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Estimation of nonisothermal kinetic parameters from a TG curve by the methods of overdetermined system and inflection point

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Abstract

Methods are described to determine nonisothermal kinetic parameters from a TG curve. The first method uses the theory of overdetermined systems while the others use the inflection points. These inflection point methods are an alternative to those described earlier by Viswanath and Gupta.

Keywords: Inflection point; Non-isothermal kinetic parameters; Overdetermined system; Thermogravimetry

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1. Introduction

A number of methods have been proposed for the evaluation of nonisothermal kinetic parameters of solid state reactions from a TG curve involving either mass loss or sometimes gain. All the available methods generally involve the assumption that a given reaction follows a simple order. The Freeman and Carroll [1] method is the only method for the estimation of the order of a reaction; however it suffers from several disadvantages [2–5]. In spite of its limited precision and disadvantages, it is widely used. In the Sharp and Wentworth [2] method, which is a derivative method, if the correct order of reaction is assumed and substituted in the Arrhenius rate equation, the logarithmic form of the equation results in a linear plot. Similarly, the Coats and Redfern [3] method is an integral method and also requires the assumption of an order

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of reaction to get a linear plot. In these two methods, the pre-exponential factor and activation energy are determined graphically.

Viswanath and Gupta [5] reported several methods for the estimation of all the kinetic parameters by considering the inflection point of the TG curve. The accuracy of the evaluation of the parameters by these methods depends on the ability to locate the inflection point accurately from the curve. We have applied this method [5] to the study of the thermal decomposition of polycarbonate bisphenol A in the presence and absence of some metal oxides [6]. In this communication, new derivative methods are reported for the estimation of all nonisothermal kinetic parameters. The first method uses the overdetermined system method. The order of reaction obtained from this method is used for the graphical method for ascertaining the correctness of the estimates of the parameters. Other methods use the inflection point as the basis for the determination of kinetic parameters.

To illustrate these methods, the data for calcium oxalate decomposition reported by Schempt et al. [7], the thermal decomposition of the solid complex formed by the ligand 2-carboxyl-2′-hydroxyl-3′,5′-dimethyl azobenzene (CHDMA) and cobalt [8], and the TG measurements on the thermal decomposition of Cu, Ni and Co sulfates have been re-examined.

2. Experimental

Thermogravimetry was carried out on a Perkin–Elmer TG Thermal System TGS2 in a flow of nitrogen gas and at a heating rate of 10 K min^{-1} in a alumina crucible at the Regional Sophisticated Instrumentation Center, Nagpur University, Nagpur. In the kinetic analysis of the TG data, it is assumed that the reaction follows a simple order.

The fraction decomposed α is defined as

$$\alpha = \frac{(W_0 - W_T)}{(W_0 - W_f)} \tag{1}$$

where W_0, W_f, and W_T, are the initial mass, final residual mass and mass of the sample at any temperature T, respectively. The logarithmic form Arrhenius rate equation is written as

$$\ln\left\{\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right\} = n\ln(1-\alpha) - \left\{\frac{E_\alpha}{RT}\right\} + \ln\left\{\frac{A}{\beta}\right\} \tag{2}$$

where n, A β and E_α are the order, pre-exponential factor, rate of heating and activation energy of a reaction, respectively.

2.1. The overdetermined system method

For x data points, there should be x equations of the above type and there are three unknowns, namely n, A and E_α, to be determined; if there are more equations than unknowns to be determined, such a set of equations forms an overdetermined system. The theory for finding the least-square solution of an overdetermined system of equations is found in a number of text-books on numerical analysis. Therefore, this theory needs no discussion here. These x equations can be resolved into three equations which can be written as

$$\sum_{i=1}^{x} \ln\left\{\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right\}_i = n\sum_{i=1}^{x}\ln(1-\alpha_i) - \left\{\frac{E_\alpha}{R}\right\}\sum_{i=1}^{x}\left\{\frac{1}{T_i}\right\} + \ln\left\{\frac{A}{\beta}\right\}x \tag{3}$$

