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Resolution of overlapping peaks and the determination of kinetic parameters for the crystallization of multicomponent system from DTA or DSC curves:
II. Isothermal kinetics

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Abstract

A computer program has been created to separate overlapping exothermic DTA (DSC) effects, obtained under isothermal conditions, occurring due to simultaneous crystallization processes, and also to calculate the kinetic parameters of the processes represented by each peak.

A graphical method for the estimation of the required parameters, i.e. initialization, and the refinement of the initial values by the least squares method is presented.

The procedure for the determination of the kinetic parameters from DTA data is demonstrated on a model system and on a kinetic analysis of mullite formation from single phase gel. The two-step mullite crystallization model was proposed and the fitting was remarkably good throughout the whole temperature range. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Computer program; Crystallization kinetics; Differential thermal analysis; Mullite; Overlapping

1. Introduction

For an analysis of solid state transformation kinetics changes of a physical property of the material subject can be measured as a function of time and temperature. Many different methods can be used for determination of the kinetic parameters of a transformation process. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are of particular value in such studies [1]. The techniques can be broadly classified into isothermal and non-isothermal methods. To give a preference to either isothermal or non-isothermal analysis should depend on the case considered. Care is required in the choice of method and in the interpretation of the data obtained [2,3].

If the sample exhibits several stages of crystallization with a small time lag, the DTA (DSC) scan obtained consists of overlapped thermal effects, e.g. exothermic peaks. The degree of overlap in an isothermal experiment can be greater than the degree of overlap in non-isothermal experiment and the range of temperatures for isothermal kinetic analysis could be more restricted by overlaps than the range of heating rates for non-isothermal kinetic analysis [3]. Moreover, the determination of peak temperature, T_p, providing data for further calculation in non-isothermal analysis, is essentially less sensitive to errors when compared with the volume fraction of transformed phase, α, the data required for isothermal analysis.

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While in non-isothermal kinetics, T_p would not be changed by a moderate overlap, in isothermal kinetics α, measured by peak integration will be dramatically erroneous even for a slight overlap. Employing the α values corresponding to a limited range of peak area will not help either, because the total value of physical property used to discern total amount of volume transformed ($\alpha=1$) is incorrect.

Numerical models for isothermal phase transformations have been presented, the models were used to compute the volume fraction transformed as a function of time and to simulate DSC traces of a glass devitrification [4]. Some attempts have been made to resolve the isothermally obtained DSC traces consisting of two partially overlapping crystallization peaks of comparable size [5].

The aim of this work was, by the same approach presented in part I of our paper [1], to find a solution for resolving an overlapped exothermic DTA (DSC) effects, obtained under isothermal conditions.

2. Theoretical

In general, isothermal methods are related through application of the Johnson–Mehl–Avrami transformation kinetics equation [6–9]. Nowadays, a modified JMA expression [10] is widely used to analyze isothermal transformation data

$$\alpha(t) = 1 - \exp[-k^n(t-\tau)^n] \tag{1}$$

The reaction kinetics is contained within the reaction constant, k, and it is related to the activation energy for the process, E, through the Arrhenius temperature dependence. The dimensionless constant, n is known as the Avrami exponent and is related to nucleation and growth mechanisms as described in part I [1], a broader insight is provided by Ranganatan and von Heimendahl [11], and τ is related to the transient time ($t>\tau$).

3. The mathematical model

In order to resolve the peaks obtained isothermally, the modified JMA expression (Eq. (1)) is taken as the basic function representing the integral function for each individual transformation. The shape of the DTA (DSC) peak is then described by the appropriate differential function

$$f(t) = q\frac{d\alpha}{dt} = qnk^n(t-\tau)^{n-1}\exp[-k^n(t-\tau)^n] \tag{2}$$

The constant, q, is introduced in order to normalize the peak. For DSC measurement $q=\Delta H$, where ΔH is the total enthalpy difference between transformed and untransformed states.

By differentiating Eq. (2) and setting it equal to 0 the dependence of t_p (time of the peak maximum) on n and k can be calculated

$$(t_p - \tau) = \frac{1}{k}\sqrt[n]{\frac{n-1}{n}} \tag{3}$$

where $(t_p-\tau)$ is the time from the beginning of the reaction ($t=\tau$) up to the maximum reaction rate ($t=t_p$). Introducing Eq. (3) into Eq. (1) yields

$$\alpha_p = 1 - \exp\left(\frac{n-1}{n}\right) \tag{4}$$

As can be seen, for the case of isothermal kinetics α_p is dependent on n. Consequently, the symmetry of the differential function (Eq. (2)), i.e. DTA or DSC peak is dependent on n. From Eq. (4) it follows that $\alpha_p=0.5$ for $n=3.2$, for $n<3.2$ the function is asymmetric for $t>t_p$, and for $n>3.2$ the function becomes to be asymmetric for $t<t_p$. The reaction rate constant, k, controls the peak broadness and consequently, the t_p value. If k is small, the reaction duration is longer, the peak is extended over long time interval and the t_p value is greater.

