(\alpha) = [-\ln(1-\alpha)]^{\chi/(\beta\chi+\lambda)} \qquad (14)$$

where β, λ and χ are the kinetic exponents of the rate equation for nucleation (0 or 1), of the growth dimension (1, 2 or 3) and of the rate equation for interface advancement (1 or 2), respectively.

In the actual process, however, the exponents β, λ and χ are to have the non-integral values, as is the case with the contracting-geometry model. The exponent β has the value $-1 < \beta < 0$ for the deceleratory part of the nucleation rate and $0 < \beta < 1$ for the acceleratory part of the nucleation rate [2]. The non-integral exponents λ and χ correspond to the exponents N and p in Figs 3 and 5, respectively. Accordingly, the nucleation-and-growth model A_m is expressed by the equation with a non-integral kinetic exponent M instead of the conventional exponent m (see Table 1). The effect of the non-integral exponent M on the shape of the A_M function is shown in Fig. 6. The accommodation function $a(\alpha)$ in Eq. (5) for the nucleation-and-growth model is written as:

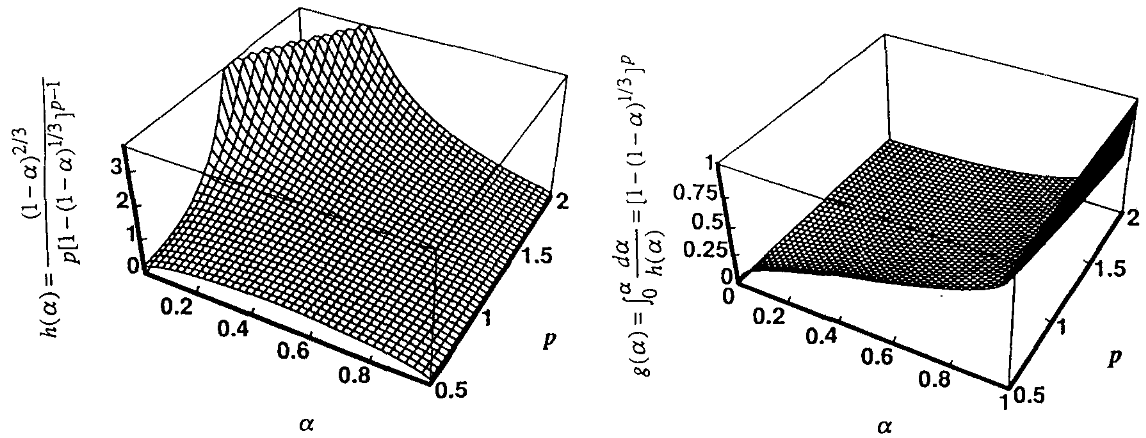

Fig. 5 Dependence of the three-dimensional contracting-geometry function on the kinetic exponent p