$$\sum_{i=i}^{x} \ln\left\{\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right\}\ln(1-\alpha_i) = n\sum_{i=1}^{x}\left\{\ln(1-\alpha_i)\right\}^2 - \left\{\frac{E_\alpha}{R}\right\}\sum_{i=1}^{x}\left\{\frac{1}{T_i}\right\}\ln(1-\alpha_i)$$
$$+\ln\left\{\frac{A}{\beta}\right\}\sum_{i=i}^{x}\ln(1-\alpha_i) \tag{4}$$

$$\sum_{i=1}^{x} \ln\left\{\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right\}_i\left\{\frac{1}{T_i}\right\} = n\sum_{i=1}^{x}\ln(1-\alpha_i)\left\{\frac{1}{T_i}\right\} - \left\{\frac{E_\alpha}{R}\right\}\sum_{i=1}^{x}\left\{\frac{1}{T_i}\right\}^2 + \ln\left\{\frac{A}{\beta}\right\}\sum_{i=1}^{x}\left\{\frac{1}{T_i}\right\} \tag{5}$$

Eqs. (3)–(5) are solved by either an analytical or a matrix method to obtain the parameters; in the present case, they are solved as described earlier [4].

The correct order of reaction obtained from the analytical solution of Eqs. (3)–(5) is substituted into Eq. (2), which can be rewritten as

$$\ln(k) = \ln\left\{\left[\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right]\bigg/\left[1-\alpha\right]^n\right\} = -\left\{\frac{E_\alpha}{RT}\right\} + \ln\left\{\frac{A}{\beta}\right\} \tag{6}$$

The plot of $\ln(k)$ against $1000/T$ results in a straight line. The results of both solutions are presented in Table 1 and plots are shown in Fig. 1. The correlation coefficient (C.R.) and percent average deviation (A.D.) [5] of the points from the regression line are also presented in Table 1.

2.2. *Inflection point methods*

In the absolute method suggested by Viswanath and Gupta [5], the (E_α/R) value obtained from the inflection equation is substituted into Eq. (2). From the plot of this equation, the order of reaction n and the pre-exponential factor A are evaluated. The n value is substituted in the inflection equation to get the activation energy of the reaction E_α.

Table 1
Nonisothermal decomposition kinetic parameters from the overdetermined system method

	Analytical solution			Graphical solution			
Compound	Order of reaction	E_α/ (kJ mol^{-1})	A/ (s^{-1})	E_α/ (kJ mol^{-1})	A/ (s^{-1})	C.R.	A.D.
Co(II)CHDMA	0.07	−5.3	1.8×10^{-4}	−5.3	1.8×10^{-4}	0.9996	0.03
CaC_2O_4	1.03	302.1	1.0×10^{19}	302.1	1.0×1^{19}	0.9996	0.34
$NiSO_4$	0.31	244.2	2.0×10^{9}	244.2	2.0×10^{9}	0.9999	0.21
$CoSO_4$	0.53	244.9	1.2×10^{9}	244.9	1.2×10^{9}	0.9998	0.22
$CuSO_4$	0.99	245.2	4.7×10^{10}	245.2	4.7×10^{10}	0.9997	0.38