In Fig. 1 the influence of Avrami exponent and rate constant on the shape of the DTA (DSC) peak has been reviewed. As can be seen, in contrast with non-isothermal kinetics, where most of the models gave peaks of uniform shape with maxima $\alpha_p=0.63$ [12,13], the situation with isothermal kinetics is completely different. This makes it harder to recognize overlapping, as well as to establish the number of overlapping peaks under isothermal conditions. This is especially true in case of high degrees of overlapping. Slight or moderate overlapping could be easily recognized due to existence of two (or more) maxima. The plot of $\ln(-\ln(1-\alpha))$ versus $\ln t$, often used to calculate n and k, should give a straight line. If linearity cannot be obtained, even by introducing τ according to Eq. (1), this could be the indicator of overlapping. Finally, by interrupting the DTA (DSC) experiment at various

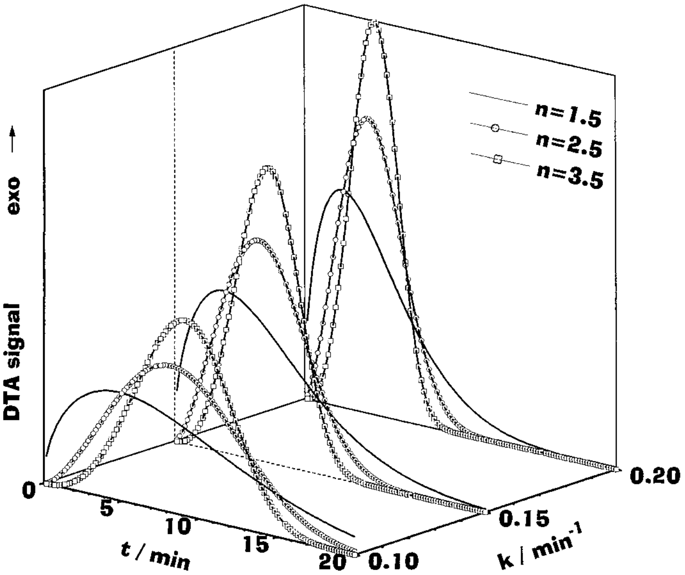

Fig. 1. A review of the influence of reaction rate constant and Avrami exponent on the shape of DTA (DSC) peak obtained under isothermal conditions.

values of α and submitting such samples to X-ray diffraction, the phases crystallizing and the crystallization path could be established.

If the experimental results (in the time interval where overlapping occurs) are the sum of those supplied by the overlapping processes, and the shape of single peak is represented by Eq. (2), then the relationship between the experimentally obtained DSC data denoted as $F(t)$ and the values corresponding to a single process are given by

$$F(t) = \sum_{i=1}^{N} w_i f_i(t) \tag{5}$$

where N is the number of overlapping peaks. In order to illustrate the complexity of the problem, four different cases of two overlapping DTA curves are shown in Fig. 2.

4. The computer model for resolving overlapping peaks in isothermal DTA and DSC

An algorithm based on Eqs. (2) and (5) was developed into computer program KINSOLID in order to resolve overlapping DTA (DSC) peaks (superimposed due to transformations occurring in the same interval of time) and to determine kinetic parameters of each individual process.

The graphical concept of initialization presented in [1] was used for estimation of initial peak parameters in order to enable corrections of the parameters before refinement and consequently, initial parameters closer to the real values. The peaks appear with the starting parameters (k=0.1 min^{-1}, n=3, τ=0 min and w=0.5), each parameter could be increased or decreased individually with variable steps across a wide range of values. The variation in n affects peak shape, the variation in k its broadness, the variation in τ its position and the variation in w its height. The aim is to adapt the two peaks sum curve to the experimental curve, as much as possible, by changing the initially estimated parameters for the contributory peaks.