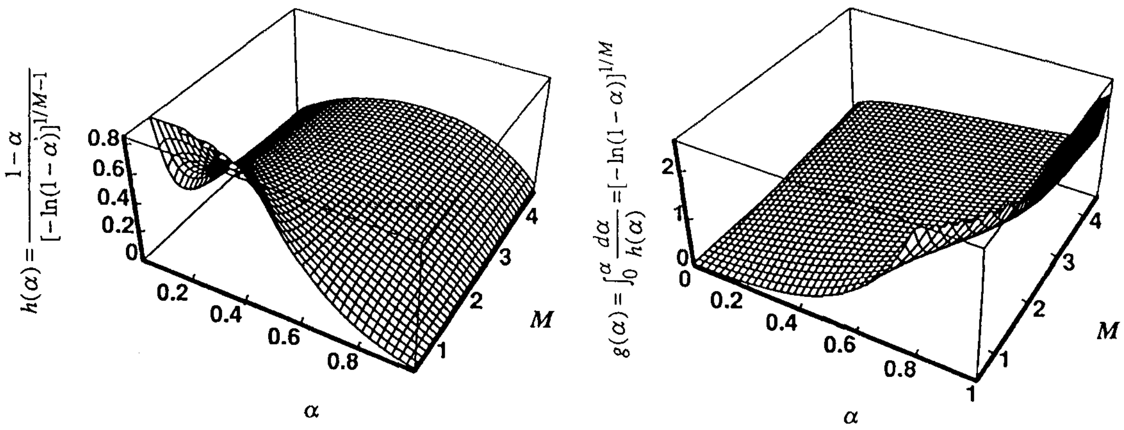

Fig. 6 Dependence of the A_M function on the non-integral kinetic exponent M

$$a(\alpha) = \frac{M}{m}[-\ln(1-\alpha)]^{(M-m)/mM} \qquad (15)$$

Figure 7 shows the polarizing microscopic view of the (100) internal surface of a partially dehydrated single crystal of $Na_3C_6H_5O_7 \cdot 2H_2O$. The anisotropy during the crystal growth is deduced as was discussed above. Employing the extended A_M function, the non-integral value M = 3.49 was obtained from the isothermal mass change traces for the thermal dehydration of a single crystal of $Na_3C_6H_5O_7 \cdot 2H_2O$ [33].

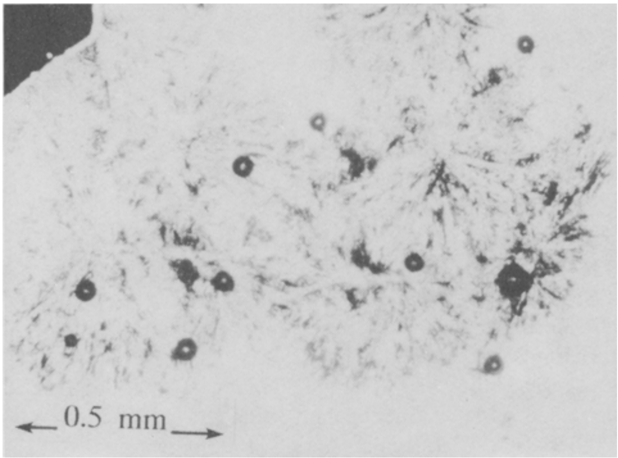

Fig. 7 Typical polarizing microscopic view of the (100) internal surface of a partially dehydrated single crystal of $Na_3C_6H_5O_7 \cdot 2H_2O$

Conclusions

When the TA curves for the solid-state process under investigation cannot fully be described by the conventional kinetic model function $f(\alpha)$, the resultant kinetic parameters are distorted as a simple mathematical consequence of Eqs (2) and (3). Employing an empirical function, such as the SB model, the apparent but characteristic kinetic parameters could be obtained. In such a kinetic approach, however, the physico-geometry of the reaction cannot be deduced from the kinetic results. If the function $h(\alpha)$ which describes the real process is expressed by the product of $f(\alpha)$ and the accommodation function $a(\alpha)$, i.e., Eq. (5), the function $h(\alpha)$ is taken as a distorted case of the conventional $f(\alpha)$. The microscopic studies of the solid-state reaction enable us to recognize the character of the accommodation function in connection with the reaction geometry, as well as the detailed interface chemistry of the process. The microscopic observation of the complex textural structure of reaction interface favours the introduction of a non-integral exponent into the kinetic expression with an appropriate accommodation function.