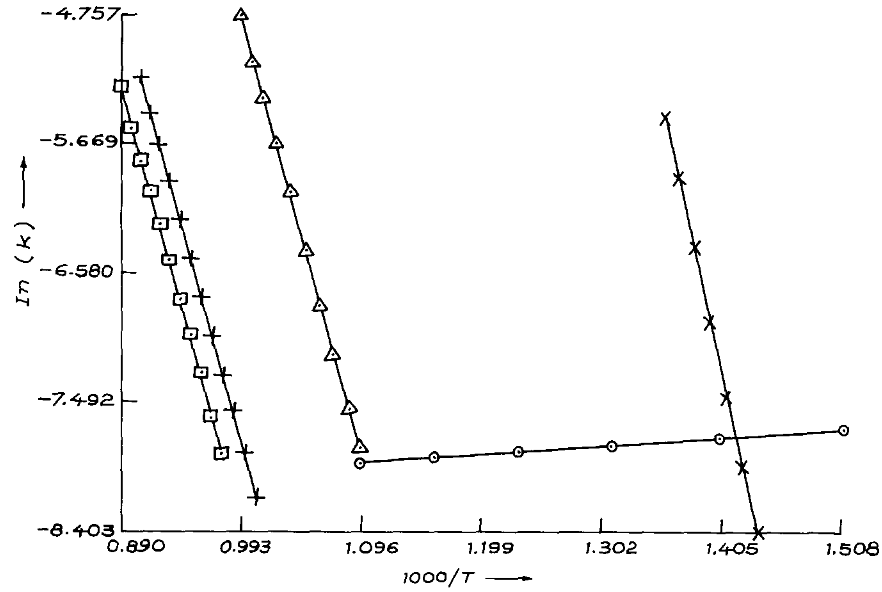

Fig. 1. Plots from the solution of the overdetermined system method: ○, Co(II)CHDMA; ×, CaC_2O_4; +, $NiSO_4$; □, $CoSO_4$; and △, $CuSO_4$.

At the inflection point, the second derivative $(d^2\alpha/dT^2) = 0$ and $(d\alpha/dT)$ is maximum. The equation at the inflection point can be written

$$(d\alpha/dT)_s = [(1-\alpha_s)/n](E_\alpha/RT_s^2) \tag{7}$$

The subscript defines the quantities at the inflection point respectively and Eq. (7) is rearranged as

$$n = (E_\alpha/RT_s^2)[(1-\alpha_s)/(d\alpha/dT)_s] \tag{8}$$

The kinetic parameters are obtained by the following methods.

2.2.1. An alternate absolute method

Eq. (8) is substituted into the logarithmic form of the Arrhenius equation which is then written

$$\ln(d\alpha/dT) = (E_\alpha/R)[\ln(1-\alpha)/\phi - 1/T] + \ln(A/\beta) \tag{9}$$

where $\phi = [T_s^2/(1-\alpha_s)](d\alpha/dT)_s$. The plot of $\ln(d\alpha/dT)$ against $1000[\ln(1-\alpha)/\phi - 1/T]$ gives a linear plot with a slope equal to (E_α/R) and intercept (A/β). By substituting the value of (E_α/R) in Eq. (8), n is obtained. Nonisothermal kinetic parameters estimated by this method for some compounds are presented in Table 2 and plots are shown in Fig. 2.

Table 2
Nonisothermal decomposition kinetic parameters from the alternate absolute method

Sample no.	Compound	Order	E/kJ mol^{-1}	A/s^{-1}	A.D.	C.R.
1	CaC_2O_4	1.08	306.5	2.2×10^{19}	0.31	0.9990
2	$NiSO_4$	0.36	250.0	4.0×10^{9}	0.36	0.9996
3	$CoSO_4$	0.39	237.2	4.9×10^{8}	0.39	0.9995
4	$CuSO_4$	1.07	251.6	9.7×10^{10}	0.26	0.9994

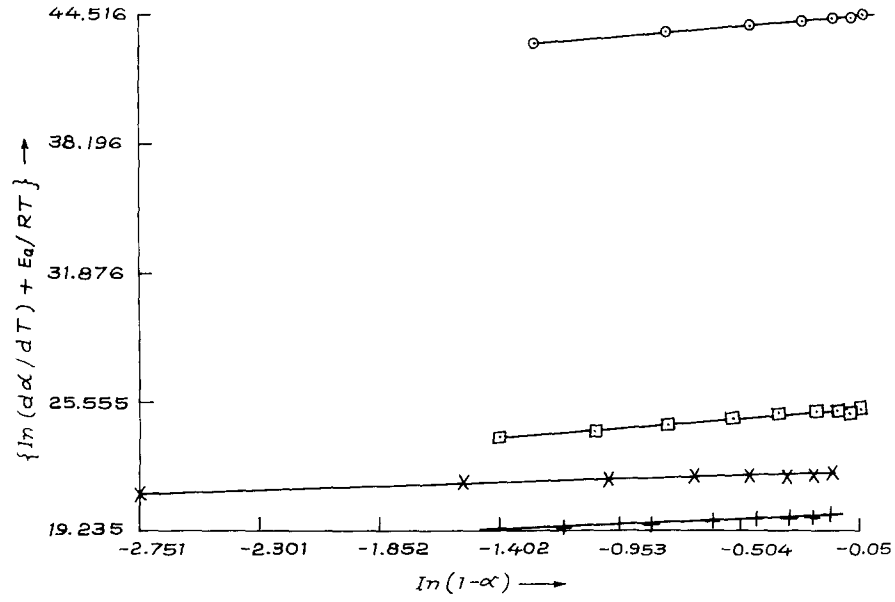

Fig. 2. Plots from the alternate absolute method: ○, CaC_2O_4; ×, $NiSO_4$; +, $CoSO_4$; and □, $CuSO_4$.