The refinement of the initial values was conducted in the same manner as in part I of our paper [1] using the equation

$$\Delta F = \sum_{i=1}^{N}\sum_{j=1}^{4} \frac{\delta F}{\delta p_{ij}} \Delta p_{ij} \tag{6}$$

ΔF is the difference between the experimentally measured and calculated curve point, Δp_{ij} is the difference

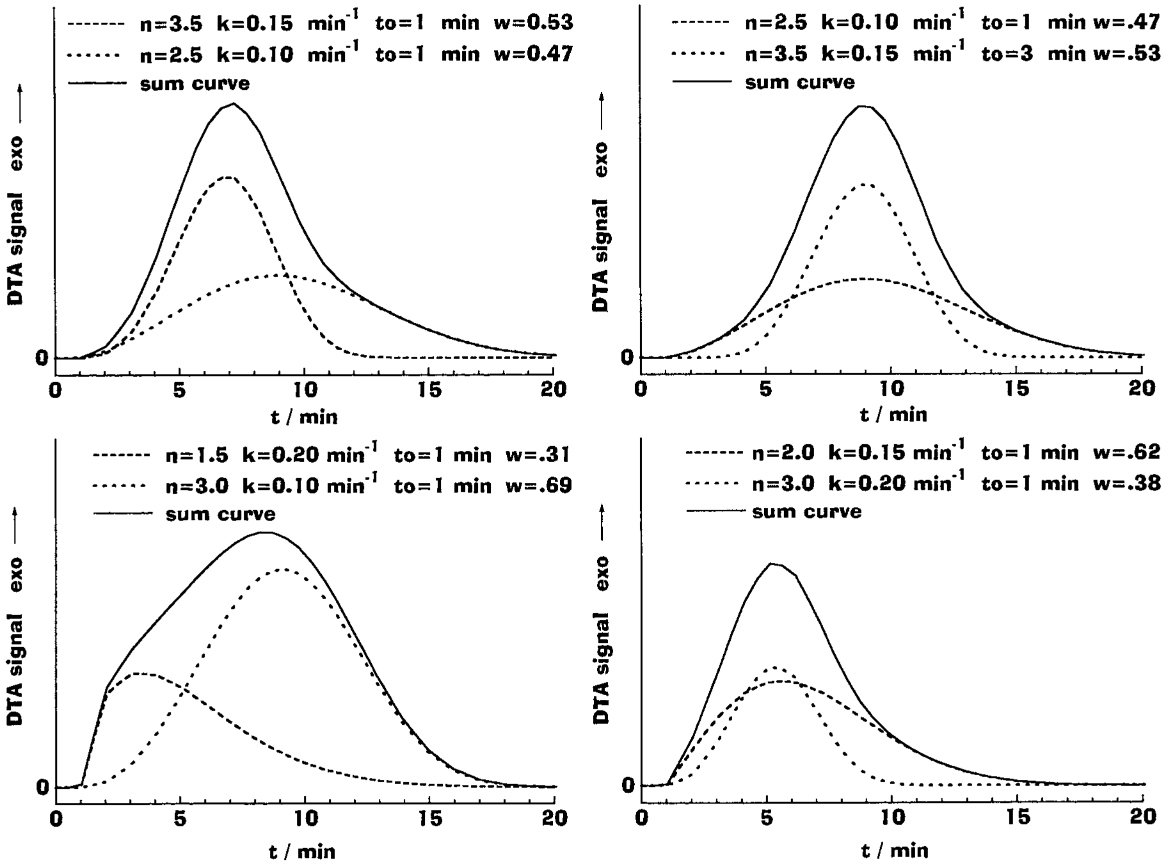

Fig. 2. Four different cases of DTA (DSC) curves overlapping in isothermal conditions obtained by computer simulation.

between most probable parameter value, p_{ij}, and the value obtained from a lower refinement cycle, p_{ijc}. The $\delta F/\delta p_{ij}$ values, where p_i denotes k_i, n_i, τ_i and w_i, respectively, are given by Eqs. (7)–(10).

$$\frac{\delta F}{\delta n_i} = C_i(t-\tau_i)^{n_i-1}\exp[-k_i^{n_i}(t-\tau_i)^{n_i}] \times \{\ln(t-\tau_i\} - k_i^{n_i}(t-\tau_i)\ln[k_i(t-\tau_i)]\} \quad (7)$$

$$\frac{\delta F}{\delta k_i} = C_i n_i k_i^{n_i-1}(t-\tau_i)^{2n_i-1}\exp[-k_i^{n_i}(t-\tau_i)^{n_i}] \quad (8)$$