References

1 M. E. Brown, D. Dollimore and A. K. Galwey, Comprehensive Chemical Kinetics, Vol. 22, (Eds. C. H. Bamford and C. F. H. Tipper), Reactions in the Solid State, Elsevier, Amsterdam 1980.
2 J. Sestak, Comprehensive Analytical Chemistry, Vol. 12, Part D (Ed. G. Svehla), Thermophysical Properties of Solids, Their Measurements and Theoretical Thermal Analysis, Elsevier, Amsterdam 1984.
3 S. F. Hulbert, J. Brit. Ceram. Soc., 6 (1969) 11.
4 H. Tanaka and N. Koga, J. Thermal Anal. 36 (1990) 2601.
5 N. Koga and H. Tanaka, Thermochim. Acta, 183 (1991) 125.
6 J. Rouquerol, J. Thermal Anal., 5 (1973) 203.
7 J. Paulik and F. Paulik, Anal. Chim. Acta, 56 (1971) 328.
8 H. Tanaka and K. Kawabata, Thermochim. Acta, 92 (1985) 219.
9 H. Tanaka and N. Koga, Thermochim. Acta, 133 (1988) 227.
10 A. K. Galwey, R. Reed and G. G. T. Guarini, Nature (London), 283 (1980) 52.
11 A. K. Galwey, Thermochim. Acta, 96 (1985) 259.
12 N. Koga, Ph. D Thesis, Univ. Chem. Technol. Pardubice (Czech Rep.), 1991.
13 N. Koga, J. Sestak and J. Malek, Thermochim. Acta, 188 (1991) 333.
14 J. Sestak and G. Berggren, Thermochim. Acta, 3 (1971) 1.
15 J. Malek, Thermochim. Acta, 138 (1989) 337.
16 J. Sestak and N. Koga, Thermochim. Acta, 203 (1992) 321.
17 N. Koga, J. Sestak and Z. Strnad, Thermochim. Acta, 203 (1992) 361.
18 J. Sestak, J. Therm. Anal., 36 (1990) 1997.
19 N. Koga and H. Tanaka, J. Phys. Chem., 93 (1989) 7793.
20 H. Tanaka, N. Koga and J. Sestak, Thermochim. Acta, 203 (1992) 203.
21 H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, Thermochim. Acta, 48 (1981) 137.
22 H. Tanaka and M. Tokumitsu, J. Thermal Anal., 29 (1984) 87.
23 H. Tanaka and N. Koga, J. Thermal Anal., 32 (1987) 1521.
24 N. Koga and H. Tanaka, J. Thermal Anal., 34 (1988) 177.
25 H. Tanaka and N. Koga, J. Phys. Chem., 92 (1988) 7023.
26 N. Koga and H. Tanaka, Solid State Ionics, 44 (1990) 1.
27 H. Tanaka and N. Koga, Thermochim. Acta, 173 (1990) 53.
28 R. Ozao and M. Ochiai, J. Ceram. Soc. Jpn., 101 (1993) 263.
29 A. K. Galwey, R. Spinicci and G. G. T. Guarini, Proc. R. Soc. London A, 378 (1981) 477.
30 V. V. Boldyrev, Y. A. Gaponov, N. Z. Lyakhov, A. A. Politov, B. P. Tolochko, T. P. Shakhtshneider and M. A. Sheromov, Nucl. Inst. Methods Phys. Res. A, 261 (1987) 192.
31 A. K. Galwey, N. Koga and H. Tanaka, J. Chem. Soc. Faraday Trans., 86 (1990) 531.
32 E. V. Boldyreva, J. Thermal Anal., 38 (1992) 89.
33 H. Tanaka, Y. Yabuta and N. Koga, React. Solids, 2 (1986) 169.

Zusammenfassung — Anhand einer mikroskopischen Untersuchung der thermischen Dehydratation einiger anorganischer Salzhydrate wurde der Grad der Koordinierung zwischen den kinetischen Informationen aus thermoanalytischen Messungen und der kinetischen Theorie von Feststoffreaktionen untersucht. Auf konventionelle kinetische Modellfunktionen $f(\alpha)$ wurde eine Akkomodationsfunktion angewendet, um die bei der Formulierung von $f(\alpha)$ vorgegebenen Diskrepanzen zwischen dem tatsächlichen und dem idealisierten Prozeß zu reduzieren. Es wurde die Wichtigkeit des nichtintegralen kinetischen Exponenten in der kinetischen Modellfunktion mit Hilfe seiner physikalisch-chemischen Bedeutung erörtert.