2.2.2. *An alternate standard method*

In this method, the slope (E_α/R) obtained from Eq. (9) is substituted in the logarithmic form of the Arrhenius rate equation. Eq. (2) may be written as

$$\ln[(\mathrm{d}\alpha/\mathrm{d}T) + (E_\alpha/R)(1/T)] = n\ln(1-\alpha) + \ln(A/\beta) \tag{10}$$

$\ln[(\mathrm{d}\alpha/\mathrm{d}T) + (E_\alpha/R)(1/T)]$ plotted against $\ln(1-\alpha)$ results in a straight line, from which n and A can be determined. Table 3 lists the results of the nonisothermal kinetic parameters for some compounds and Fig. 3 depicts the plots.

2.2.3. *An additional standard method*

The n value obtained from Eq. (8) is substituted in the logarithmic form of the Arrhenius rate equation which is Eq. (6). The plot of $\ln(k)$ against $(1000/T)$ results in

Table 3
Nonisothermal decomposition kinetic parameters from the alternate standard method

Sample no.	Compound	n	A/s^{-1}	A.D.	C.R.
1	CaC_2O_4	1.07	2.3×10^{19}	0.05	0.9981
2	$NiSO_4$	0.32	3.9×10^{9}	0.04	0.9991
3	$CoSO_4$	0.50	5.1×10^{8}	0.20	0.9995
4	$CuSO_4$	1.07	9.7×10^{10}	0.26	0.9994

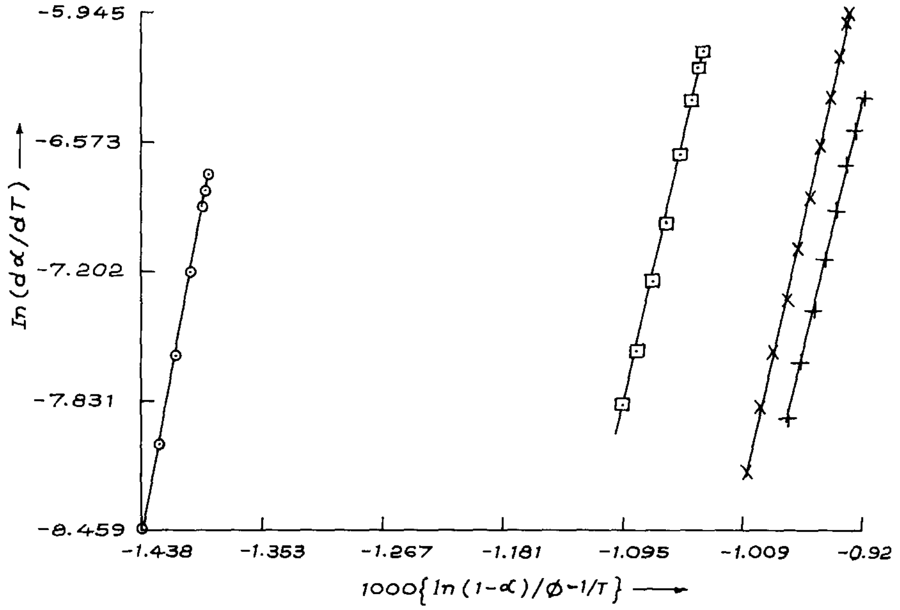

Fig. 3. Plots from the alternate standard method: ○, CaC_2O_4; ×, $NiSO_4$; +, $CoSO_4$; and □, $CuSO_4$.

a straight line, from which E_α and A are determined. Table 4 lists the results obtained using n values from the alternate absolute method and Fig. 4 depicts the plots. Similarly, n obtained from the alternate standard method can also be used to obtain such plots.