$$\frac{\delta F}{\delta \tau_i} = C_i(t-\tau_i)^{n_i-2}\exp[-k_i^{n_i}(t-\tau_i)^{n_i}] \times [(1-n_i)-(t-\tau_i)^{n_i}n_i k_i^{n_i}] \quad (9)$$

$$\frac{\delta F}{\delta C_i} = (t-\tau_i)^{n_i-1}\exp[-k_i^{n_i}(t-\tau_i)^{n_i}] \quad (10)$$

where C is multiplicative constant

$$C_i = w_i n_i k_i^{n_i} \quad (11)$$

The application of Eq. (2) to M experimental items of data give a system of M equations with $4N$ unknowns, where $M \gg 4N$. The best values for Δp_{ij} are obtained by the least-squares method and the most reliable values for p_{ij} are obtained from Eq. (12).

$$p_{ij} = p_{ijc} + \Delta p_{ij} \quad (12)$$

The first three parameters (n, k and τ) have to be refined first, subsequently the multiplicative constant (C) is refined.

One refinement cycle consists of 6–10 such refinement processes, depending on ε

$$\varepsilon = \frac{\sigma_{n-1}-\sigma_n}{\sigma_n} \quad (13)$$

where σ_n is the standard deviation between calculated and experimental curve for the *n*th refinement process. The cycle ends either when the number of refinement processes reaches 10 or it is larger than 6 and $0 \leq \varepsilon < 0.01$. If the sum curve does not have a tendency for progressive adaptation to the shape of the experimentally obtained curve the standard deviation value increases ($\varepsilon < 0$) and the refinement process is interrupted. Then the initial parameters estimation should be repeated with different assumptions.

Since the parameters n, k and τ are mutually dependent (Eq. (3)) there is a significant possibility of compensating one wrong initialisated parameter with another. To avoid this possibility, the program takes into consideration several values of parameters n_i and k_i close to the initialized value and performs a refinement cycle for each value. Values giving the lowest system standard deviation are taken for the further calculations. Such a procedure is repeated a few more times, each time in a narrower range of parameter values.

The process proceeds in the previously described cycles until the initially set maximal permitted ε, or maximal permitted number of refinement cycles, is reached. The required number of refinement cycles depend on system and the initial parameters estimation.

The experimental curve can, thus, be resolved into component parts, each representing an individual process with known kinetic parameters. The standard deviation values for parameters k and n are also calculated.

For mathematical reasons the refinement calculations could be conducted just for the values of $t > \tau_{\min}$, where $\tau_{\min}$ is the lowest τ value obtained during the refinement process.

The program KINSOLID is written in Borland C++ language, version 2.0. The program uses ASCII files data obtained by on-line measurements, each representing one DTA or DSC curve. Results (separated peaks and calculated parameters) could be printed out or saved as an ASCII file.

5. Results and discussion

In order to verify the validity of the program presented, it was tested on a model system of two overlapping exothermic peaks with the preset parameters listed in Table 1. The results of applying the program developed on a model system are shown in Fig. 3. Very good agreement between simulated and calculated curves and between preset and calculated values of parameters are observed (Table 1).

The program has also been applied in the determination of the kinetic parameters for crystallization of premullite single phase gel. The gel was prepared by using tetraethoxysilane and aluminum nitrate nonahydrate, Al/Si=3/1 [14]. The kinetic parameters for crystallization were evaluated on dried gels heated in the DSC apparatus (NETZSCH STA 409, air atmosphere, Pt pan, empty pan as standard) from room temperature at a heating rate of 30°C min^{-1} to selected temperatures between 937 and 959°C and held at the attained temperature until completion of crystallization. The curves recorded at higher annealing temperatures exhibit two overlapping maxima, whereas scans recorded at lower temperatures are similar to a single thermal event, representative scans for each case are shown in Fig. 4. Therefore, the experimental data were submitted to analysis by the developed program. The satisfactory matching

Table 1
Preset parameter values of the model system, initial values and the values of the model system calculated by program[a]

	$k(1)$ (min^{-1})	$n(1)$	$\tau(1)$ (min)	$w(1)$	$k(2)$ (min^{-1})	$n(2)$	$\tau(2)$ (min)	$w(2)$
Preset	0.150	3.5	1.0	0.53	0.100	2.5	1.00	0.47
Initial	0.140	3.6	0.6	0.50	0.090	2.4	1.00	0.50
Calculated[b]	0.144	3.61	0.68	0.52	0.100	2.56	1.18	0.48
Calculated[c]	0.149	3.50	0.97	0.54	0.099	2.54	0.96	0.46

[a] The parameters denoted by (1) corresponds to the first peak and parameters denoted by (2) correspond to the second peak. The initially set ε was 0.001. The number of refinement procedures until the set ε has been attained was 4.