3. Discussion

In Tables 2 and 3, kinetic parameters for the thermal decomposition of Co(II) CHDMA complex are not presented because it was found to be a zero-order reaction which gives an inflection point at infinite T only, as is evident from Eq. (7). Therefore, the order of reaction is a function of the parameters at the inflection point, such as C_s,

Table 4
Nonisothermal decomposition kinetic parameters from the additional standard method

Sample no.	Compound	E/kJ mol^{-1}	A/s^{-1}	A.D.	C.R.
1	Co(II)CHDMA	−7.8	1.1×10^{-4}	0.12	0.9955
2	CaC_2O_4	307.2	2.4×10^{19}	0.33	0.9996
3	$NiSO_4$	250.4	4.2×10^{9}	0.28	0.9997
4	$CoSO_4$	226.0	1.4×10^{8}	0.46	0.9990
5	$CuSO_4$	251.6	9.6×10^{10}	0.28	0.9997

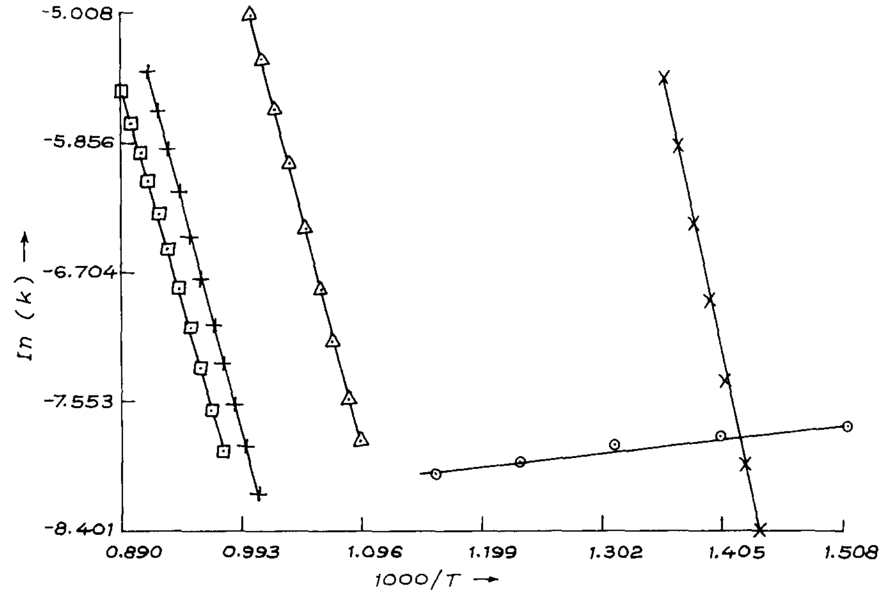

Fig. 4. Plots from the additional standard method: ○, Co(II)CHDMA; ×, CaC_2O_4; +, $NiSO_4$; □, $CoSO_4$; and △, $CuSO_4$.

T_s, E_α, and $(d\alpha/dt)_s$. The parameters obtained for the thermal decomposition of the compounds by all the methods are in good agreement, except for Co(II)CHDMA complex. Therefore, the parameters calculated from the overdetermined system method give more accurate results, as the A.D. values are lower while the C.R. values are higher than for other methods.

The pre-exponential factor A for the Co(II)CHDMA complex is almost zero and the activation energy is small. This may indicate that this is a weak complex and its decomposition is kinetically favored. In the present treatment of nonisothermal kinetics, it is assumed that (a) a reaction follows a simple order, (b) the temperature dependence of the rate of mass loss is governed by the Arrhenius equation, and (c) the reaction mechanism takes no account of the solid state decomposition reaction, the kinetic parameters of which may vary with various factors. However, the entire analysis is based on the criterion of the degree of fit of the data.