[b] After the first refinement cycle.

[c] Final values.

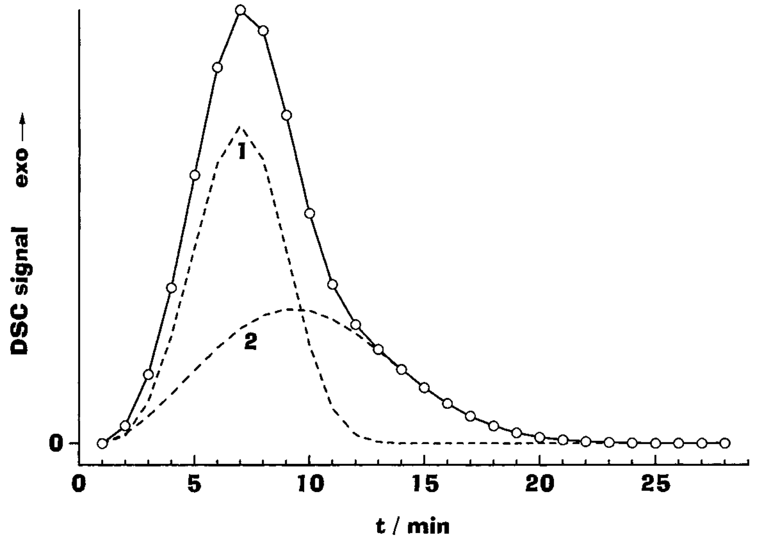

Fig. 3. Simulated DTA (DSC) curve of the model system (○), separated peaks (- - -), and the sum curve (—).

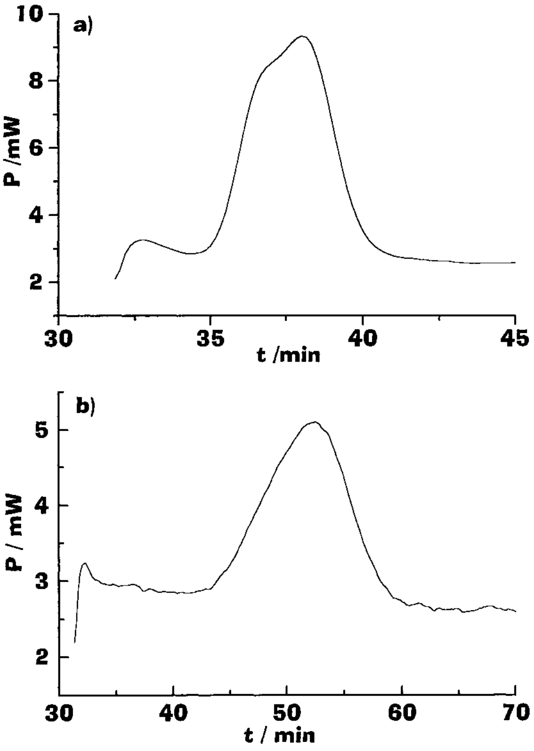

Fig. 4. Isothermal DSC scans of premulite gels annealed at (a) 959°C and (b) 947°C.

between experimental and calculated curve was obtained under the assumption of the existence of two overlapping exothermic peaks (Fig. 5.). Table 2 gives *k*, *n*, τ and *w* values of the resolved peaks calculated by the KINSOLID program for DSC curve obtained at an annealing temperature of 947°C.

Applying the program to the entire set of curves, two independent linear functions $\ln k$ versus $1/T_i$

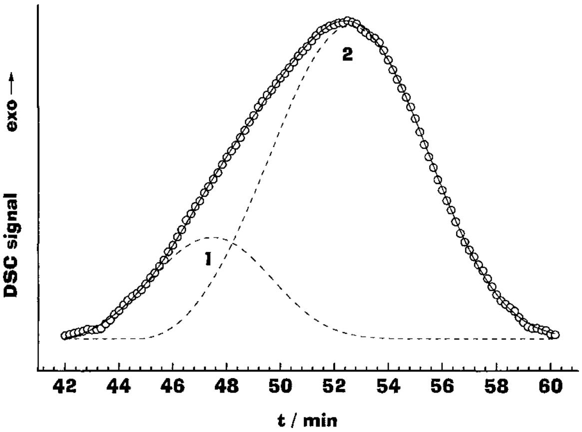

Fig. 5. Isothermal DSC curve of gel sample on annealing at 947°C (○), fitted data under the assumption of two-step crystallization process (- - -) and sum curve (—).

Table 2
Parameter values k, n, τ and w of the resolved peaks calculated by the developed program for DSC curve of sample held at annealing temperature of 947°C[a]

	$k(1)$ (min^{-1})	$n(1)$	$\tau(1)$ (min)	$w(1)$	$k(2)$ (min^{-1})	$n(2)$	$\tau(2)$ (min)	$w(2)$
Initial	0.132	3.40	37.50	0.25	0.114	3.30	46.50	0.75
Calculated[b]	0.143	3.44	40.40	0.22	0.112	3.30	45.23	0.78
Calculated[c]	0.146	3.31	41.67	0.20	0.116	3.35	44.80	0.80

[a] The parameters denoted by (1) corresponds to the first peak and parameters denoted by (2) correspond to the second peak. The initially set ε was 0.001. The number of refinement procedures until the set ϵ has been attained was 5.

[b] After the first refinement cycle.

[c] Final values.

were calculated (Fig. 6) which gave $E(1)$ (1053±51 kJ mol^{-1}) and $E(2)$ (1028±22 kJ mol^{-1}) values, determined from the slope. According to these results, two-step crystallization model fits the experimental data, i.e. two transformation processes follow one after another with a small time lag. Since in the samples studied mullite was the only phase crystallizing [14], the two exothermic processes could be explained by the two-step mullite crystallization process proposed by Li and Thomson [15] in their study of single phase premullite gel. According to Tkalcec et al. [14] phase separation has to be assumed to cause such crystallization behavior. The apparent activation energies reveal a consistency with those determined by Wei and Halloran [16] (E_a=1070±200 kJ mol^{-1}), for diphasic, and Huling and Messing [17] (E_a=1091±71 kJ mol^{-1}) for hybrid gels.

6. Conclusions

A new computer program KINSOLID for separating overlapped DSC (DTA) peaks obtained under isothermal conditions was created. From such separated peaks the kinetic parameters for the processes represented by each peak could be calculated.

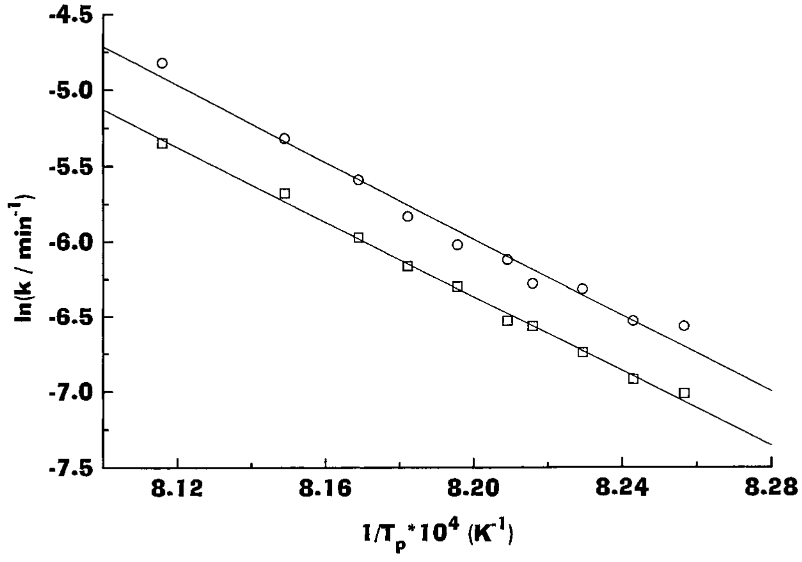

Fig. 6. Arrhenius plots for gel samples heated from room temperature up to various temperatures from 937 to 959°C. The reaction constants have been calculated by the developed program. First peak (○), second peak (□).

The program was tested on a model system consisted of two peaks with high degree of overlapping. Very good matching between simulated and calculated curves was obtained.

The program was also tested on DSC scans of mullite crystallization from single phase gel. It was shown that the DSC exotherms obtained have arisen from two crystallization processes and have been resolved into two separated peaks. Resolving was successfully achieved and values of k, n, τ and w were determined for both processes. Arrhenius plots for the entire set of curves revealed the consistency of calculated data and enabled the calculation of activation energies for the processes.

The applying of KINSOLID program[1] on DTA or DSC data can be successful only if the proposed mathematical model corresponds to the kinetic process.

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[1] The program KINSOLID could be obtained from the corresponding author by e-mail.