Furthermore, it may be noted that the physical properties and the chemical stoichiometry change during nonisothermal analysis. Such changes may result in a change in the activation energy. Therefore, in the method it is desirable to define a region in the space (α, T) for which E_α is constant in the analysis of the TG experiments. A constant activation energy suggests that a single mechanism will describe the kinetics in this region. Conversely, if E_α is changing, it is certain that a change in kinetics or a physical or chemical change, or both, is taking place. Hence, in the data analysis by these methods, the criterion of the fit reasonably exhibits the constancy of E_α in the range of temperature. A change in kinetics of the decomposing spectrum frequently results from a shift in a physical-diffusion-limited case to a chemical-reaction-limited case, or vice versa [9]. It can be observed that the direct fitting of thermoanalytical data leads to more exact kinetic parameters compared to the usual methods of linearizing. The large variation in the values of A may be attributed to enthalpy-entropy compensation. As the E_α increases, A must increase so that the reaction is thermodynamically (entropy) favored. This will mean that the magnitude of n, A, and E_α provide the understanding of the reactivity of solids. In solid state reactions, the crystal is an association of molecules/atoms/ions with long-range interaction between them; the relative arrangement determines the physical and chemical properties as well as the disturbances and the reactivity of solids [10].

All thermal decomposition reactions can be classified into two groups. The first includes chemical reactions in which rupture and formation of new bonds occur locally. The second group covers reactions in which changes are transferred within a path length much longer than interatomic distances. The change can be carried by electrons or ions. Reactions which belong to the first group usually start at the surface. The second group of reactions involves the volume of the crystal [11]. Thus defects may play an important role in solid state reactions. The creation and distribution of defects are entropy-favored. Therefore, a large value of A indicates that the reaction is a surface reaction. The process involves a mechanism which is due to a large disturbance in the solids (entropy-favored), such as the nucleation and growth of active centers on the surface or the diffusion of species (electron or ion) through the lattice. Thus the rate constant is related to the formation of the active centers at the surface.

It has been shown by Mental and Anderson [12] that the decomposition of CaC_2O_4 is a first-order process, that there is an electron transition from oxalate to metal (Ca) through interstitial defects, and that the reaction is a surface reaction which occurs at the interface separating the parent crystal and the product.

The decomposition of $NiSO_4$ leads to the product NiO and order is 1/3. This gives the functional form of the rate law similar to the Arvami–Erofeev mechanism of nucleation and growth. Koga and Tanaka [13] reported that the decomposition of $NiSO_4$ proceeds by surface and random nucleation and growth near the reaction front as well as in bulk.

The decomposition of $CoSO_4$ is characterized by a contracting area geometry model and is affected by the distribution of the active surface centers. The decomposition of $CuSO_4$ is first order and during dehydration, reaction zones are produced in $CuSO_4$ [14].

4. Conclusions

The methods described here are useful for the determination of the activation energy and other kinetic parameters for the overall processes which take place in the decomposition process. However, formulation of a realistic mechanism for a solid state decomposition reaction requires at least the knowledge of the relationships between the rate and the rate-forcing variables such as pressure, gaseous flow, gaseous composition, physical and geometric properties of the sample, etc.

References

[1] E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
[2] J.H. Sharp and S.A. Wentworth, Anal. Chem., 41 (1969) 2060.
[3] A.W. Coats and J.P. Redfern, Nature, 201 (1964) 8.
[4] S.G. Viswanath, S.S. Umare and M.C. Gupta, Thermochim. Acta, 233 (1994) 47.
[5] S.G. Viswanath and M.C. Gupta, Thermochim. Acta (1996), in press.
[6] M.C. Gupta and S.G. Viswanath, J. Therm. Anal., (1995), in press.
[7] J.M. Schempt, F.E. Freberg, D.J. Royer and F.M. Angelonic, Anal. Chem., 38 (1966) 520.
[8] H.R. Choudhari, Structural Studies of Metal Complexes, Ph.D. Dissertation, Nagpur University, Nagpur, 1981.
[9] J.H. Flynn, in H.H.G. Jellinek (Ed.), Aspects of Degradation and Stabilization of Polymers, Elsevier Scientific Publication, New York, 1978, p. 573.
[10] H.S. Ray, High Temperature Chemistry, B.A.R.C., Bombay, Vol. 6, 1985.
[11] V.V. Boldyrev, Kinet. Catal., 1 (1960) 203.
[12] J. Mental and H. Anderson, J. Therm. Anal., 40 (1993) 1307.
[13] N. Koga and H. Tanaka, J. Therm. Anal., 40 (1993) 1165.
[14] V.V. Boldyrev, J. Therm. Anal., 40 (1993) 1041.